

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON ORGANIC CHEMISTRY.

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BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Development of Organic Chemistry in the Last Forty Years. CARL GRAEBE (*Ber.*, 1907, 40, 4638—4644).—A lecture delivered before the German Chemical Society. W. H. G.

Fractional Distillation of Higher Normal Paraffins from Lignite in the Vacuum of the Cathode Light. FRIEDRICH KRAFFT (*Ber.*, 1907, 40, 4779—4784).—An examination of a Saxon paraffin wax of a complicated character. The apparatus used consists essentially of a small flask for distillation provided with a long neck in which the thermometer bulb can be immersed in the liquid or vapour at will; for details, the original should be consulted. The first fractionation of 450 grams resulted in the collection of five fractions, and each fraction was carefully redistilled. After repeated fractionation, the following eighteen hydrocarbons were isolated and their molecular weights by the boiling-point method determined.

		B. p., 0 mm.	M. p.	D liquid.
C ₁₉ H ₄₀	Nonadecane	109·0°	31·8—32·0°	—
C ₂₀ H ₄₂	Icosane	117·5	36·3—36·6	0·7775
C ₂₁ H ₄₄	Heneicosane	125·5	39·9—40·2	0·7778
C ₂₂ H ₄₆	Docosane	130·5	44·0—44·5	0·7776
C ₂₃ H ₄₈	Tricosane	138·0	47·2—47·5	0·7799
C ₂₄ H ₅₀	Tetracosane	145·5	50·7—51·3	0·7781
C ₂₅ H ₅₂	Pentacosane	152·5	53·8—54	0·7785
C ₂₆ H ₅₄	Hexacosane	160	56·8—57	0·7787
C ₂₇ H ₅₆	Heptacosane	167	about 59·4	0·7789
C ₂₈ H ₅₈	Octacosane	173·5	„ 61·6	0·7792
C ₂₉ H ₆₀	Nonacosane	179	63·6—64·1	0·7797
C ₃₀ H ₆₂	Triacontane	186	65·6	0·7797
C ₃₁ H ₆₄	Hentriacontane ...	193·5	68·4	0·7799
C ₃₂ H ₆₆	Dotriacontane	201	69·8	0·7798
C ₃₃ H ₆₈	Tritriacontane	208	71·8	0·7801
C ₃₄ H ₇₀	Tetraatriacontane ...	215	about 73	0·7806
C ₃₅ H ₇₂	Pentatriacontane...	222	„ 74	0·7813
C ₃₆ H ₇₄	Hexatriacontane about	230	„ 76	0·7819

There is a series of still higher homologues present in this paraffin, b. p. 250—290°/0 mm., and a portion boiling above 300°, the hydrocarbons of which must contain at least fifty carbon atoms. W. R.

Electro-Syntheses [with Ethylene and Acetylene]. SIMA M. LOSANITSCH (*Ber.*, 1907, 40, 4656—4666).—See this vol., ii, 32.

Isomeric Change of *iso*Butyl Alcohol Effected by Nitrous Acid. LOUIS HENRY (*Compt. rend.*, 1907, 145, 899—902).—The isomeric change which certain aliphatic amines undergo when their salts are treated with metallic nitrites has been examined in the cases of *n*-propylamine (Meyer and Forster, *Abstr.*, 1876, 543) and $\beta\beta$ -dimethylpropylamine (Tissier, *Abstr.*, 1891, 998; Freund and Lenze, *Abstr.*, 1891, 1172); in the first case, a mixture of *n*- and *iso*-propyl alcohols is obtained containing 58% of the secondary alcohol, whilst in the second case the tertiary alcohol, dimethylethylcarbinol, is the sole product of the reaction. The author has extended the investigation to the intermediate homologue, *isobutylamine*, and finds that on treatment with sodium nitrite in a slightly acid solution it is converted into a mixture of *isobutyl* alcohol and trimethylcarbinol, of which 75% is the tertiary alcohol. These three amines contain respectively the groupings: $-\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, $>\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$, and $>\text{C}\cdot\text{CH}_2\cdot\text{NH}_2$, and the results show that when they are converted into alcohols by the action of nitrous acid they suffer a partial or complete isomeric change, whereby the resulting alcohol has the hydroxyl attached to that carbon atom which in the original compound was associated with the least number of hydrogen atoms. M. A. W.

Action of Magnesium Organic Compounds on Tiglic Aldehyde. PAUL ABELMANN (*Ber.*, 1907, 40, 4589—4590).— γ -Methyl- Δ^7 -pentene- β -ol, $\text{CHMe}:\text{CMe}:\text{CHMe}\cdot\text{OH}$, obtained from magnesium methyl bromide and tiglic aldehyde, is a colourless liquid, b. p. 139—141°. Its *acetate*, $\text{C}_8\text{H}_{14}\text{O}_2$, has b. p. 153—155°.

δ -Methyl- Δ^8 -hexene- γ -ol, $\text{CHMe}:\text{CMe}:\text{CHEt}\cdot\text{OH}$, obtained from magnesium ethyl bromide and tiglic aldehyde, has b. p. 154—155°/80 mm. Its *acetate*, $\text{C}_9\text{H}_{16}\text{O}_2$, has b. p. 167—170°.

$\gamma\eta$ -Dimethyl- Δ^8 -octene- δ -ol, $\text{CHMe}:\text{CMe}:\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$, obtained from magnesium *iso*amyl bromide and tiglic aldehyde, has b. p. 202—204°. A. McK.

Esterification of Phosphoric Acid by Glycerol. GEORGES PRUNIER (*Bull. Soc. chim.*, 1907, [iv], 1, 1046—1048).—The rate of esterification of phosphoric acid by glycerol has been investigated under varying conditions of concentration, temperature (110°, 130°, or 150°), and pressure, and the nature of the products determined.

The results show that care must be taken to eliminate water as it is formed, and this may be accomplished by heating the reaction mixture under reduced pressure or by exposing a comparatively large evaporating surface.

The limit appears to be reached when 80% of the acid is esterified, and this point is arrived at more quickly at the higher temperatures. The extent to which esterification proceeds is increased as the concentration of alcohol and acid is increased and as the time of operation is extended. At atmospheric pressure, the best result (78%) is obtained at 110° and using 60% phosphoric acid and glycerol of 60°B.

At the higher temperatures and under reduced pressure, the chief product is the di-ester, this being replaced, in part, by the mono-ester when esterification is slow (namely, at higher pressures and lower temperatures), and by the tri-ester when the operation is conducted at a still higher temperature. No method is yet available for the separation of the mono- from the di-ester. Mercurous and mercuric glycerophosphates have been prepared for the first time. T. A. H.

Action of Sodium Ethoxide on Trichloromethylsulphonyl Chloride. ALEXANDER CRUM BROWN and THOMAS F. COWIE (*Proc. Roy. Soc. Edin.*, 1907, 27, 369—370).—The action of an ethereal solution of trichloromethylsulphonyl chloride on sodium ethoxide results in the production of ethyl ether, sodium chloride, sodium carbonate, sodium sulphite, and small quantities of ethyl carbonate, ethyl orthocarbonate, and sodium ethyl sulphite. The most probable explanation of the reaction, which also takes place when solutions of the two compounds in absolute alcohol are mixed, is that the ester $\text{C}(\text{OEt})_3 \cdot \text{SO}_2 \cdot \text{OEt}$ is formed, and acted on by sodium ethoxide, thus: $\text{C}(\text{OEt})_3 \cdot \text{SO}_2 \cdot \text{OEt} + \text{NaOEt} = \text{C}(\text{OEt})_4 + \text{NaSO}_2 \cdot \text{OEt}$ or $\text{CO}(\text{OEt})_2 + \text{OEt}_2 + \text{NaSO}_2 \cdot \text{OEt}$. Further action of sodium ethoxide on the carbonic esters and sodium ethyl sulphite results in the formation of ether, sodium carbonate, and sodium sulphite. W. H. G.

Complex Iridium Salts. Irido-oxalates. CESARE GIALDINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 648—655. Compare *Abstr.*, 1907, i, 1005).—*Silver irido-oxalate*, $\text{Ag}_3\text{Ir}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, prepared from the corresponding potassium salt and silver nitrate, forms silky, yellow needles, exploding at 145—150°, and exhibits cryoscopic behaviour in water, indicating that it undergoes dissociation into three Ag ions and the complex ion: $\text{Ir}(\text{C}_2\text{O}_4)_3$.

The *pyridine* salt, $(\text{C}_5\text{H}_5\text{N})_3\text{Ir}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, and the *barium* salt, $\text{Ba}_3[\text{Ir}(\text{C}_2\text{O}_4)_3]_2$, were also prepared.

Salts of the type $\text{M}''' \text{R}(\text{C}_2\text{O}_4)_2$, such as are formed by tervalent iron, aluminium, and chromium, do not appear to be formed with iridium. T. H. P.

Acids of High Melting Point in Japanese Wax, in Particular, Nonadecamethylenedicarboxylic Acid. RICHARD SCHAAL (*Ber.*, 1907, 40, 4784—4788).—Eberhardt's acid, m. p. 117·5°, from Japan wax has the composition $\text{C}_{21}\text{H}_{40}\text{O}_4$ (*Diss. Strasburg*, 1888; compare also Geitel and van der Want, *Abstr.*, 1900, i, 271). The acids in Japan wax, when carefully fractionated in the vacuum of the cathode light, give dicarboxylic acids of high m. p. After recrystallisation from 75% methyl alcohol and redistillation in a vacuum, two fractions are obtained of b. p. 180—210° and 210—245°/0 mm. and m. p. 98—100°

and 107—112° respectively. From the latter fraction, Eberhardt's acid was isolated; the *silver* salt, $C_{21}H_{38}O_4Ag_2$, *ethyl* ester, $C_{21}H_{38}O_4Et_2$, m. p. 53°, and *diamide*, $C_{21}H_{38}O_4(NH_2)_2$, m. p. 174—175°, were prepared. The acid has been identified as *n-nonadecamethylene-dicarboxylic acid*, $CO_2H \cdot [CH_2]_{19} \cdot CO_2H$, by converting the acid into *n-nonodecane* by baryta. From the fraction of b. p. 180—210° by repeated fractionation and treatment with baryta, *n-octadecane* and *n-heptadecane* have been identified, thus establishing the presence of the two lower homologues of nonadecamethylenedicarboxylic acid.

W. R.

Syntheses of *r*-Erythric Acid and of Inactive Erythritol. ROBERT LESPIEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 1112—1120).—The syntheses were effected as already described (Abstr., 1904, i, 471; 1905, i, 566; 1907, i, 173), but fuller details are now given of the methods employed and further data regarding some of the substances obtained. *r*-Erythrolactone is soluble in water or alcohol, insoluble in ether, and does not boil even under reduced pressure (20 mm.) without decomposition. It forms, from acetone, large monoclinic prisms [$a : b : c = 1.6886 : 1.1394$; $\beta = 92^\circ 53'$] (measurements by Wyruboff). The *hydrazide* of the corresponding acid has m. p. 145—146°, and the *brucine* salt has m. p. 210° (decomp.). These figures differ considerably from those recorded for corresponding compounds of the *d*-acid recorded by Ruff (Abstr., 1900, i, 139).

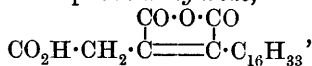
A yield of 30% of the theoretical of inactive erythritol is obtained under the conditions already described (Abstr., 1907, i, 173), but varied by using a large excess of sodium amalgam (fifty times the weight of the erythrolactone employed).

It is pointed out that the formation of inactive erythritol from *r*-erythrolactone probably takes place in the same manner as the production of *i*-tartaric acid from maleic acid.

T. A. H.

Agaricic Acid. HERMANN THOMS and J. VOGELSANG (*Annalen*, 1907, 357, 145—170).—A résumé is given of the work of previous authors on agaricic acid. It is now found that, contrary to Jahn's statement (Abstr., 1884, 354), agaricic acid is a tribasic hydroxy-acid and has the formula: $C_{22}H_{40}O_7 \cdot \frac{1}{2}H_2O$, $[\alpha]_D - 8.84^\circ$, and loses $\frac{1}{2}H_2O$ on prolonged heating at 100°; the *potassium* salt has $[\alpha]_D - 9.82^\circ$. The *trimethyl* ester, $C_{25}H_{46}O_7$, crystallises in needles, m. p. 63—64°. The *triethyl* ester, $C_{28}H_{52}O_7$, crystallises in needles, m. p. 36—37° (Siedler and Winzheimer, Abstr., 1902, i, 487). These esters form only oily acetyl derivatives. *Methyl benzoylagaricate*, $OBz \cdot C_{19}H_{36}(CO_2Me)_3$, prepared by heating the trimethyl ether with benzoyl chloride at 170°, forms colourless crystals, m. p. 39—40°. On hydrolysis with boiling alcoholic potassium hydroxide, the esters yield agaricic acid, which is partly decomposed, yielding stearic acid; this is formed also by heating agaricic acid with alcoholic potassium hydroxide at 150—160°. The action of hot concentrated sulphuric acid on agaricic acid leads to the formation of methyl heptadecyl ketone (Krafft, Abstr., 1880, 34), which forms an *oxime*, $C_{19}H_{39}ON$, m. p. 76—77°.

When heated in a current of hydrogen at 140° for six hours, agaricic acid yields the amorphous *anhydride*,



whilst at $155\text{--}160^{\circ}$ it loses carbon dioxide and forms the *anhydride*, $\text{CO}\cdot\text{O}\cdot\text{CO}$
 $\text{CMe}=\text{C}\cdot\text{C}_{16}\text{H}_{33}$, which separates from aqueous methyl alcohol in colourless crystals, m. p. $35\text{--}36^{\circ}$, does not react with bromine in chloroform solution, but decolorises potassium permanganate in cold aqueous alcoholic sodium carbonate solution. It is concluded that agaricic

acid has the structure: $\text{C}_{16}\text{H}_{33}\cdot\begin{array}{c} \text{CO}_2\text{H} \\ | \\ \text{C} \\ | \\ \text{H} \end{array}\text{---}\begin{array}{c} \text{CO}_2\text{H} \\ | \\ \text{C} \\ | \\ \text{OH} \end{array}\text{---}\begin{array}{c} \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \end{array}$.

G. Y.

Dissociation Processes in the Sugar Group. I. Behaviour of Carbohydrates toward's Fehling's Solution and other Oxidising Agents. JOHN U. NEF (*Annalen*, 1907, 357, 214—312. Compare Abstr., 1905, i, 3).—The product of the action of Fehling's solution and of aqueous copper acetate on dextrose and levulose, considered previously to consist chiefly of *d*- $\alpha\beta\gamma$ -trihydroxy-*n*-butyric acid, has been found to be a mixture of monobasic hydroxy-acids which have now been separated and identified. Similarly, mixtures of products are formed by the action of aqueous sodium hydroxide on formaldehyde and on the di-, tri-, tetra-, pent-, and hex-oses. The amounts of the various products formed were determined quantitatively in all the cases.

1. *Products of the Oxidation of Arabinose by means of Copper Hydroxide and Sodium Hydroxide.*—If sodium hydroxide and sufficient of the hexose to reduce the copper completely are added to an aqueous solution of copper sulphate and the mixture heated, the oxidation of dextrose or levulose commences at 40° , but that of *d*-mannose not below 92° , whilst *l*-arabinose occupies an intermediate position. Contrary therefore to the usual view, *d*-mannose, dextrose, and levulose cannot be in complete equilibrium in alkaline solution, since if they were they must undergo oxidation under the same conditions and yield the same products. The amount of the hexose required for complete reduction of the copper and the proportions in which the products are formed varies with the amount of sodium hydroxide added.

Oxidation of *l*-arabinose with copper hydroxide in alkaline solution leads to the formation of carbon dioxide, formic acid, and a number of non-volatile acids, which after acidification and evaporation of the oxidation filtrate are extracted partly by ether and partly by ethyl acetate. The ethereal extract yields *l*-glycollic acid and traces of oxalic acid, which are separated as the calcium salts, *l*-ribonic acid, which is isolated as the phenylhydrazide, and a residue containing glycollic, glyceric, *dl*-erythronic, and *dl*-threonic acids. The ethyl acetate extract yields *l*-arabonic acid and small amounts of *l*-ribonic acid.

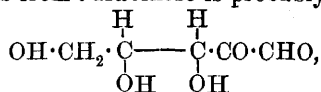
Glycollic acid is identified by formation of its *phenylhydrazine* salt, which crystallises slowly, but almost completely, from alcohol in

hexagonal plates, m. p. 100—101°, and decomposes slowly at the ordinary temperature, quickly at 100°, evolving gas.

As arabonic and ribonic acids occur, not only amongst the oxidation products of *l*-arabinose, but also together with *d*-gluconic and mannonic acids in the oxidation products of dextrose, lævulose, and mannose, their salts were studied with the object of finding methods of separation. *l*-Arabonic acid forms sparingly soluble, crystalline salts with *brucine*, decomp. 155°, *quinine*, m. p. 164°, and *strychnine*, decomp. 125—130°, and a sparingly soluble, resinous salt with *morphine*. *Brucine d-gluconate*, decomp. 120—125° when dried in air, 150—155° when dried over sulphuric acid in a vacuum. *d*-Gluconic and *l*-arabonic acids are separated by means of the *cinchonine* salts; the *d*-gluconate crystallises almost completely from alcohol, whilst the *l*-arabonate forms a readily soluble gum. The calcium salts are less satisfactory as a means of separation, since their solubilities are often modified to a marked extent by the presence of other hydroxy-acids.

l-Ribonic acid forms a crystalline lactone, phenylhydrazide, and cadmium salt; the *brucine*, *cinchonine*, and *strychnine* salts are readily soluble in alcohol. *l*-Arabonic and *l*-ribonic acids are separated best by conversion into the phenylhydrazides; on digestion with absolute alcohol, *l*-arabonylphenylhydrazide remains undissolved, whilst *l*-ribonylphenylhydrazide crystallises from the filtrate on concentration. These hydrazides are hydrolysed by dilute alkalis at 100°; isomerisation of the hydroxy-acid does not take place during the hydrolysis.

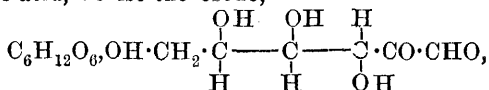
As the intermediate product in the formation of $\alpha\beta\gamma\delta$ -tetrahydroxyvaleric acids from *l*-arabinose is probably the pentosone,



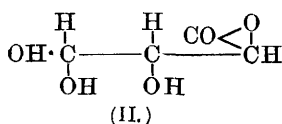
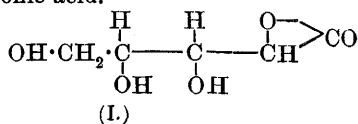
the comparatively small amount of *l*-ribonic acid formed is remarkable.

The hexosone, $\text{OH}\cdot\text{CH}_2\cdot\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{CO}\cdot\text{CHO}$, formed from *d*-

mannose, dextrose, or lævulose, yields *d*-gluconic acid with only traces of *d*-mannonic acid, whilst the osone,



from maltose, yields chiefly glucosido-*d*-mannonic acid. It is argued from the point of view of the author's dissociation hypothesis that the pentosone from *l*-arabinose must undergo an unsymmetrical "benzilic acid transformation" forming (I), from which *l*-arabonic acid is derived together with only small amounts of (II), which yields *l*-ribonic acid.



Similar arguments are employed to explain the formation of optically active lactic acid by the action of enzymes on hexoses, and of *l*-alanine from *l*-bromopropionic acid (Fischer, Abstr., 1907, i, 192).

Glycollic, glyceric, *dl*-erythronic, and *dl*-threonic acids are formed probably, not only by oxidation of *l*-arabinose, but also from all aldo- and keto-pentoses and -hexoses. These acids are separated by conversion into a mixture of strychnine glycollate and *dl*-erythronate, m. p. 125—160°, and a mixture of brucine *l*-threonate, *dl*-glycerate, and *dl*-erythronate, m. p. 190—207°, the *d*-threonic acid remaining in the alcoholic filtrate. When heated with acetic anhydride, glycollic acid forms *acetylglycollic acid*, which crystallises in needles, m. p. 68—70°, and is readily soluble in water, whereas *dl*-erythronic acid forms an oily *acetyl* derivative, insoluble in water. This difference is utilised to separate the acids from the mixture of strychnine salts. The acids from the mixture of brucine salts are separated in the same manner. The soluble acetylated oil on hydrolysis yields *dl*-glyceric acid, forming an optically active calcium salt, m. p. 135°; the insoluble oil on hydrolysis yields a mixture of *dl*-erythronic and *l*-threonic acids, which are separated by means of their brucine salts. *Brucine l-threonate*, needles, m. p. 200°, sparingly soluble, hot alcohol. *Brucine d-threonate* melts at a low temperature, and is readily soluble. *l-Threonylphenylhydrazide*, flat needles, m. p. 158°, $[\alpha]_D^{20} - 26.88^\circ$, on hydrolysis with 10% potassium hydroxide yields *l-threonic acid* as a laevorotatory syrup.

It is shown that when heated with hydrochloric acid at 100°, and thereafter treated as in the separation of the oxidation products of *l*-arabinose, *dl*-erythronic acid remains unchanged, and that the same products of oxidation are obtained when carbohydrates are heated with alkalis and a limited amount of mercuric oxide in place of copper hydroxide, from which it is concluded that the four trihydroxybutyric acids are formed directly from pentoses or hexoses, and not through intermediate formation of aldotetroses.

dl-Erythrolactone (m. p. 89—90°: Ruff, Abstr., 1901, i, 449; 91°: Lespieau, Abstr., 1905, i, 566), formed by treating the calcium salt with oxalic acid, crystallises in monoclinic prisms [$a:b = 1.6509$: about 1; $\beta = 86^\circ 35'$], m. p. 92—95°, b. p. 195—200°/14 mm. (slight decomp.). *dl*-Erythronylphenylhydrazide, $C_{10}H_{14}O_4N_4$, formed by the action of phenylhydrazine on the lactone, crystallises in white plates, m. p. 150—151°. *Dibenzoyl-dl-erythrolactone*, $C_{18}H_{14}O_6$, forms transparent crystals, m. p. 118°.

The mechanism of the reactions by which the products of the oxidation of *l*-arabinose by copper hydroxide in alkaline solution are formed is discussed.

2. *Products of the Oxidation of d-Mannose, Dextrose, and Lævulose by Copper Hydroxide and Sodium Hydroxide.*—The oxidation of *d*-mannose, dextrose, and lævulose leads to the formation of the same products as are obtained from *l*-arabinose with the exception that *d*-gluconic acid and smaller amounts of *d*-mannonic acid are obtained in place of *l*-arabonic and *l*-ribonic acids. Moreover, *dl*-glyceric acid is formed in larger, glycollic acid in smaller, amounts than from the pentose. As *d*-gluconic and *d*-mannonic acids form insoluble hydrazides

with phenylhydrazine in cold alcoholic solution, the non-volatile acids formed from the hexoses are separated in the same manner as those from *l*-arabinose.

When heated with hydriodic acid, D 1·96, at 100°, glyceric acid yields β -iodopropionic acid; as glycollic, lactic, and erythronic acids do not undergo this reaction, it is utilised in the determination of the glyceric acid present in mixtures.

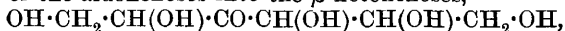
On digestion with cinchonine in aqueous solution, gluconic acid is partly transformed into a *polymeric anhydride*, which is obtained as a viscid oil, is very sparingly soluble in alcohol, and remains unchanged when heated with 10% sodium hydroxide or hydrochloric acid at 100°, but is gradually converted into gluconylphenylhydrazide by the action of an excess of phenylhydrazine at 100°. Calcium *d*-gluconate has $[\alpha]_D^{20} + 10\cdot5^\circ$ ($+9\cdot9^\circ$: Alberda van Ekenstein, Jorissen, and Reicher, Abstr., 1897, ii, 129).

3. *Behaviour of Carbohydrates in Dilute Alkali Hydroxide Solution towards Excess of Silver Oxide.*—When treated with an excess of silver oxide in aqueous alkali solution, the carbohydrates, whether di-, tri-, tetra-, pent-, or hex-oses, yield carbon dioxide, oxalic acid, and formic acid, only the proportions varying with the individual carbohydrate and probably with the concentration. Ten grams of each of the following substances were oxidised with an excess of silver oxide in presence of baryta in aqueous solution; the numbers given are grams of the oxidation products in the order: carbon dioxide, oxalic acid, formic acid.

Dextrose, 2·256, 8·534, 3·845; *l*-xylulose, 2·6, 8·273, 3·53; *d*-galactose, 2·995, 6·447, 4·3625; *l*-arabinose, 2·934, 8·02, 3·7294; erythritol, 2·256, 8·92, 3·427; glycerol, 5·056, 3·372, 4·8852; glycolylaldehyde, formed by heating trihydroxybutyric acid at 56–60°, 5·336, 5·362, 2·622; ethylene glycol, 4·324, 3·308, 3·1202; glycollic acid, 3·26, 6·094, 1·11228.

As erythritol is oxidised only when the mixture is gently heated, the carbon dioxide might be formed by oxidation of formic acid, but it is found that the formation of carbon dioxide from formic acid when treated with silver oxide and baryta commences and that only slowly at 110°. Ethylene glycol is oxidised completely only at 110°. The experiment with glycollic acid shows this to be a possible intermediate product in the oxidation of the carbohydrates.

4. *The Action of Alkali Hydroxides on Carbohydrates.*—The transformation of the aldohexoses into the β -keto-hexoses,



or *dl*-lactic acid, by the action of alkalis (compare Bruyn and Alberda van Ekenstein, Abstr., 1896, i, 116; 1898, i, 225), and the theory of the formation of the saccharinic acids are discussed.

It is shown that the amount of lactic acid formed depends, not only on the individual carbohydrate, but also on the concentration of the alkali.

The stereoisomeric parasaccharinic acids are $\alpha\omega$ -hydroxyethyltrihydroxybutyric acids, and must form two pairs of optical isomerides, *Brucine dl*-parasaccharinate crystallises in needles, m. p. 193–194°;

the corresponding acid is a viscid syrup, which forms a *phenylhydrazide*, m. p. 125°. G. Y.

Sugars. W. ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1907, 4, 743—748).—*l*-Arabinose has been prepared from the leaves of *Adonis vernalis*; *l*-xylose from the seed envelope of *Sterculia foetida*, from buckwheat bran (*Polygonum fagopyrum*), and from rushes (*Scirpus lacustris*). Ribonic acid and arabonic acid were separated by fractional crystallisation of their phenylhydrazides, and pure ribonolactone obtained (m. p. 80°). From *d*-lyxose were prepared methyl-lyxoside, m. p. 80°, $\alpha_D + 40.2^\circ$, and benzyl-lyxoside, m. p. 44°, $\alpha_D + 80.5^\circ$.

Calcium amalgam is no better than sodium amalgam for the reduction of sugars. *p*-Nitrophenylhydrazine can be employed in the identification of sugars from glucosides. A. J. W.

Nature of Iodide of Starch. M. KATAYAMA (*Zeitsch. anorg. Chem.*, 1907, 56, 209—217. Compare Mylius, Abstr., 1887, 568; Padoa and Savari, Abstr., 1905, 1, 416).—The influence of the concentration of starch, iodine, and potassium iodide on the formation of iodide of starch has been investigated by bringing the components together in varying proportions and determining the quantity of iodide of starch produced by means of colorimetric measurements, the assumption being made that the depth of the colour is proportional to the concentration of the compound.

It is shown that, in dilute solution, the starch iodide concentration is proportional to the concentrations of iodine and starch respectively, but varies in a somewhat complicated manner with the iodide concentration. In very dilute solution, it is proportional to the second or third power of the iodide concentration, but the effect is proportionately smaller as the concentration increases, and depends also on the starch concentration.

From the observations, the conclusion is drawn that iodide of starch is to be regarded as a solid solution of iodine in starch and not as a chemical compound. G. S.

Hydrocelluloses. CARL G. SCHWALBE (*Ber.*, 1907, 40, 4523—4527; *Zeitsch. angew. Chem.*, 1907, 20, 2166—2172. Compare Abstr., 1907, i, 390).—The reducing power of a cellulose derivative can be determined as follows. After treatment with the Fehling's solution (*loc. cit.*) and thorough washing, the mass is extracted with dilute acetic acid and the copper estimated in the extract. The cellulose is again immersed in Fehling's solution, thoroughly washed, the blue copper-cellulose-alkali compound decomposed with acid, and a second copper estimation made. The difference between the two copper estimations gives the reducing power of the cellulose. The values have been determined for various cellulose products, including cotton-satin, mercerised cotton, viscose silk, Chardonnnet silk, parchment paper, hydro- and oxy-celluloses. The hydrocelluloses give values differing from those obtained for celluloses treated with alkali.

The water of hydration in several cellulose products has been estimated by boiling the dry material with toluene; the water passes over with the first drops of the toluene, and may be absorbed by calcium chloride. The results obtained agree with the formula $2C_6H_{10}O_5 \cdot H_2O$ for mercerised cotton, and $6C_6H_{10}O_5 \cdot H_2O$ for hydrocellulose (Gladstone, *Trans.*, 1852, 5, 7). It thus appears that alkalis have a hydrating effect, but acids both a hydrating and a hydrolysing effect.

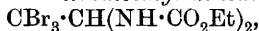
The celluloses and their derivatives are divided into the following groups. 1. Celluloses and their hydrates, with very little reducing action and not dyed by basic colours. 2. Hydrocelluloses and their hydrates, with distinct reducing properties, but not dyed by basic colours. 3. Oxycelluloses and their hydrates, strong reducing properties and strongly dyed by basic colours. J. J. S.

Putrescine. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1907, 53, 545—546).—The constitution of putrescine as tetramethylenediamine is confirmed by the fact that when the hydrochloride is distilled it yields pyrrolidine chloride and ammonium chloride. J. J. S.

Chemistry of Putrefaction. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1907, 54, 1—31).—From the products of prolonged putrefaction of ox pancreas, the fraction of bases which are precipitated by alcoholic mercuric chloride solution, but not by alcoholic picric acid solution, yielded, besides pentamethylenediamine, three new bases, which were isolated as aurichlorides.

Marcitine, $C_8H_{19}N_3$, yields an *aurichloride*, $C_8H_{19}N_3 \cdot 2HAuCl_4$, m. p. 175—178°. *Putrine*, $C_{11}H_{26}O_3N_2$, gives an *aurichloride*, $C_{11}H_{26}O_3N_2 \cdot 2HAuCl_4$, forming orange-coloured, anhydrous, microscopic crystals, m. p. 109—110°. *Putridine* is either an isomeride of muscarine or of betaine, or it is an isomeride of putrine. The *aurichloride*, which was not obtained quite pure, forms yellow, rhombic leaflets, containing 1 or $2H_2O$ (according to the formula adopted), and melts at 85—87°. G. B.

Bromination of Urethane. OTTO DIELS and FELIX OCHS (*Ber.*, 1907, 40, 4571—4575).—*Tribromoethylidenediurethane*,



m. p. 166—167°, obtained by heating urethane with bromine and iron, is decomposed by dilute hydrochloric acid at 160°, yielding glyoxylic acid, carbon dioxide, ethyl chloride and bromide, and ammonium bromide. Nitric acid, D 1.4, decomposes the substance, forming ethyl nitrate and bromal. The constitution of tribromoethylidenediurethane is determined also by its formation from bromal and urethane at 95° in the presence of a few drops of concentrated sulphuric acid.

Di bromourethane, $NBr_2 \cdot CO_2Et$, b. p. 100—104°/10—11 mm., is obtained in a slightly impure condition as a heavy, transparent, reddish-brown oil by decomposing Hantzsch's compound,



(*Abstr.*, 1894, i, 363), with dilute sulphuric acid at 0°. C. S.

Thiocarbamide. HERMANN GROSSMANN (*Chem. Zeit.*, 1907, 31, 1195—1196).—The addition of thiocarbamide to solutions of tartaric

acid, dextrose, raffinose, cane-sugar, and mannitol has practically no effect on their optical rotatory power, showing that thiocarbamide does not exist as a base in aqueous solutions.

It is shown that the sulphur in thiocarbamide and similar compounds may be readily estimated by treating the substance in an open vessel with concentrated nitric acid together with a little hydrochloric acid, and precipitating as barium sulphate. W. H. G.

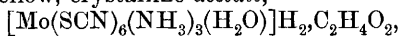
Action of Dry Ammonia on Ethyl Oxalate. ISAAC K. PHELPS, L. H. WEED, and C. R. HOUSUM (*Amer. J. Sci.*, 1907, [iv], 24, 479—482).—It has been stated by Liebig (*Annalen*, 1834, 9, 129) that dry ammonia acts with difficulty on ethyl oxalate to form ethyl oxamate and oxamide, the greater part of the ethyl oxalate being unaffected.

Experiments are now described which show that when cold anhydrous ethyl oxalate is treated with excess of dry ammonia, a mixture of ethyl oxamate and oxamide is produced, only a small quantity of the oxalate remaining unchanged. If contact between the reagents is facilitated by means of a medium, such as alcohol or light petroleum, the final product consists entirely of oxamide.

E. G.

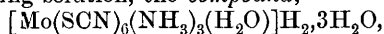
Compounds of Quadrivalent Molybdenum. JULIUS SAND and JOHANNA MAAS (*Ber.*, 1907, 40, 4504—4513).—Sand and Burger obtained a series of salts in which molybdenum was considered to function as a quadrivalent element by electrolytic reduction of ammonium molybdate in presence of ammonium thiocyanate (*Abstr.*, 1906, i, 487). The present paper contains the results of a further investigation of the zinc salt, $[\text{Mo}(\text{SCN})_6(\text{NH}_3)_4]\text{Zn}$, described by these authors.

The action of boiling acetic acid on the zinc salt leads to the formation of a yellow, crystalline *acetate*,



in which two of the ammonia groups are co-ordinated, on the one hand, with molybdenum and, on the other, with hydrogen. The curve representing the molecular conductivity of the acetate rises rapidly with increasing dilution, and closely resembles the corresponding curve for hydrofluosilicic acid. The acetate dissolves in concentrated aqueous ammonium thiocyanate, and is extracted from this by ether, forming a yellow solution which is stable if the ether has been previously dried over sodium, but otherwise becomes dark green, and finally black on exposure to air.

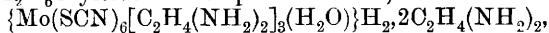
On reduction of a solution of ammonium molybdate and thiocyanate in hydrochloric acid with a current not exceeding two amperes and cooling the resulting solution, the *compound*,



separates in yellow needles, which lose water and become dark over sulphuric acid in a vacuum. If the crude product from the electrolytic reduction is dissolved in absolute alcohol, addition of benzene precipitates a *compound*, $[\text{Mo}(\text{SCN})_6(\text{NH}_3)_3(\text{H}_2\text{O})]\text{H}_2\cdot \frac{1}{2}\text{C}_2\text{H}_6\text{O}\cdot 2\text{H}_2\text{O}$, or $[\text{Mo}(\text{SCN})_6(\text{NH}_3)_3(\text{H}_2\text{O})]\text{H}_2\cdot \frac{2}{3}\text{C}_2\text{H}_6\text{O}\cdot \text{H}_2\text{O}$. Similarly, recrystallisation

of the crude reduction product from propyl alcohol leads to the formation of the compound, $[\text{Mo}(\text{SCN})_6(\text{NH}_3)_3(\text{H}_2\text{O})]\text{H}_2, \frac{2}{3}\text{C}_3\text{H}_8\text{O}, \text{H}_2\text{O}, \frac{1}{3}\text{HCl}$. When treated with acetic acid, the three preceding compounds yield the acetate obtained from the zinc salt, or, with propionic acid, the propionate, $[\text{Mo}(\text{SCN})_6(\text{NH}_3)_3(\text{H}_2\text{O})]\text{H}_2, \frac{2}{3}\text{C}_3\text{H}_6\text{O}_2, \text{H}_2\text{O}$.

When boiled with alcoholic ethylenediamine, the compound containing $\frac{1}{2}$ or $\frac{2}{3}\text{C}_3\text{H}_8\text{O}$ yields the complex substance,



which forms yellow crystals, m. p. $106-107^\circ$, gives with ammonia a derivative containing both ammonia and ethylenediamine, forms a yellow zinc salt with aqueous zinc chloride, and is converted by acids into thiocyanates containing smaller proportions of the diamine.

The quadrivalency of the molybdenum atom in the yellow series of thiocyanates is confirmed by heating Sand and Burger's zinc salt with concentrated hydrochloric acid in a current of carbon dioxide, when thiocyanic acid is slowly evolved and the product on addition of manganese sulphate and dilute sulphuric acid and titration with potassium permanganate gives results agreeing with those calculated for the conversion of quadrivalent into hexavalent molybdenum.

G. Y.

Hydroxycarbamides and Carbamidoximes. I. A. CONDUCHÉ (*Ann. Chim. Phys.*, 1907, [viii], 12, 533—574).—Mainly a detailed account of work already published (Abstr., 1905, i, 289; 1906, i, 593). In view of the fact that *isohydroxycarbamide*, m. p. $70-72^\circ$, condenses

with aldehydes to form carbamidoximes of the type $\text{O} < \begin{smallmatrix} \text{CHR} \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, whilst the isomeride, m. p. 140° , does not react with aldehydes, the author suggests that *isohydroxycarbamide* has the constitution: $\text{OH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, that of its isomeride being represented by the formula $\text{OH} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{OH}$ (compare Francesconi and Parrozzani, Abstr., 1902, i, 139).

M. A. W.

Action of Semicarbazide on Unsaturated Compounds. II. HANS RUPE and E. HINTERLACH (*Ber.*, 1907, 40, 4764—4770. Compare Rupe and Lotz, Abstr., 1903, i, 841; Rupe and Schlochoff, Abstr., 1904, i, 144).—The addition of hydroxylamine to compounds is not so much affected by constitutional influences as is the addition of semicarbazide. It was not found possible to add on semicarbazide to a cyclic, unsaturated ketone. The action of semicarbazide on ethylidenacetone, *isovalerylidenacetone*, and heptylidenacetone respectively is described. The semicarbazide-semicarbazones of these compounds are unstable; when boiled with alcohol, or with water, they are decomposed, either into their components, or the unsaturated ketones undergo further decomposition, whilst the hydrazodicarbonamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, of Thiele is produced. Ethyl ethylidenacetate combines with semicarbazide to form the semicarbazide-semicarbazone in very small yield. Ethyl crotonate combines comparatively readily with semicarbazide.

Ethylideneacetonesemicarbazide-semicarbazone,

$\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$,
obtained from ethylidene acetone and semicarbazide, crystallises from alcohol in needles, m. p. 126° .

*iso*Valerylideneacetone, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{COMe}$, obtained from *isovaleraldehyde* and acetone, is a yellow oil with b. p. $72-73^\circ/12 \text{ mm.}$, whilst Barbier and Bouveault give $180^\circ/750 \text{ mm.}$ Its *semicarbazide-semicarbazone*,

$\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CH}_2 \cdot \text{CHMe}_2) \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$,
crystallises from alcohol in rhombic leaflets, m. p. 157° .

Heptylideneacetone, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{COMe}$, obtained from heptaldehyde and acetone, boils at $125-126^\circ/12 \text{ mm.}$, and forms needles, m. p. $16-17^\circ$. Its *semicarbazide-semicarbazone*,

$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2) \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$,
crystallises from alcohol in tiny needles, m. p. $156-157^\circ$.

Ethyl ethylideneacetoacetate semicarbazide-semicarbazone,

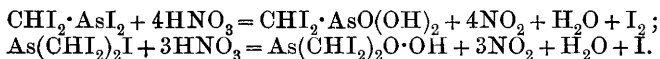
$\text{CMe}(\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2) \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CHMe} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$,
forms leaflets, m. p. 168° .

The compound, $\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, obtained from ethyl crotonate and semicarbazide, crystallises from alcohol in cubes, m. p. 127° . The main product of the action is, however, the compound, $\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, which crystallises from alcohol in tiny, stellate needles, m. p. 151° .

A. McK.

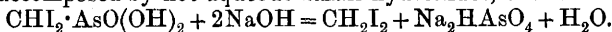
Action of Amorphous Arsenic on Alkyl-halide Derivatives.

VICTOR AUGER (*Compt. rend.*, 1907, 145, 808—811).—The amorphous arsenic, obtained by reducing a hydrochloric acid solution of arsenious oxide with stannous chloride or sodium hypophosphite, is of very great chemical activity. When heated in a sealed tube at 160° with carbon tetrachloride, arsenic trichloride and carbon tetrachloride are formed; with chloroform, the products are arsenic trichloride, hydrogen chloride, and amorphous carbon, and with ethylene bromide, or iodide, ethylene and arsenic tribromide or tri-iodide. When methyl iodide is treated with amorphous arsenic at the ordinary temperature or on a water-bath, there are formed arsenic tri-iodide, tetramethylarsonium iodide, a large quantity of methylarsine iodide, AsMeI_2 , and a trace of cacodyl iodide. Ethyl iodide reacts more slowly, giving 16% of AsI_3 , 16% of AsEt_2I , and 60% of AsEtI_2 . The higher aliphatic iodides also react with amorphous arsenic. At the temperature of the water bath, amorphous arsenic reacts explosively with iodoform, but in the presence of a neutral solvent (benzene or toluene) the reaction: $3\text{MeI} + 2\text{As} = \text{CHI}_2 \cdot \text{AsI}_2 + \text{As}(\text{CHI}_2)_2\text{I}$ takes place quantitatively. The dense, black oil formed is oxidised by cold nitric acid according to the equations:



Di-iodomethylarsonic acid, $\text{CHI}_2 \cdot \text{AsO}(\text{OH})_2$, crystallises in large, yellow, efflorescent tablets containing $1\text{H}_2\text{O}$. It forms dibasic salts; that of *silver* is an insoluble, white precipitate, which is decomposed by

boiling nitric acid, forming arsenic acid and liberating iodine. The acid is decomposed by hot aqueous alkali hydroxides, thus :



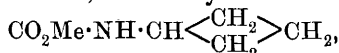
It is also decomposed by hydrochloric acid.

Tetraiodocacodylic acid, $\text{As}(\text{CHI}_2)_2\text{O} \cdot \text{OH}$, forms small, sulphur-yellow crystals, insoluble in water, but soluble in boiling nitric acid or much acetic acid. It is completely decomposed by prolonged boiling with the former acid. With hot alkali, the reaction is similar to that with the first acid. The sodium salt crystallises from 90% alcohol in large, yellow tablets containing $6\text{H}_2\text{O}$. E. H.

Convenient Method for the Preparation of *cyclo*Propane.

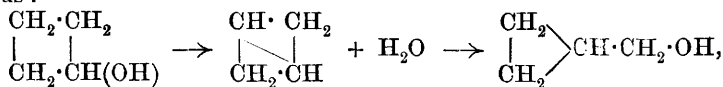
HUGO HAEHN (*Arch. Pharm.*, 1907, 245, 518—519).—*cyclo*Propane is readily prepared by heating 16 grams of amyl alcohol and 10 grams of trimethylene bromide with 3.3 grams of zinc wool; about 650 c.c. of the compound, containing traces of propylene, are obtained by this method in an hour. W. H. G.

Constitution of *cyclo*Butene. NICOLAI ZELINSKY and JOHANNES GUTT (*Ber.*, 1907, 40, 4744—4749. Compare Willstätter and Bruce, *Abstr.*, 1907, i, 1018).—*cyclo*Butanecarboxylic acid has D_4^{20} 1.0683, not D_4^{20} 1.0538, as given by Brühl. It was converted first into its acid chloride, then into its amide, and finally into the *wrethane*,



m. p. 19° , b. p. $95\text{--}96^\circ/12\text{ mm.}$, and D_4^{20} 1.0593; when distilled with calcium hydroxide, it forms *cyclobutylamine*, $\text{C}_4\text{H}_9\text{N}$, D_4^{20} 0.8328, D_4^{10} 0.8422, and n_D^{19} 1.4363.

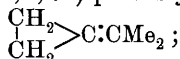
*cyclo*Butanol, obtained by the action of a slight excess of potassium nitrite on an aqueous solution of the preceding amine, has b. p. $123^\circ/740\text{ mm.}$, D_4^{20} 0.9159, and n_D^{20} 1.4328. After *cyclobutanol* had been oxidised by an aqueous solution of chromic acid, the product was submitted to steam distillation, and the first 10 c.c. of the distillate saturated with potassium carbonate. The oil, obtained in this manner, coloured magenta-sulphurous acid red, and boiled at $90\text{--}110^\circ$; the semicarbazone obtained from it had m. p. 216° (decomp.), whereas *cyclobutanonesemicarbazone* has m. p. 201° according to Kijner. A partial isomerisation of *cyclobutanol* had accordingly taken place, thus :



dicyclobutane resulting as an intermediate product.

It is probable that, under the conditions employed by Willstätter and Bruce, *dicyclobutane* would result from the dry distillation of the product, obtained by the interaction of silver oxide and *cyclobutylammonium iodide*. All the transformations of the "*cyclobutene*" of Willstätter and Bruce could be accounted for on the basis of the *dicyclic* structure referred to. A. McK.

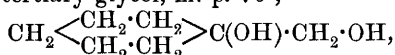
Scission of the Trimethylene Ring by Catalytic Reduction. NICOLAI ZELINSKY (*Ber.*, 1907, 40, 4743—4744. Compare Willstätter and Bruce, *Abstr.*, 1907, i, 1018).—With the view of studying the behaviour of the trimethylene ring when unsaturated derivatives of cyclopropane are reduced by hydrogen in the presence of nickel according to Sabatier and Senderens, the author examined the reduction of dimethylmethylenecyclopropane. The latter hydrocarbon (*Abstr.*, 1901, i, 660; 1902, i, 70) probably has the formula:



it has b. p. 69—69.5°/718 mm., and has n_D^{17} 1.4264. When the mixture of its vapour and hydrogen is passed over nickel at 160°, the action: $\text{C}_6\text{H}_{10} + 2\text{H}_2 = \text{C}_6\text{H}_{14}$ takes place, the trimethylene ring being disrupted. The resulting hydrocarbon has b. p. 59—59.5°/732 mm., D_4^{17} 0.6583, and n_D^{17} 1.3723. The b. p. is the same as that of β -methylpentane, so that the trimethylene ring appeared to be disrupted between the secondary and tertiary carbon atoms.

A. McK.

Isomeric Rearrangement. Methylenecyclohexane. ALEXEI E. FAWORSKY and I. BORGMANN (*Ber.*, 1907, 40, 4863—4875).—Methylcyclohexanol, prepared from phenol by a modification of Sabatier's method in which nickel is replaced by nickelised asbestos, forms a *bromide*, b. p. 163—165.5°, D_0^0 1.3604. *cycloHexylcarbinol*, prepared by the Grignard method, has b. p. 184—186°/784 mm., D_0^0 0.9445, and yields an *acetate*, b. p. 199—201°/740 mm. The *iodide*, $\text{CH}_2 \langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \rangle \text{CH} \cdot \text{CH}_2\text{I}$, formed by the action of saturated hydriodic acid, has b. p. 102—104°/28 mm. or 213°/743 mm., and D_0^0 1.555. When treated with alcoholic potash by Butleroff's method, it yields *methylenecyclohexane*, $\text{CH}_2 \langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \rangle \text{C} : \text{CH}_2$, b. p. 102—103°/760 mm., D_0^0 0.8184, which forms an additive *dibromide*, $\text{C}_7\text{H}_{12}\text{Br}_2$, b. p. 121.5—123°/27 mm., D_0^0 1.7156; this, when hydrolysed, forms a primary tertiary glycol, m. p. 76°,



which is converted into an aldehyde on heating with 1% sulphuric acid.

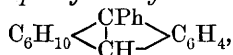
Methylenecyclohexane chloronitrosite forms colourless, plate-like crystals, m. p. 118° (heated slowly) or 145° (heated quickly) with decomposition; the *piperidide*, $\text{C}_7\text{H}_{12}\text{ON} \cdot \text{C}_6\text{NH}_{10}$, has m. p. 127.5—128°. Oxidation of the hydrocarbon with potassium permanganate leads to the formation of the glycol just mentioned, which has been described previously by Wallach.

Methylenecyclohexane remains unaltered when heated with quinoline, but in presence of quinoline and quinoline hydriodide it is converted into methyl- Δ^1 -cyclohexene, b. p. 109.5—110°, which forms a *chloronitrosite*, $\text{C}_7\text{H}_{12}\text{NOCl}$, m. p. 97.5° (decomp. 115°).

The hydrocarbons described by Zelinsky and Gutt, by Sabatier, and

by Wallach as methylenecyclohexane are shown to have been isomerides of this compound. E. F. A.

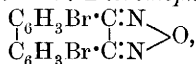
The Hydroanthracenes and their Derivatives. MARCEL GODCHOT (*Ann. Chim. Phys.*, 1907, [viii], 12, 468—533).—A detailed account of work already published (compare Abstr., 1904, i, 987; 1905, i, 201; 1906, i, 76, 494; 1907, i, 308, 836, 840, 841). The following facts are new: 9-benzylhexahydroanthracene (Abstr., 1907, i, 308) can also be prepared by the action of magnesium benzyl chloride on hexahydroanthrone; 9-phenylhexahydroanthracene,



similarly prepared from magnesium phenyl bromide and hexahydroanthrone, is a yellow oil, b. p. 235°/15 mm., and dissolves in ether or benzene to form beautiful blue, fluorescent solutions. M. A. W.

Phenanthrene Series. XXII. 2:7-Dibromophenanthrene and 2:7-Dibromophenanthraquinone. JULIUS SCHMIDT and ROBERT MEZGER (*Ber.*, 1907, 40, 4560—4566).—The bromination of α -tetrahydrophenanthrene (Abstr., 1907, i, 1022) in chloroform yields 2:7-dibromophenanthrene, $\text{C}_{14}\text{H}_8\text{Br}_2$, m. p. 199—200°, which separates from alcohol in long, colourless needles; the position of the halogen is determined by the oxidation of the compound to 2:7-dibromophenanthraquinone (Abstr., 1904, i, 1034).

2:7-Dibromophenanthraquinone dioxime, $\text{C}_{14}\text{H}_8\text{O}_2\text{N}_2\text{Br}_2$, m. p. 290° (decomp.), crystallises in yellow needles; the diacetyl derivative, $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_2\text{Br}_2$, m. p. 250° (decomp.), forms sulphur-yellow needles, and is hydrolysed very readily. 2:7-Dibromophenanthrafurazan,

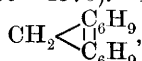


m. p. 306°, is obtained from the dioxime, benzoyl chloride, and sodium hydroxide, and forms colourless needles.

With reference to the question of colour and constitution, a comparison of the preceding compounds with the corresponding compounds of phenanthraquinonedioxime (Abstr., 1907, i, 630, 1022) shows that one and the same quinonoid nucleus can yield colourless or coloured derivatives according as the nuclear carbon atoms are attached to hydrogen or to bromine.

Saturated solutions of 9-bromophenanthrene and of picric acid, mixed at the ordinary temperature, yield yellow needles of the *picrate*, $\text{C}_{14}\text{H}_9\text{Br} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, m. p. 118°. C. S.

Hydrogenation of Fluorene. JULIUS SCHMIDT and ROBERT MEZGER (*Ber.*, 1907, 40, 4566—4570).—*Decahydrofluorene*,

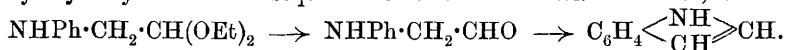


b. p. 258°/737 mm., is obtained from fluorene, hydriodic acid (D 1.96), and red phosphorus at 175° in an atmosphere of carbon dioxide, or from fluorene under Sabatier and Senderens' conditions at 150°. It has D_4^{20} 1.012, n_D^{20} 1.5060, gives yellow to violet colorations with warm

concentrated sulphuric acid, and a dark violet coloration with potassium dichromate and concentrated sulphuric acid, changing to bluish-green by dilution.

Liebermann and Spiegel's fluorene perhydride (Abstr., 1889, 719) and Guye's compound (Abstr., 1891, 314) are shown to be the decahydride. C. S.

Anilinoacetal. ALFRED WOHL and M. LANGE (*Ber.*, 1907, 40, 4727—4730. Compare Wohl, Abstr., 1888, 443).—Anilinoacetal was prepared in the hope that it would be possible to obtain indole from it by hydrolysis and subsequent removal of 1 mol. of water, thus:



This condensation could not, however, be effected.

Anilinoacetal, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, cannot be prepared by heating aniline and chloroacetal together, but may be obtained by adding these two substances to finely-divided sodamide suspended in ether; it is an oil, b. p. 92—94°/0.24—0.30 mm. Hydrolysis of this compound by acids does not result in the liberation of the corresponding aldehyde; instead, water splits off with the alcohol group and polymerisation ensues, the *substance*, $(\text{C}_8\text{H}_7\text{N})_6$, being produced. It is a greyish-white, amorphous substance, decomposing at 248°, and does not give the pine-shaving reaction.

A mixture of alcohol, sodium ethoxide, sodium iodide, formanilide, and chloroacetal heated under pressure at 150—160° for ten hours yields the *acetal*, $\text{CHO} \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, but it cannot be separated from unaltered formanilide. W. H. G.

Phenyl Derivatives of Primary Aromatic Amines. IRMA GOLDBERG [and FRL. C. SISOEFF] (*Ber.*, 1907, 40, 4541—4546. Compare Abstr., 1906, i, 426; Lambé, Abstr., 1907, i, 941).—Practically all primary arylamines are converted into corresponding diphenylamine derivatives when boiled with bromobenzene, potassium carbonate, and cuprous iodide in nitrobenzene solution for some hours. The cuprous iodide can be replaced with advantage by a mixture of potassium iodide and copper, and better yields are obtained when the acetyl derivatives of arylamines are used.

The following have been prepared by this method: acetyldiphenylamine; *acetylphenyl-p-tolylamine*, m. p. 52°; phenyl-*p*-tolylamine; *acetylphenyl-m-xylylamine* [$\text{Me}_2 : \text{NAc} = 1 : 3 : 4$], m. p. 115°; *phenyl-m-xylylamine* [$\text{Me}_2 : \text{NH} = 1 : 3 : 4$], m. p. 43°; *m-nitrodiphenylamine*, m. p. 112°; *o-nitrodiphenylamine*, m. p. 75°, and *p-nitrodiphenylamine*, m. p. 133°. J. J. S.

Coloured and Colourless Modifications of the Silver Salts of Halogen Phenols. ARTHUR HANTZSCH and KARL SCHOLTZE (*Ber.*, 1907, 40, 4875—4883. Compare Torrey and Hunter, this vol., i, 1030).—Salts of phenols which do not contain halogen are colourless and easily decompose; as halogen is introduced their stability is increased, and the salts of the tri-, tetra- and penta-halogen phenols are almost as stable as silver acetate. Coloured salts, varying from yellow to orange-red, exist of some of these, which sometimes contain

water, but in other cases are anhydrous, and have then the same composition as the colourless salts. The coloured silver salts are the primary form, as they result at once when the alkali salts are precipitated by silver nitrate; the colourless salts are quite stable, but they can to some extent be converted into the coloured salts by carefully acidifying their solutions in pyridine or ammonia. The coloured salts are most readily transformed into the colourless forms in presence of a moist solvent, but they are quite stable when completely dry.

The silver salts of *o*-, *m*-, and *p*-chlorophenol are colourless and decompose very rapidly; that of 2:4-dichlorophenol behaves similarly. Silver dichloro-*p*-cresol, m. p. 39°, is of a deep yellow colour, which becomes green as decomposition takes place. Silver-2:4:6-trichlorophenol is more stable, and cannot be converted into a colourless salt; the yellow compound crystallises with a molecule of water. Silver tetra- and penta-chlorophenol are yellow and orange respectively; the latter is not convertible into a colourless modification.

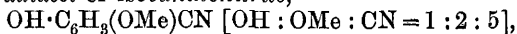
The silver salts of *p*-bromo- and 2:4-dibromo-phenol are colourless. Silver-2:6-dibromo-*p*-cresol forms a primary, labile, orange-coloured salt, $C_6H_2MeBr_2OAg, 3H_2O$, decomposing at 135°, which, when moist, very rapidly goes over into the stable, colourless salt. Silver-2:4:6-tribromophenol was obtained in orange-red and colourless modifications (compare Torrey and Hunter, *loc. cit.*). The coloured salt only slowly changes into the colourless form; both modifications form an ammoniate, $C_6H_2Br_3OAg, 2NH_3$. The silver salts of tetra- and penta-bromophenol and of tetrabromo-*p*-cresol are colourless.

The silver salts of *p*-iodo- and 2:4-di-iodo-phenol are colourless, as also are those of 2:6-di-iodo-*p*-cresol and 2:4:6-tri-iodophenol. E. F. A.

Position of the Iodine in the Two Known Iodoguaiacols. ERISIO MAMELI (*Gazzetta*, 1907, 37, ii, 366—379).—The structure of the 4-iodoguaiacol, m. p. 43°, prepared by Mameli and Pinna (*Arch. Farm. sper. Sci. affini*, 1907, 6, 193) by reducing benzeneazoguaiacol, diazotising the 4-aminoguaiacol, and decomposing the diazo-salt in presence of cuprous iodide, is confirmed. The compound, described by Tassilly and Leroide (*Abstr.*, 1907, i, 515) as 4-iodoguaiacol, is really 5-iodoguaiacol, its constitution having been based on that of Cousin's 4-nitroguaiacol (*J. Pharm. Chim.*, 1899, [vi], 9, 276), which Paul (*Abstr.*, 1906, i, 843) has shown to be 5-nitroguaiacol.

The positions of the iodine in these two iodoguaiacols have been further verified as follows. Cousin's nitroguaiacol (*loc. cit.*) was reduced to aminoguaiacol, which was diazotised and the diazo-derivative decomposed with cuprous cyanide; hydrolysis of the resulting 5-cyanoguaiacol (*vide infra*) yielded the corresponding known acid, isovanillic acid. Similar treatment of the aminoguaiacol from which the author and Pinna (*loc. cit.*) prepared their iodoguaiacol resulted in the formation of vanillic acid.

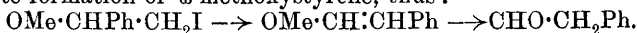
5-Cyanoguaiacol or isovanillonitrile,



crystallises from water in shining, brick-red needles, m. p. 124°, dissolves readily in ether and sparingly in alcohol or benzene, and gives a violet coloration with ferric chloride. T. H. P.

Iodohydrins and Alkyl iodohydrins derived from Styrene. MARC TIFFENEAU (*Compt. rend.*, 1907, 145, 811—813).—By the action of iodine and yellow mercuric oxide on styrene in the presence of ether, phenylethylene iodohydrin, $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CHI}$, is alone formed, but in the presence of an alcoholic solvent an alkyl iodohydrin, $\text{OR}\cdot\text{CHPh}\cdot\text{CH}_2\text{I}$, is also produced. In all cases, the hydroxyl combines with the carbon atom nearer to, the iodine with that farther from, the aromatic group (compare Abstr., 1906, i, 965). The constitution of the alkyl iodohydrins is proved by their transformation by alcoholic potash into α -alkyloxystyrenes: $\text{OR}\cdot\text{CHPh}\cdot\text{CH}_2\text{I} \rightarrow \text{OR}\cdot\text{CPh}\cdot\text{CH}$. Phenylethylene iodohydrin (compare Abstr., 1907, i, 404) has b. p. 148—152°/18 mm., and D_0 1.667; it soon decomposes, forming acetophenone.

When heated with sodium methoxide, *phenylethylene ω -methyl ether*, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{OMe}$, b. p. 132°/18 mm., 237—238°/760 mm., D_0 1.080, and a compound, $\text{C}_{16}\text{H}_{16}\text{O}_2$, b. p. 195—197°/18 mm., D_0 1.098, which combines with bromine and easily decomposes into acetophenone, are formed. With alcoholic potash, the iodohydrin gives the *ω -ethyl ether*, b. p. 242—243°/760 mm., D_0 1.054, and a substance, b. p. 187—190°/15 mm. *Phenylethylene methyl iodohydrin*, $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}_2\text{I}$, b. p. 135—138°(corr.)/14 mm., is transformed by alcoholic potash into *α -methoxystyrene*, b. p. 196—197°(corr.), D_0 1.0178, and by silver nitrate or acetate into phenylacetaldehyde, probably by the intermediate formation of *ω -methoxystyrene*, thus:

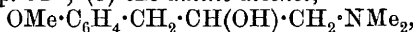


Phenylethylene ethyl iodohydrin, $\text{OEt}\cdot\text{CHPh}\cdot\text{CH}_2\text{I}$, b. p. 142—144°/16 mm., D_0 1.530, is converted by alcoholic potash into *α -ethoxystyrene*, b. p. 209—210°(corr.), D_0 0.991. *Phenylethylene amyl iodohydrin*, $\text{OC}_5\text{H}_{11}\cdot\text{CHPh}\cdot\text{CH}_2\text{I}$, b. p. 170—175°/15 mm., is transformed by alcoholic potash into *α -amyloxystyrene*, b. p. 255—259°, D_0 0.943, and by silver nitrate into phenylacetaldehyde and amyl alcohol.

E. H.

Presence of *p*-Methoxycinnamaldehyde in Essential Oil of Tarragon, and some Derivatives of Estragole. MAURICE DAUFRESNE (*Compt. rend.*, 1907, 145, 875—877).—Essential oil of tarragon contains from 4.5% to 0.5% of *p*-methoxycinnamaldehyde, which is isolated from the higher boiling fractions as a yellow oil, b. p. 171°/15 mm., D 1.137, and forms an *oxime*, m. p. 154°, and a semi-carbazone, m. p. 220°. Contrary to the experience of Scholtz and Wiedemann (Abstr., 1903, i, 437), the author finds that the synthetical compound prepared by the condensation of anisaldehyde with acetaldehyde has the same physical constants.

The iodohydrin of estragole yields (1) estragole oxide on treatment with powdered potassium hydroxide (compare Fournneau and Tiffeneau, Abstr., 1905, i, 591; 1906, i, 20); (2) *γ -*p*-methoxyphenylpropane- $\alpha\beta$ -diol*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{OH}$, on treatment with 15% solution of aqueous potassium hydroxide, this compound has b. p. 200—205°/20 mm. and m. p. 52°; (3) the *amino-alcohol*,



by reaction with dimethylamine, this alcohol has b. p.

166—167°/12 mm., D_0 1.038, and the hydrochloride of the *benzoyl* derivative has m. p. 98°; the corresponding *diethylamino*-compound, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NEt}_2$, has b. p. 187—189°/15 mm. or 308—310°/755 mm., D_0 0.946, and does not yield a crystalline benzoyl derivative.

The *methyl iodohydrin* of estragole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe}) \cdot \text{CH}_2\text{I}$, b. p. 178—180°/14 mm., D_0 1.459, yields the *methyl ether* of the corresponding vinyl alcohol, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}(\text{OMe}) \cdot \text{CH}_2$, by the action of boiling potassium hydroxide solution; this compound has b. p. 144—145°/15 mm. or 262—264°(corr.)/760 mm., D_0 1.073, and is hydrolysed by dilute sulphuric acid, forming anisylacetone.

M. A. W.

Cubebin. I. EFISIO MAMELI (*Gazzetta*, 1907, 37, ii, 483—506).—Previous work on cubebin is first discussed. From ten samples of cubebin of different ages and origins, the author succeeded, by various methods of purification, in preparing products exhibiting the same physical properties, and thus establishing the individuality of cubebin.

Pure cubebin has m. p. 132°, $[\alpha]_D^{25} - 45.45^\circ$ in chloroform or benzene, and empirical formula $\text{C}_{10}\text{H}_{10}\text{O}_3$. The mean molecular weight in freezing acetic acid is 265.71, and in boiling alcohol 329.07, the formula being hence $\text{C}_{20}\text{H}_{20}\text{O}_6$. From the known chemical reactions of cubebin, it is assumed to have the annexed formula.

T. H. P.

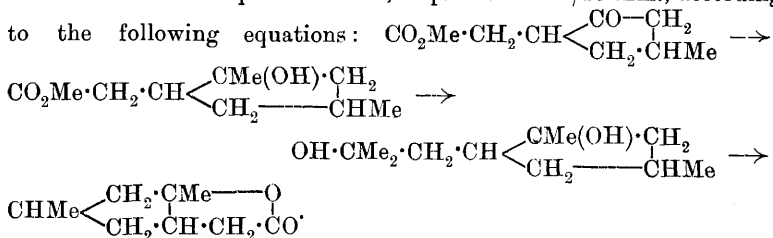
Salicylic Ester of Cholesterol. L. GOLODETZ (*Chem. Zeit.*, 1907, 31, 1215).—*Cholesteryl salicylate*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_{26}\text{H}_{43}$, prepared in a 60% yield by heating salicylic acid with cholesterol at 160—170°, separates from a mixture of ether and alcohol in white crystals, m. p. 173°, and is hydrolysed by boiling alcoholic potassium hydroxide, forming cholesterol and salicylic acid.

G. Y.

Synthesis of β -Campholenolactone; the Lactone of 2:4-Dimethylcyclopentane-2-olacetic Acid. GUSTAVE BLANC (*Compt. rend.*, 1907, 145, 930—932).—Preliminary to attempting the synthesis of β -campholenolactone from $\alpha\alpha$ -dimethyladipic acid, the author has synthesised the similarly constituted compound, the lactone of 2:4-dimethylcyclopentane-2-olacetic acid, from methyl- β -methyladipate by means of the following series of reactions. Methyl β -methyladipate, when treated with sodium, yields a compound which, according to Dieckmann (*Abstr.*, 1894, i, 173), should be *methyl methylcyclopentane-4-one-3-carboxylate*, $\text{CO}_2\text{Me} \cdot \text{CH} \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix}$, but

the possibility of the methyl group being adjacent to the carbonyl is not precluded. The sodium derivative of this ester reacts with ethyl bromoacetate to form the compound, $\text{CO}_2\text{Me} \cdot \text{CH} \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix}$, a colour-

less liquid, b. p. 165—168°/10 mm., which, on hydrolysis, yields *methylcyclopentane-4-one-3-acetic acid*, a viscous liquid, b. p. 195°/25 mm., forming a *semicarbazone*, m. p. 205°. The *methyl* ester of this acid is a sweet smelling, mobile liquid, b. p. 128°/14 mm., forms a *semicarbazone*, m. p. 190°, and by the action of magnesium methyl iodide yields a non-crystalline *glycol*, which is converted by the action of alkalis into the required *lactone*, b. p. 127—130°/13 mm., according



M. A. W.

Unsaturated Compounds. V. Addition of Mercaptans to Unsaturated Acids. THEODOR POSNER [with ROBERT BAUMGARTH] (*Ber.*, 1907, 40, 4788—4794. Compare *Abstr.*, 1904, i, 160; 1905, i, 279; 1906, i, 955; 1907, i, 55, 212).—Previous work has shown that addition of mercaptan to an unsaturated ketone occurs at the ethylenic linking. Unsaturated hydrocarbons show, in general, the same behaviour, but there are exceptions, notably stilbene and diphenylbutadiene, and, of the fifteen diolefines examined, in thirteen cases addition only occurred at one double bond. The work has been extended to unsaturated acids of the acrylic series. In all cases, the resulting sulphide produced by the interaction of the acids and mercaptans was not isolated as such, but oxidised to sulphone by potassium permanganate.

β-Phenylsulphonepropionic acid, $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained by the union of acrylic acid and thiophenol in glacial acetic acid during four weeks, crystallises from dilute alcohol in white leaflets, m. p. 56—57°. The position of the phenylsulphone group and, inferentially, that of the other sulphone groups, is shown to be the β by the preparation of β -phenylsulphone- β -phenylpropionic acid from cinnamic acid and thiophenol (compare Kohler and Reimer, *Abstr.*, 1904, i, 234). The *silver* salt, $\text{C}_{15}\text{H}_{13}\text{O}_3\text{SAg}$, is white, the *amide*, $\text{C}_{15}\text{H}_{15}\text{O}_3\text{NS}$, crystallises from water, m. p. 123—124°, and the *anilide*, $\text{C}_{21}\text{H}_{19}\text{O}_3\text{NS}$, has m. p. 157—158°. The *ethyl* ester, $\text{C}_{17}\text{H}_{15}\text{O}_4\text{S}$, forming white needles, m. p. 54—55°, is prepared from the acid; it could not be obtained from ethyl cinnamate and thiophenol. *β-Ethylsulphone-β-phenylpropionic acid*, $\text{SO}_2\text{Et}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, forms white crystals, m. p. 139—140°. The influence of the phenyl group in the β -position is to facilitate the addition; when the phenyl is also in the α -position, addition still occurs, but the α -phenylcinnamic acid and thiophenol have to be heated in a solution of glacial acetic acid, saturated with hydrogen chloride, under pressure for seven hours at 130°. The *β-phenylsulphone-αβ-diphenylpropionic acid*, $\text{SO}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, so derived crystallises from alcohol; m. p. 233—234°. The inference is drawn

that as stilbene does not form an additive compound with thiophenol, the carboxyl group exercises an influence. It is noteworthy that neither α -methyl- nor α -ethyl-cinnamic acid give products with thiophenol, and all three α -substituted cinnamic acids are not reactive towards ethyl mercaptan. Further, β -furfurylacrylic acid and mercaptans could not be made to unite.

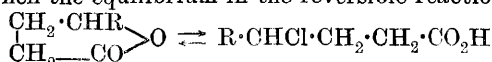
No additive product is obtained when *o*-nitrocinnamic acid and thiophenol are heated under pressure in glacial acetic acid solution saturated with hydrogen chloride at 100° for nine hours, but, when heated at 110° for eighteen hours, β -phenylsulphone- β -*o*-nitrophenyl propionic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{SO}_2\text{Ph}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is finally obtained as yellow crystals, m. p. 157—160°; the corresponding meta- and para-derivatives have m. p. 170° and 197—200° respectively. β -Phenylsulphone-*o*-tolylpropionic acid, $\text{SO}_2\text{Ph} \cdot \text{CH}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, obtained in a similar manner to the nitro-compounds, forms white, rectangular plates, m. p. 164—165°; the *m*-tolyl and *p*-tolyl derivatives have m. p. 235—236° and 210°. W. R.

Action of Potassium Hypochlorite on Cinnamamide. II. R. A. WEERMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 10, 308—309. Compare Abstr., 1907, i, 132).—The action of an alkaline solution of potassium hypochlorite on a methyl-alcoholic solution of cinnamamide results in the formation of methyl styrylcarbamate, b. p. 181—182°/14 mm.; m. p. 122—123° (corr.). Thiele and Pickard (Abstr., 1900, i, 29) give m. p. 115°. When similarly treated, *o*-nitrocinnamamide yields methyl *o*-nitrostyrylcarbamate,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{NH} \cdot \text{CO}_2\text{Me}$,
bright yellow needles, m. p. 149—150°.

W. H. G.

The Synthesis of Substituted Aromatic Acids. III. JOHAN F. EYKMAN (*Chem. Weekblad*, 1907, 4, 727—738. Compare Abstr., 1904, i, 669; 1905, i, 528).—Aliphatic lactonic acids, such as hexylparaconic acid, do not react with aromatic hydrocarbons in presence of aluminium chloride, even when the mixture is maintained at 40—50° for several weeks, indicating that the possibility of condensation depends on the nature of the group attached to the lactone ring. Since γ -cyanovalerolactone is also unaffected by these reagents, the non-reactivity cannot be due to the union of the CO_2H -group in hexylparaconic acid with the β -C-atom. Although monochloroacetic acid does not form condensation products by the Friedel and Crafts reaction, γ -chlorobutyric acid, like γ -butyrolactone (Abstr., 1907, i, 378), condenses with benzene and toluene to form γ -phenylbutyric acid and γ -tolylbutyric acid respectively, indicating that the γ -halogen-substituted acid is an intermediate product. The non-reactivity of hexylparaconic acid and γ -valerolactone is explained by the fact that when the equilibrium in the reversible reaction :



is greater on the side of the lactone, condensation does not take place. The condensation of Δ^8 -acids supports the view of the intermediate

production of hydrogen chloride additive products in the condensation with lactones.

Δ^β -Phenylcrotonic acid condenses with benzene to form $\gamma\gamma$ -diphenylbutyric acid (m. p. 107°), identical with that obtained from phenylbutyrolactone (Abstr., 1904, i, 669) and by reduction of dichloro- and dibromo-diphenylcrotonic acids (Hill and Dunlap, Abstr., 1897, i, 572). It is uncertain whether $\beta\gamma$ -diphenylcrotonic acid is also formed.

Allylacetic acid yields with benzene, γ -phenylvaleric acid, a non-crystallisable liquid, unlike that (m. p. 13°) obtained from the isomeric valerolactone. The difference may be due to the presence of a small proportion of δ -phenylvaleric acid.

Δ^β -Hydrosorbic acid, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, yields with benzene a liquid acid, probably a mixture of γ - and β -phenylhexoic acids. Allylcyanide gives with benzene a nitrile, possibly a mixture of γ - and β -phenylbutyronitriles, which hydrolyses to an oily acid, partly crystalline (m. p. about 50°). γ -Phenylbutyric acid melts at 51.7° . Δ^β - and Δ^α -Hydropiperic acids resinify. Allylmalonic acid does not form an aromatic substituted acid, so that an $\alpha\text{-CO}_2\text{H}$, like a $\beta\text{-CO}_2\text{H}$ and a $\gamma\text{-CN}$ group, prevents the condensation. α -Angelolactone,

$\text{CH}_3\cdot\overset{\text{O}}{\text{C}}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}$, yields with benzene, $\gamma\gamma$ -diphenylvaleric acid, colourless needles, m. p. 115° , and with toluene an oil,
 $\text{CH}_3\cdot\text{C}(\text{C}_6\text{H}_5)_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

β -Campholenic acid gives with benzene, β -phenyldihydrocampholenic acid, colourless crystals, m. p. about 90° , b. p. 190° (4 mm.). Crotonic acid yields with benzene a syrupy acid (b. p. 280°), possibly a mixture of α - and β -phenylbutyric acids.

*iso*Lauronic acid and benzene give a phenyldihydroisolauronic acid, colourless crystals (m. p. 119°), different from that obtained by Burcker (Abstr., 1895, i, 108) from camphoric anhydride, but probably having the constitution assigned by Blanc (Abstr., 1900, i, 329) to Burcker's acid.

The action of toluene and of anisole on camphoric anhydride is also under examination.

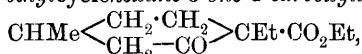
A. J. W.

β -Phenylcinnamic Acid ($\beta\beta$ -Diphenylacrylic Acid). HANS RUPE and E. BUSOLT (*Ber.*, 1907, 40, 4537—4540. Compare Kohler and Johnstin, Abstr., 1905, i, 215).—*Ethyl β -hydroxy- $\beta\beta$ -diphenylpropionate*, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is readily obtained by the action of dilute acid on the product formed by the condensation of benzophenone, ethyl bromoacetate, and zinc in the presence of benzene. It crystallises from dilute alcohol in glistening prisms, m. p. 87° . The corresponding *acid*, $\text{C}_{15}\text{H}_{14}\text{O}_3$, obtained by hydrolysing the ester with methyl-alcoholic potash, crystallises from dilute alcohol in pearly needles, m. p. 212° , and, when heated with sodium acetate and acetic anhydride, yields β -phenylcinnamic acid, m. p. 162° (Kohler and Johnstin, 155°). It can be distilled without decomposition at atmospheric pressure. The *ammonium*, *magnesium*, and *calcium* salts are somewhat sparingly soluble. When oxidised, the acid yields benzophenone.

J. J. S.

Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. VII. Influence of the Alkyl Groups on the Synthesis and Degradation of 1-Alkylcyclohexane-2-one-1-carboxylic Esters. ARTHUR KÖTZ [and, in part, ARTHUR BIEBER, LEOPOLD HESSE, and ADOLF SCHWARZ] (*Annalen*, 1907, 357, 192—208. Compare Abstr., 1906, i, 58, 59).—It has been shown in the previous parts of this investigation that the alkylation of *cyclopentane*- and *cyclohexane*-2-one-1-carboxylic esters by means of sodium ethoxide and an alkyl iodide takes place with diminishing velocity, as does also the ketonic and acid hydrolyses of the resulting alkyl derivative, as the weight of the alkyl increases. These generalisations are further illustrated in the present paper in the case of ethyl methylcyclohexane-3-one-4-carboxylate (Kötz and Hesse, Abstr., 1906, i, 88) and its derivatives.

Ethyl 1-methyl-4-ethylcyclohexane-3-one-4-carboxylate,



b. p. 126°/10 mm., prepared by the action of ethyl iodide on the potassium derivative of ethyl methylcyclohexane-3-one-4-carboxylate in xylene, forms a *semicarbazide*, $\text{C}_{13}\text{H}_{23}\text{O}_3\text{N}_3$, crystallising in white needles, m. p. 160°.

Ethyl 1-methyl-4-isopropylcyclohexane-3-one-4-carboxylate is prepared best by heating the potassium derivative of the same ester with isopropyl chloride in xylene under pressure at 120°.

When boiled with alcoholic potassium hydroxide, the *cyclohexane*-2-one-1-carboxylic esters yield *cyclohexane*-2-ones; in this manner, 1:4-dimethylcyclohexane-2-one has been obtained from ethyl 1:4-dimethylcyclohexane-2-one-1-carboxylate (Kötz and Hesse, *loc. cit.*), and 1-methyl-4-ethylcyclohexane-3-one (Haller, Abstr., 1905, i, 214) from ethyl 1-methyl-4-ethylcyclohexane-3-one-4-carboxylate.

Substituted pimelic esters are formed by boiling *cyclohexane*-2-one-1-carboxylic esters with sodium ethoxide in alcoholic solution. The following three esters have been prepared in this manner.

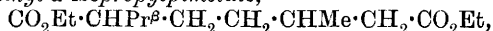
Ethyl αδ-dimethylpimelate, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, b. p. 152—153°/12 mm., from ethyl 1:4-dimethylcyclohexane-2-one-1-carboxylate, on hydrolysis with dilute hydrochloric acid, yields *αδ-dimethylpimelic acid*; the *silver salt*, $\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$, was analysed.

Ethyl δ-methyl-α-ethylpimelate,



from ethyl 1-methyl-4-ethylcyclohexane-3-one-4-carboxylate, is obtained as a colourless oil, b. p. 142—144°/10 mm., and, on hydrolysis with methyl-alcoholic potassium hydroxide, yields *δ-methyl-α-ethylpimelic acid*, which forms a hygroscopic, brown mass; the *silver salt*, $\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ag}_2$, was analysed.

Ethyl δ-methyl-α-isopropylpimelate,

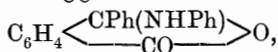


from ethyl 1-methyl-4-isopropylcyclohexane-3-one-4-carboxylate, is obtained as a transparent liquid, b. p. 151—153°/9 mm., and, on hydrolysis with methyl-alcoholic potassium hydroxide, yields the corresponding *acid*; the *silver salt*, $\text{C}_{11}\text{H}_{18}\text{O}_4\text{Ag}_2$, was analysed.

G. Y.

Acid-anilides, Anilo-acids, and ψ -Anilides. HANS MEYER (*Monatsh.*, 1907, 28, 1211—1230).—The numerous isomeric condensation products with primary bases of the type of aniline, which can be derived theoretically from *o*-aldehydo- and keto-acids by elimination of water from the components, have been studied previously in the aromatic series only in the case of the aldehydo-acids. The present paper contains an account of the substances obtained by the action of aniline on benzoylbenzoic acids.

o-Benzoylbenzoic acid reacts with aniline, forming, chiefly, *o*-benzoylbenzoyl- ψ -anilide, $C_6H_4 \begin{smallmatrix} \text{CPh(OH)} \\ \text{CO} \end{smallmatrix} \text{NPh}$ or, less probably,



which crystallises from acetone in colourless leaflets, m. p. 221° , dissolves in hot dilute alkalis, forming a slightly yellow solution, behaves as a ψ -acid on titration with potassium hydroxide in presence of phenolphthalein, and forms an oily, yellow potassium salt. When dissolved in alkalis and precipitated by acids, the ψ -anilide forms a hydrate, which may have the structure: $NHPh \cdot CPh(OH) \cdot C_6H_4 \cdot CO_2H$. It separates in colourless crystals, m. p. about 195° , loses only traces of water when heated in a steam-bath, and can be recrystallised unchanged from solvents boiling at low temperatures, but, on recrystallisation from boiling alcohol or glacial acetic acid, loses H_2O , forming the ψ -anilide, m. p. 221° . Reduction of the ψ -anilide with zinc and acetic acid leads to the formation of phenylphthalideanilide, $C_6H_4 \begin{smallmatrix} \text{CHPh} \\ \text{CO} \end{smallmatrix} \text{NPh}$, which is formed also by heating phenylphthalide with aniline and aniline hydrochloride; it separates from methyl alcohol in dull crystals, m. p. 195° , becomes electrified when rubbed, and gives Tafel's anilide reaction.

A substance, $CO \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NPh} \end{smallmatrix} \text{CPh} \cdot O \cdot \text{CPh} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NPh} \end{smallmatrix} CO$, formed as a by-product in the action of aniline on *o*-benzoylbenzoic acid, crystallises from alcohol in needles, m. p. 196° , is insoluble in aqueous alkalis, forms an intense orange-yellow solution in concentrated sulphuric acid, and, like the ψ -anilide, does not give Tafel's anilide reaction.

p-Benzoylbenzoic acid forms only a salt when heated with aniline. The anilide, $COPh \cdot C_6H_4 \cdot CO \cdot NHPh$, is prepared by the action of *p*-benzoylbenzoyl chloride on aniline; it crystallises in needles, m. p. 171° , and gives a bluish-red coloration with concentrated sulphuric acid and potassium dichromate.

o-Benzoylbenzoylanilide, formed together with the ψ -anilide by heating *o*-benzoylbenzoyl chloride containing small amounts of thionyl chloride with aniline in benzene solution, separates from acetic acid in colourless crystals, m. p. 195° , and gives a red coloration with concentrated sulphuric acid. A mixture of this anilide with the substance, m. p. 195° , obtained as a by-product in the preparation of the ψ -anilide from the acid, commences to sinter at 160° , m. p. 170° . The anilide is considered to be a secondary product of the action of benzoylbenzoyl chloride or of the thionyl chloride on the ψ -anilide, as this is transformed into the anilide when treated with thionyl chloride,

acetyl chloride, or boiling acetic anhydride. Reduction of the anilide by means of zinc and acetic acid leads to formation of phenyl-phthalide.

When boiled with acetic anhydride, opianyl- ψ -anilide, which does not behave as a ψ -acid on titration, is transformed into *opianylanilide*, m. p. 179°, which is insoluble in alkalis, and gives a rosaniline red with concentrated sulphuric acid.

Acetophenonecarboxylic acid reacts with aniline, forming a crystalline *substance*, m. p. 203°, which is not identical with the product of the action of phthalylacetic acid on aniline. G. Y.

Determination of the Constitution of Isomeric Derivatives of *o*-Keto-acids. HANS MEYER (*Monatsh.*, 1907, 28, 1231—1237).—From the discovery of isomeric esters of aromatic *o*-keto-acids has arisen amongst others the question whether such isomerism is limited to the ortho-series or may possibly occur in the meta- and para-series. Whilst it is difficult to establish a conclusion based only on negative evidence, it seemed of importance to show in a special case that the present methods of investigation give no indication of such isomerism. There remains then to be determined the constitution of the representatives of each series of derivatives as also of the free acids.

Methyl *p*-benzoylbenzoate, m. p. 107°, is obtained from *p*-benzoylbenzoic acid by all methods of esterification. *p*-Benzoylbenzoic acid does not form a mixed anhydride with acetic acid as does the *o*-acid.

The action of methyl sulphate on *o*-benzoylbenzoyl- ψ -anilide in alkaline solution, $\text{NPh} \cdot \text{CPh}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{K}$, leads to the formation of an *ester*, which forms greenish-yellow crystals, m. p. 132°, and must have the constitution: $\text{NPh} \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$; when heated with 10% acetic acid, it yields methyl benzophenone-*o*-carboxylate, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, which is identical with Plaskuda's ester, m. p. 52°. The constitution of this ester establishes, also, the constitutions of its isomerides and analogues.

Whilst the action of *o*-benzoylbenzoyl chloride, prepared by means of thionyl chloride, on aniline leads to the formation of a mixture of the anilide and ψ -anilide, the former only is obtained from aniline and the crystalline acid chloride prepared by means of phosphorus pentachloride.

The normal esters of both *p*-aldehydo- and *o*-keto-acids are formed by means of diazomethane or of the silver salt, and usually melt at a lower temperature than the ψ -esters. But whilst the action of thionyl chloride on the *o*-aldehydo-acids leads to the formation of normal acid chloride, the ψ -acid chloride is formed by the action of thionyl chloride on *o*-benzoylbenzoic acid. Wegscheider (*Abstr.*, 1906, i, 86) considers the free *o*-aldehydo-acids to have in aqueous solution a ψ -structure. Acids of the type of *o*-benzoylbenzoic acid, on the other hand, must have the normal structure. Such acids, however, undergo transformation readily with changes of temperature. Although at higher temperatures *o*-benzoylbenzoic acid forms the ψ -anilide, at the ordinary temperature it is a strong acid, having the conductivity constant $100k = 0.0379$ with $v = 1024$, or 0.0358 with $v = 2048$; $\mu_\infty = 374.5$.

G. Y.

Benzoquinoneoximecarboxylic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1907, 40, 4739—4743).—The authors have prepared benzoquinoneoximecarboxylic acid from 5-nitroso-*N*-methylanthranilic acid, $\text{NHMe}\cdot\text{C}\begin{smallmatrix} \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{H})\cdot\text{CH} \end{smallmatrix}\text{C}\cdot\text{NO}$, which is obtained from *o*-nitrosomethylaminobenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{NO})\text{Me}$, and alcohol or glacial acetic acid containing hydrogen chloride. The precautions to be observed in the isolation of the free acid from its hydrochloride are described. The acid separates from alcohol in dark green prisms with a blue lustre or in needles; it separates from glacial acetic acid in green needles. It begins to decompose about 100° ; when reduced, it forms a colourless compound, which very quickly becomes blue.

Benzoquinoneoximecarboxylic acid, $\text{OC}\begin{smallmatrix} \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{H})\cdot\text{CH} \end{smallmatrix}\text{C}\cdot\text{N}\cdot\text{OH}$, obtained by boiling 5-nitroso-*N*-methylanthranilic acid with aqueous sodium carbonate, has m. p. $162\text{--}163^\circ$; it crystallises from benzene in dark green scales, and from water, when crystallised quickly, in dark green needles. Its aqueous solution decomposes when filtered through ordinary filter paper. The acid decomposes on contact with air. It reacts with phenylhydrazine, semicarbazide, hydroxylamine, and aniline respectively.

A. McK.

Hydropinenealdehyde. JOSEF HOUBEN and HANS DOESCHER (*Ber.* 1907, 40, 4576—4579).—With the object of comparing derivatives of pinene hydrochloride and bornyl chloride with derivatives of *isobornyl* chloride, the author has prepared hydropinenealdehyde, $\text{C}_{10}\text{H}_{17}\cdot\text{CHO}$. For this purpose, methylformanilide was obtained by boiling methylaniline with anhydrous formic acid for six hours; it has b. p. $263^\circ/760$ mm. and $121^\circ/11$ mm. It was then boiled for eight hours with magnesium pinene hydrochloride (Houben, *Abstr.*, 1906, i, 21), when the following reaction takes place: $\text{C}_{10}\text{H}_{17}\cdot\text{MgCl} + \text{CHO}\cdot\text{NMePh} = \text{C}_{10}\text{H}_{17}\cdot\text{CH}(\text{OMgCl})\cdot\text{NMePh}$. The resulting magnesium compound, when decomposed in the usual manner, forms methylaniline hydrochloride and hydropinene aldehyde: $\text{C}_{10}\text{H}_{17}\cdot\text{CH}(\text{OMgCl})\cdot\text{NMePh} \rightarrow \text{C}_{10}\text{H}_{17}\cdot\text{CH}(\text{OH})\cdot\text{NMePh} \rightarrow \text{C}_{10}\text{H}_{17}\cdot\text{CHO} + \text{NHMePh}\cdot\text{HCl}$. *Hydropinenealdehyde*, isolated by aid of its sodium hydrogen sulphite compound, has an odour of camphor, undergoes oxidation with remarkable ease, and is very volatile with steam; m. p. above 120° , but indefinite, owing to the rapid oxidation of the aldehyde. Its *oxime*, $\text{C}_{10}\text{H}_{17}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, crystallises from light petroleum in needles, has m. p. $60\text{--}61^\circ$, and b. p. $143^\circ/13$ mm.

The *semicarbazone*, $\text{C}_{10}\text{H}_{17}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, separates from benzene in small needles, m. p. 220° .

A. McK.

Action of Organo-magnesium Pyridine Compounds on Aldehydes. BERNARDO ODDO (*Gazzetta*, 1907, 37, ii, 356—366).—The interaction of benzaldehyde and the pyridine compound of magnesium methyl iodide (compare *Abstr.*, 1904, i, 920) yields: (1) styrene; (2) phenylmethylcarbinol, and (3) the *ether*, $\text{O}(\text{CHPhMe})_2$, b. p. $240\text{--}245^\circ/20$ mm., $D_{25}^{25} 1.1154$, which has the normal molecular weight in freezing benzene, and when heated or treated with 10% potassium

hydroxide solution yields a crystalline compound, m. p. 90—92°, or 95°, according to its method of preparation.

The action of the pyridine compound of magnesium phenyl bromide on benzaldehyde yields: benzyl alcohol, benzyl ether, tetraphenylethane, diphenylcarbinol, and the ether, $O(CHPh)_2$. T. H. P.

Syntheses of Aromatic Aldehydes. II. The Hydrogen Cyanide Method. LUDWIG GATTERMANN (*Annalen*, 1907, 357, 313—383. Compare Abstr., 1906, i, 589).—The hydrogen cyanide method for the synthesis of aromatic aldehydes permits of the introduction of the aldehydo-group, CHO, into phenols, ethers, or other derivatives of phenols. The aldehydo-group is introduced into monohydric phenols in the para-position to the hydroxyl if this is occupied by hydrogen, the *p*-hydroxy-aldehydes being formed in 50% to 90% yields. If the para-position is already occupied by a substituting group, *o*-hydroxy-aldehydes are formed in small yields in the benzene series, but readily in the β -naphthols. The dihydric phenols with the hydroxyls in the meta-position to each other, and dihydroxynaphthalenes with both hydroxyls in β -positions, readily yield aldehydes with the aldehydo-group in the ortho-position to one of the hydroxyls. Catechol and quinol, on the other hand, yield only small amounts of an aldehyde, or do not undergo the reaction. Also, in the case of the trihydric phenols, pyrogallol, and hydroxyquinol, the aldehydo-group is readily introduced into the ortho-position to one, or in phloroglucinol to two, of the hydroxyls.

In the ethers of the phenols, the alkyloxy-groups have a similar, but weaker, effect on the orientation of the aldehydo-group. Thus the monomethyl ethers of the *m*-dihydroxybenzenes yield *p*-hydroxy-*o*-methoxy-aldehydes. The ethers of catechol readily form aldehydes, differing in this from the free phenol. Two aldehydo-groups are introduced only into the ethylene and trimethylene ethers of monohydric phenols and naphthols, and into dialkyloxydiphenyls.

Directions are given for the preparation of anhydrous hydrogen cyanide; this is condensed with the phenol in ethereal solution by means of hydrogen chloride alone or together with zinc chloride, or with phenols or phenol ethers in benzene solution, or in absence of a solvent, by means of aluminium chloride and hydrogen chloride. The following new aldehydes are described.

Hydroxytolualdehyde [Me:CHO:OH = 1:3:4], m. p. 56°, prepared from *p*-cresol, is volatile in steam; the *azine*, $C_{16}H_{16}O_2N_2$, crystallises in yellow needles, m. p. 232°.

p-Hydroxy-*m*-ethylbenzaldehyde, $C_9H_{10}O_2$, prepared from *o*-ethylphenol, crystallises in colourless needles, m. p. 172—173°; the *azine*, $C_{18}H_{20}O_2N_2$, forms yellow needles, m. p. 262°.

4-Hydroxy-2:5-dimethylbenzaldehyde, from *p*-xylenol in an 80% yield, crystallises in colourless needles, m. p. 132—133°. The *oxime*, $C_9H_{11}O_2N$, colourless needles, m. p. 155°; the *phenylhydrazone*, colourless leaflets, m. p. 164°; the *azine*, $C_{18}H_{20}O_2N_2$, yellow needles, m. p. 280° (decomp.); the *condensation product* with aniline, $C_{15}H_{15}ON$, crystallises in colourless needles, m. p. 143°. When heated with aniline hydrochloride in alcoholic solution, the aldehyde forms the

hydrochloride of an additive compound, $C_{15}H_{18}O_2NCl$, which crystallises in orange-red needles, decomp. about 240° . The action of the calculated amount of potassium nitrate on the aldehyde in concentrated sulphuric acid solution at -10° , leads to the formation of *3-nitro-4-hydroxy-2:5-dimethylbenzaldehyde*, $C_9H_9O_4N$, crystallising in colourless leaflets, m. p. 188° ; the *oxime*, $C_9H_{10}O_4N_2$, orange-red needles, decomp. 160° ; the *azine*, $C_{18}H_{18}O_6N_4$, orange needles, decomp. 237° ; the *aniline condensation product*, $C_{15}H_{14}O_3N_2$, forms ruby-red crystals with blue fluorescence, m. p. 136° . *4-Hydroxy-2:5-dimethylcinnamic acid*, $C_{11}H_{12}O_3$, crystallises in colourless needles, m. p. 171° .

4-Hydroxy-2:3-dimethylbenzaldehyde, from 1:2:3-xenol in a 60% yield, crystallises from toluene in colourless leaflets, m. p. 172° ; the *phenylhydrazone*, $C_{15}H_{16}ON_2$, silvery scales, m. p. 165° ; the *azine*, $C_{18}H_{20}O_2N_2$, yellow needles, m. p. 254° .

4-Hydroxy-3:5-dimethylbenzaldehyde, m. p. $115-116^\circ$ (114° : Thiele and Eichwede, Abstr., 1900, i, 501), forms an *azine*, $C_{18}H_{20}O_2N_2$, crystallising in yellow needles, m. p. $262-263^\circ$.

4-Hydroxy-2:6-dimethylbenzaldehyde, from *s*-xylene in an almost quantitative yield, crystallises in colourless needles, m. p. $189-190^\circ$. The *oxime*, colourless leaflets, m. p. 196° ; the *azine*, yellow needles, m. p. 240° .

2-Hydroxy-4:5-dimethylbenzaldehyde, colourless leaflets, m. p. 70° , volatile with steam; the *phenylhydrazone*, colourless needles, m. p. 195° ; the *azine*, yellow, crystalline powder, m. p. 317° (decomp.). On fusion with potassium hydroxide, the aldehyde yields *4:5-dimethylsalicylic acid*, m. p. 199° .

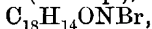
p-Carvacrolaldehyde, m. p. 96° , formed from carvacrol and hydrogen cyanide by the aluminium chloride method, is identical with Nordmann's aldehyde (Abstr., 1885, 162). Lustig's aldehyde (Abstr., 1886, 346) is probably the *o*-aldehyde. The *phenylhydrazone* of the *p*-aldehyde, $C_{17}H_{20}ON_2$, crystallises in glistening leaflets, m. p. 109° ; the *azine*, $C_{22}H_{28}O_2N_2$, yellow crystals, m. p. $238-240^\circ$; the *methyl ether*, b. p. 275° , formed by the action of potassium hydroxide and methyl iodide on the aldehyde, yields an *azine*, $C_{24}H_{32}O_2N_2$, yellow crystals, m. p. $184-185^\circ$, and on oxidation with alkaline permanganate is converted into the acid described by Gattermann and Obörländer (Abstr., 1899, i, 510).

When treated with hydrazine sulphate in dilute alcoholic solution, 1:4-hydroxynaphthaldehyde forms an *additive compound*,



which is obtained as a dark red substance, decomp. $220-236^\circ$, and when dissolved in alcohol loses water, forming the *azine*, $C_{22}H_{16}O_2N_2$, crystallising in yellow needles, m. p. 236° .

3-Bromo-4-hydroxy-1-naphthaldehyde, $C_{11}H_7O_2Br$, prepared by the action of bromine on 1:4-naphthaldehyde in cooled glacial acetic acid solution, crystallises in colourless needles, m. p. 145° , and forms *condensation products* with aniline, $C_{17}H_{12}ONBr$, leaflets, with red and green fluorescence, m. p. 180° (decomp.), with *p*-toluidine,



crystals with green and red lustre, m. p. 168° , and with *p*-xylydine, $C_{19}H_{16}ONBr$, red, monoclinic plates, m. p. 206° (decomp.).

With hydrogen cyanide and aluminium chloride in benzene solution, *ar*-tetrahydro-*a*-naphthol forms an *aldehyde*, $C_{11}H_{12}O_2$, which crystallises in yellow leaflets, m. p. 138—139°. The *condensation product* with aniline, $C_{17}H_{17}ON$, yellow to orange-red plates, m. p. 189°; the condensation product with *p*-toluidine, $C_{18}H_{19}ON$, yellow leaflets, m. p. 209—210°; the *azine*, $C_{22}H_{24}O_2N_2$, yellow needles, decomp. about 260°; the *methyl ether*, $C_{12}H_{14}O_2$, colourless needles, m. p. 58—59°.

2-Chloro-4-hydroxybenzaldehyde, $C_7H_5O_2Cl$, in a 50% yield, from *m*-chlorophenol, crystallises in colourless needles, m. p. 146·5°. The *oxime*, $C_7H_6O_2NCl$, stout crystals, m. p. 194°; the *azine*,

$C_{14}H_{10}O_2N_2Cl_2$,
yellow needles, m. p. 255° (decomp.).

2-Bromo-4-hydroxybenzaldehyde, formed in a 10% yield, crystallises in slightly yellow needles, m. p. 159·5°. The *oxime*, stout crystals, m. p. 128·5°, does not form an indoxazen derivative; the *azine*, needles, m. p. 260°.

Resorcyaldehyde condenses with aniline, forming a *product*,

$C_{13}H_{11}O_2N$,
crystallising in lemon-yellow needles, m. p. 131°. With aniline hydrochloride, the aldehyde forms an *additive* compound, $C_{13}H_{14}O_3NCl$, which crystallises in light yellow needles, and decomposes when heated. The *additive* compound, $C_{14}H_{14}O_5NCl$, formed with *p*-aminobenzoic acid in presence of hydrochloric acid, is obtained in yellow crystals, and decomposes when heated. The action of fuming nitric acid on the aldehyde in glacial acetic acid leads to the formation of 5-nitro-2:4-dihydroxybenzaldehyde, $C_7H_5O_5N$, which crystallises in yellowish-brown prisms, m. p. 148—149°. 3:5-Dinitro-2:4-dihydroxybenzaldehyde, $C_7H_4O_7N_2$, prepared by the action of fuming nitric acid on resorcyaldehyde, forms slightly yellow crystals, m. p. 170°. Both these aldehydes form intensely yellow or orange salts with alkalis, and give the typical aldehyde reactions; the crystalline derivatives mostly decompose when heated.

Chlororesorcyaldehyde, formed from chlororesorcinol, is obtained in the form of its *hydrate*, $C_7H_7O_4Cl$, which melts below 100°, and when more highly heated yields a sublimate of the aldehyde in colourless needles, m. p. 157°. The *oxime*, $C_7H_6O_3NCl$, colourless needles, m. p. 184°; the *azine*, $C_{14}H_{10}O_4N_2Cl_2$, yellow needles, m. p. above the b. p. of sulphuric acid; the *phenylhydrazone*, $C_{13}H_{11}O_2N_2Cl$, brownish-red needles, m. p. 185—193° (decomp.).

Cresorcyaldehyde, formed in a 90% yield from cresorcinol, crystallises from benzene in colourless needles, m. p. 146·5°. The *azine*, $C_{16}H_{16}O_4N_2$, yellow needles, m. p. 303° (decomp.).

1:5-Dihydroxy-4-naphthaldehyde, $C_{11}H_8O_3$, from 1:5-dihydroxynaphthalene, crystallises in yellow needles, m. p. 195—210°. 1:5-Dihydroxy-4-naphthylideneaniline, $C_{17}H_{13}O_2N$, forms dark red crystals, m. p. 195—196°.

2:7-Dihydroxy-1-naphthaldehyde, formed in an almost quantitative yield from 2:7-dihydroxynaphthalene, is obtained in the form of its *hydrate*, $C_{11}H_{10}O_4$, which crystallises in light yellow needles, m. p. 210—215° (decomp.), and over sulphuric acid in a vacuum, or more

quickly at 120° , loses H_2O , becoming yellowish-red. 2:7-Dihydroxy-1-naphthylideneaniline, $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$, crystallises in golden needles, m. p. $195-196^{\circ}$, when quickly heated.

2:6-Dihydroxy-1-naphthaldehyde, $\text{C}_{11}\text{H}_8\text{O}_3$, crystallises in light yellow needles, m. p. $185-190^{\circ}$ (decomp.). The naphthylideneaniline, $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$, forms orange-red needles with green lustre, and is partially melted at 215° , but not completely at 235° . The phenylhydrazone, $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$, crystallises in golden needles, and commences to decompose at 200° , m. p. about 230° .

Trihydroxybenzylideneaniline, $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}$, crystallises in ruby-red needles, m. p. 198° . The additive compound of pyrogallolaldehyde and aniline hydrochloride, $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CH}(\text{OH})\cdot\text{NHPh}\cdot\text{HCl}$, crystallises in yellow needles, m. p. 245° , and when boiled with water is converted into the benzylideneaniline.

Dihydroxycoumarin diacetate, $\text{C}_{12}\text{H}_{10}\text{O}_6$, prepared by heating phloroglucinolaldehyde with acetic anhydride and sodium acetate at $160-170^{\circ}$ under pressure, crystallises in needles, m. p. 138° , and when heated with dilute sulphuric acid yields dihydroxycoumarin, $\text{C}_9\text{H}_6\text{O}_4$, crystallising in yellow needles, m. p. above 250° (partial decomp.). The solutions of this are not fluorescent; it forms yellow salts with aqueous alkalis, ammonia, or calcium or barium hydroxide, and with aqueous ferric chloride gives a green coloration, becoming red, and a precipitate.

4-Hydroxy-2-methoxybenzaldehyde is formed in a 75% yield from resorcinol monomethyl ether, whilst anisaldehyde is obtained in an almost quantitative yield from anisole.

Orcinol monomethyl ether forms 4-hydroxy-6-methoxy-2-methylbenzaldehyde, $\text{C}_9\text{H}_{10}\text{O}_3$, which crystallises in colourless needles, m. p. 188° , and is not volatile with steam. The oxime, colourless needles, m. p. 127° ; the phenylhydrazone, $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$, yellow plates, m. p. 159° ; the azine, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, yellow leaflets, m. p. 253° (decomp.).

p-Ethoxybenzaldehyde, $\text{C}_9\text{H}_{10}\text{O}_2$, formed in an almost quantitative yield from phenetole, is obtained as a colourless oil, b. p. 249° , $D_{21}^{25} 1.08$, has a pleasant odour, and on oxidation with alkaline permanganate is converted into *p*-ethoxybenzoic acid. The oxime, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 83° ; the azine, $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$, crystallises in yellow leaflets, m. p. 172° , forming a turbid liquid, clearing at 197° ; the condensation product with benzidine, $\text{C}_{30}\text{H}_{28}\text{O}_2\text{N}_2$, crystallises in yellow leaflets, m. p. 248° to a turbid liquid, clearing when heated above the b. p. of sulphuric acid.

3-Chloro-4-methoxybenzaldehyde, $\text{C}_8\text{H}_7\text{O}_2\text{Cl}$, from *o*-chloroanisole, crystallises in colourless needles, m. p. 53° , and on oxidation yields 3-chloro-4-methoxybenzoic acid. The oxime, $\text{C}_8\text{H}_8\text{O}_2\text{NCl}$, forms colourless needles, m. p. 115° .

2-Chloro-4-methoxybenzaldehyde, from *m*-chloroanisole, is identical with Tiemann's aldehyde (Abstr., 1891, 704).

2-Chloro-4-ethoxybenzaldehyde, from *m*-chlorophenetole, crystallises in colourless needles, m. p. 66.5° . The oxime, $\text{C}_9\text{H}_{10}\text{O}_2\text{NCl}$, colourless needles, m. p. 89.5° .

2-Bromo-4-ethoxybenzaldehyde, from *m*-bromophenetole, crystallises in colourless needles, m. p. 69.5° .

4- β -Bromoethoxybenzaldehyde, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, formed in a 50% yield from β -bromoethoxybenzene, crystallises in colourless needles, m. p. 52° . The *oxime*, $\text{C}_9\text{H}_{10}\text{O}_2\text{NBr}$, colourless leaflets, m. p. 108° ; the *phenylhydrazine*, $\text{C}_{15}\text{H}_{15}\text{ON}_2\text{Br}$, silvery needles, m. p. 127° ; the *azine*, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2\text{Br}_2$, yellow needles, m. p. $176\cdot5^\circ$. 4- β -Bromoethoxybenzoic acid, $\text{C}_9\text{H}_9\text{O}_3\text{Br}$, prepared by oxidation of the aldehyde with permanganate in alkaline solution, crystallises in needles, m. p. 177° . When heated with potassium acetate and absolute alcohol at 150° under pressure, the bromo-aldehyde is converted into *p*- β -hydroxyethoxybenzaldehyde, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, which crystallises in colourless needles, m. p. 34° ; the *oxime*, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, colourless needles, m. p. 98 — 99° ; the *phenylhydrazine*, $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$, colourless needles, m. p. 102 — 103° ; the *azine*, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, light yellow needles, m. p. 184° , forming a turbid liquid, and clearing at 207° .

Methoxytolualdehyde [$\text{Me}:\text{CHO}:\text{OMe}=1:3:6$], b. p. 251° (Abstr., 1898, 476), is prepared from *o*-tolyl methyl ether; the *oxime*, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$, m. p. 68 — 70° , is formed together with traces of its *stereoisomeride*; the *azine*, $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$, yellow, nacreous leaflets, m. p. 172 — 173° . The corresponding 4-ethoxy-aldehyde (*loc. cit.*) crystallises from light petroleum in glistening needles, m. p. 33 — 34° ; the *oxime*, colourless needles, m. p. 92 — 93° ; the *azine*, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$, yellow leaflets, m. p. 155 — 156° ; the *condensation product* with benzidine, $\text{C}_{32}\text{H}_{32}\text{O}_2\text{N}_2$, yellow leaflets, m. p. 238° , forming a turbid liquid.

o-Tolyl β -bromoethyl ether, $\text{C}_9\text{H}_{11}\text{OBr}$, solidifies at -90° , b. p. 213 — $125/9$ mm. β -Bromoethoxy-*m*-tolualdehyde, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ [$\text{Me}:\text{CHO}:\text{C}_2\text{H}_4\text{Br}=1:3:6$], crystallises in colourless needles, m. p. 39° ; the *oxime*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{NBr}$, colourless needles, m. p. 73° ; the *azine*, $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_2\text{Br}_2$, yellow needles, m. p. 136° . 6- β -Hydroxyethoxy-*m*-tolualdehyde, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHO}$, prepared by the action of potassium acetate and alcohol on the β -bromo-compound, crystallises from benzene in slightly yellow needles, m. p. 61 — 62° ; the *oxime*, $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}$, colourless needles, m. p. 115° ; the *azine*, yellow needles, m. p. 184° .

Methoxytolualdehyde [$\text{Me}:\text{CHO}:\text{OMe}=1:2:5$], b. p. 257° (Abstr., 1898, i, 477), on oxidation, yields *m*-homoanisic acid; the *oxime*, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 81° ; the *azine*, golden needles, m. p. 141° ; the *condensation product* with benzidine, $\text{C}_{30}\text{H}_{28}\text{O}_2\text{N}_2$, yellow leaflets, m. p. 171° , forming a turbid liquid, which clears above the b. p. of sulphuric acid.

Ethoxytolualdehyde [$\text{Me}:\text{CHO}:\text{OEt}=1:2:5$], from *m*-tolyl ethyl ether, forms a strongly refracting, colourless oil, b. p. 260 — 262° ; the *oxime*, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$, stout crystals, m. p. 84° ; the *azine*, golden leaflets, m. p. 142° ; the *condensation product* with benzidine, $\text{C}_{32}\text{H}_{32}\text{O}_2\text{N}_2$, golden leaflets, m. p. 167° (turbid), clears above 300° .

Methoxytolualdehyde [$\text{Me}:\text{CHO}:\text{OMe}=1:3:4$], b. p. 250° (Abstr., 1898, i, 477), prepared from *m*-tolyl methyl ether, contains a small amount of the *isomeride* [$\text{Me}:\text{CHO}:\text{OMe}=1:2:4$], since, on oxidation, it yields an acid, m. p. 67° , accompanied by traces of a more sparingly soluble acid, m. p. 192 — 193° . The *oxime*, $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 144 — 145° .

Ethoxytolualdehyde [$\text{Me}:\text{CHO}:\text{OEt} = 1:3:4$], from *p*-tolyl ethyl ether, crystallises from light petroleum in colourless needles, m. p. 32—33°; the *oxime*, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$, colourless needles, m. p. 87°; the *azine*, yellow prisms, m. p. 154—155°.

4-Methoxy-2:6-dimethylbenzaldehyde, $\text{C}_{10}\text{H}_{12}\text{O}_2$, prepared from *s*-xylene methyl ether, b. p. 194·5°, crystallises in colourless needles, m. p. 18°, b. p. 271—272°; the *oxime*, colourless leaflets, m. p. 121·5°. *s*-Xylene ethyl ether, b. p. 208°, yields 4-ethoxy-2:6-dimethylbenzaldehyde, m. p. 279—280°, which does not solidify when cooled; the *oxime*, colourless needles, m. p. 100°. *v*-m-Xylene methyl ether, b. p. 182—183°, yields chiefly 4-hydroxy-3:5-dimethylbenzaldehyde, m. p. 116°, together with small amounts of the corresponding methoxy-aldehyde, $\text{C}_{10}\text{H}_{12}\text{O}_2$, b. p. 257°. *v*-m-Xylene ethyl ether, b. p. 194·5°, yields only moderate amounts of 4-ethoxy-3:5-dimethylbenzaldehyde, m. p. 265·5°.

4-Phenoxybenzaldehyde, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, from phenyl ether, solidifies in a freezing mixture, b. p. 191—193°/22 mm., and on oxidation with alkaline permanganate yields *p*-phenoxybenzoic acid. The *oxime*, $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}$, crystalline powder, m. p. 86°; the *azine*, sulphur-yellow leaflets, m. p. 143°; the *phenylhydrazone*, yellow leaflets, m. p. 123°.

4-Methoxy-1-naphthaldehyde, prepared by boiling 1:4-hydroxy-naphthaldehyde with methyl iodide and alcoholic potassium hydroxide, is obtained as a colourless liquid, b. p. 212°/40 mm., and, on oxidation, yields Gattermann and Hess's acid, m. p. 232° (Abstr., 1888, 574). With hydrazine sulphate, the aldehyde yields the *additive* compound, $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{C}_{10}\text{H}_6\cdot\text{OMe}$, which forms dark red needles, decomp. 160—182°, and, when heated with alcohol, loses $2\text{H}_2\text{O}$, forming the *azine*, $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2$, crystallising in light yellow needles, m. p. 182°; this again forms the *additive* compound on treatment with mineral acids. The corresponding *ethoxy-aldehyde*, $\text{C}_{13}\text{H}_{12}\text{O}_2$, forms yellow crystals, m. p. 75°; the *azine*, yellow needles, m. p. 209°.

2-Methoxy-1-naphthaldehyde, $\text{C}_{12}\text{H}_{10}\text{O}_2$, prepared from β -naphthyl methyl ether or 2-hydroxy-1-naphthaldehyde, crystallising in stout prisms, m. p. 83·5°; the *azine*, $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2$, crystallises from nitrobenzene in golden prisms with blue lustre, m. p. 255—256°. The corresponding *ethoxy-aldehyde* crystallises from glacial acetic acid in long needles, m. p. 110°; the *azine*, $\text{C}_{26}\text{H}_{24}\text{O}_2\text{N}_2$, golden crystals, m. p. 184°.

The aldehyde formed from veratrole crystallises in yellow needles, m. p. 43—44° (42°: Tiemann, this Journ., 1876, i, 76); the *oxime*, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, forms spherical aggregates, m. p. 88—89°; the *azine*, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, yellow leaflets, m. p. 189—190°; the *additive* compound with aniline hydrochloride, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}(\text{OH})\cdot\text{NHPh}\cdot\text{HCl}$, light yellow needles, m. p. 112°.

3:4-Diethoxybenzaldehyde, $\text{C}_6\text{H}_3(\text{OEt})_2\cdot\text{CHO}$, prepared from catechol diethyl ether, is obtained as an oil, b. p. 278—280°, and, on oxidation, yields protocatechuic acid diethyl ether; the *azine*, $\text{C}_{22}\text{H}_{28}\text{O}_4\text{N}_2$, yellow leaflets, m. p. 169—170°.

2:4-Dimethoxybenzaldehyde (Abstr., 1898, i, 477) forms an *oxime*,

$C_9H_{11}O_8N$, colourless needles, m. p. 106° , and an *azine*, $C_{18}H_{20}O_4N_2$, yellow needles, m. p. 195° .

2:5-Dimethoxybenzaldehyde, formed from benzoquinol dimethyl ether, crystallises in colourless needles, m. p. 53° . 2:5-Diethoxybenzaldehyde, colourless needles, m. p. 62.5° .

4:5-Dimethoxy-2-methylbenzaldehyde, $C_{10}H_{12}O_3$, formed from homocatechol dimethyl ether, crystallises in colourless needles, m. p. 76° , and, on oxidation, yields a *carboxylic acid*, $C_{10}H_{12}O_4$, crystallising in colourless needles, m. p. $146-147^\circ$, together with *m*-hemipinic acid. The *oxime*, $C_{10}H_{13}O_3N$, colourless needles, m. p. 124° ; the *azine*, yellow, rhombic plates, m. p. 228° . The corresponding methoxyethoxyaldehyde, $C_{11}H_{14}O_3$, m. p. $33-34^\circ$, b. p. $293-294^\circ$; the *oxime*, colourless leaflets, m. p. 116.5° .

The aldehyde prepared from cresorcinol dimethyl ether, b. p. 211° , crystallises in colourless needles, m. p. 116.5° ; the *oxime*, $C_{10}H_{13}O_3N$, nacreous leaflets, m. p. 145° . The isomeric aldehyde from orcinol dimethyl ether forms colourless needles, m. p. 62° ; the *azine*, $C_{10}H_{24}O_4N_2$, yellow leaflets, m. p. 193° ; the phenylhydrazone, $C_{16}H_{18}O_2N_2$, yellow needles, m. p. $100-101^\circ$.

The additive compound of asarylaldehyde and aniline hydrochloride, $C_{16}H_{20}O_4NCl$, crystallises in orange-yellow needles, m. p. 188° .

Catechol ethylene ether, prepared by the action of potassium hydroxide and ethylene dibromide on catechol, is a colourless oil, b. p. $110-111^\circ/31$ mm. or $99-100^\circ/17$ mm., and has an aromatic odour. Contrary to Moureu's statement (Abstr., 1898, i, 644), catechualdehyde ethylene ether has no odour; it is oxidised by permanganate, yielding proto-catechuic acid ethylene ether, m. p. 135.5° . The *azine*, $C_{18}H_{16}O_4N_2$, forms yellow needles, m. p. $190-191^\circ$.

Ethylene ether of 4-hydroxybenzaldehyde, $C_2H_4(O \cdot C_6H_4 \cdot CHO)_2$, prepared from phenyl ethylene ether, crystallises in colourless needles, m. p. $117-118^\circ$; the aniline derivative, $C_{28}H_{24}O_2N_2$, glistening leaflets, m. p. $183-184^\circ$; the phenylhydrazone, $C_{28}H_{26}O_2N_4$, brown leaflets, m. p. $217-218^\circ$. The corresponding trimethylene ether, $C_{17}H_{16}O_4$, crystallising in yellow needles, m. p. $135-136^\circ$, is formed from phenyl trimethylene ether, and also by the action of trimethylene dibromide on sodium *p*-hydroxybenzaldehyde; the dioxime, $C_{17}H_{18}O_4N_2$, colourless needles, m. p. $153-154^\circ$; the disemicarbazone, $C_{19}H_{22}O_4N_6$, colourless needles, m. p. $297-298^\circ$; the *azine*, $C_{17}H_{16}O_2N_2$, is obtained as a yellow, insoluble substance, m. p. above 360° , and is probably polymolecular.

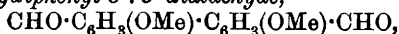
Ethylene ether of 6-hydroxy-*m*-tolualdehyde, $C_2H_4(O \cdot C_6H_3Me \cdot CHO)_2$, crystallises in colourless needles, m. p. 150° ; the *oxime*, yellow needles, m. p. $191-192^\circ$; the phenylhydrazone, $C_{30}H_{30}O_2N_4$, yellow crystals, m. p. 231° ; the aniline derivative, $C_{30}H_{28}O_2N_2$, colourless needles, m. p. 161° ; the *p*-toluidine derivative, $C_{32}H_{32}O_2N_2$, colourless needles, m. p. 156° . *o*-Tolyl trimethylene ether, $C_{17}H_{20}O_2$, forms a colourless oil, b. p. $225^\circ/28$ mm. or $341-343^\circ/760$ mm. The corresponding *di*-4:4'-aldehyde, $C_{19}H_{20}O_4$, crystallises in colourless needles, m. p. 114° .

Ethylene ether of 5-hydroxy-*o*-tolualdehyde, from *m*-tolyl ethylene ether, m. p. 91° , crystallises from glacial acetic acid in yellow leaflets,

m. p. 125—126°. *p*-Xylenol ethylene ether, $C_{18}H_{22}O_2$, crystallises in colourless needles, m. p. 82—83°, and forms a dialdehyde, $C_{20}H_{22}O_4$, obtained in a 66% yield and crystallising in colourless needles, m. p. 163°. α -Naphthyl trimethylene ether, $C_{23}H_{20}O_2$, crystallises in colourless needles, m. p. 103—104°. Trimethylene ether of 1:4-hydroxynaphthaldehyde, $C_{25}H_{20}O_4$, forms yellow needles, m. p. 159—160°; the oxime, $C_{25}H_{22}O_4N_2$, glistening leaflets, m. p. 192—193°; the aniline derivative, $C_{27}H_{30}O_2N_2$, is obtained as a yellow, crystalline precipitate, m. p. 188—189°. β -Naphthyl trimethylene ether, colourless leaflets, m. p. 148—149°; the dialdehyde, brown needles, m. p. 186—187°.

Guaiacol ethylene ether, $C_{16}H_{18}O_4$, crystallises in strongly refracting needles, m. p. 139—140°; the trimethylene ether, $C_{17}H_{20}O_4$, crystallises in colourless leaflets; m. p. 111°. An aldehyde could not be obtained from either of these ethers. Vanillin trimethylene ether, $C_{19}H_{20}O_6$, prepared by the action of sodium ethoxide and trimethylene dibromide on vanillin, crystallises in silvery needles, m. p. 145—146°, and is odourless; the oxime, $C_{19}H_{22}O_6N_2$, colourless needles, m. p. 161—162°; the aniline derivative, $C_{31}H_{30}O_4N_2$, yellow needles, m. p. 183—184°.

2:2'-Dimethoxydiphenyl-5:5'-dialdehyde,



prepared from 2:2'-dimethoxydiphenyl, crystallises in colourless needles, m. p. 130°. 2:2'-Diethoxydiphenyl, $C_{16}H_{18}O_2$, prepared by heating *o*-iodophenetole with copper powder, crystallises in colourless leaflets, m. p. 36—37°; the dialdehyde, $C_{18}H_{18}O_4$, forms colourless needles, m. p. 128°.

G. Y.

Methylation of Vanillin by Methyl Sulphate. HERMAN DECKER and OTTO KOCH (*Ber.*, 1907, 40, 4794—4795).—A simpler and better method of obtaining veratraldehyde than that employed by Perkin and Robinson is described (*Trans.*, 1907, 91, 1079). The method consists in using 0.9 mol. of potassium hydroxide, as the sodium vanillate is sparingly soluble, and gradually adding the alkaline solution to a hot solution of 1 mol. of vanillin and 0.9 mol. of methyl sulphate. The yield is 97%, and the unused vanillin can be recovered. In this method, excess of alkali is avoided, and consequent alteration of the aldehyde prevented. This procedure is applicable to phenols generally.

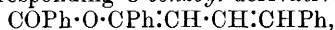
W. R.

Distillation of Calcium Azelate and the Formation of Azelaone. CARL D. HARRIES and LUDWIG TANK (*Ber.*, 1907, 40, 4555—4559).—Working with the products obtained from azelaic acid, the authors show that the substance prepared by the distillation of the calcium salt is not azelaone (*cyclooctanone*), but a complex mixture of isomeric, probably hepta-, hexa-, and penta-cyclic, ketones (compare Derlon, *Abstr.*, 1898, i, 638; Wallach, *Abstr.*, 1907, i, 602).

C. S.

Phenylisocrotophenone. HEINRICH WIELAND and HANS STENZL (*Ber.*, 1907, 40, 4825—4833).— α -Dinitro- α -diphenyl- Δ^8 -butylene- $NO_2 \cdot CHPh \cdot CH : CH \cdot CHPh \cdot NO_2$, is readily formed when a solution of

nitric peroxide in pure ether and light petroleum is gradually added to a suspension of diphenylbutadiene in absolute ether surrounded by a freezing mixture. On the addition of light petroleum or ether to its benzene solution, it is deposited in the form of snow-white needles, m. p. 158° (decomp.). When an ethereal suspension of the dinitro-derivative is poured on to dilute aqueous ammonia and repeatedly shaken, nitrous acid is eliminated and *a*-nitro-*ad*-diphenylbutadiene, $\text{NO}_2\cdot\text{CPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}$, is formed. It crystallises from hot alcohol or glacial acetic acid in well-developed, golden-yellow, glistening prisms, m. p. 111 — 112° , and dissolves in concentrated sulphuric acid to a deep red solution. When reduced with stannous chloride and aqueous alcoholic hydrochloric acid under special conditions, the nitro-derivative yields *phenylisocrotophenone*, $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHPh}$. This crystallises from hot alcohol in small, colourless needles, m. p. 93° . It does not give a coloration with ferric chloride, and dissolves in concentrated sulphuric acid to a colourless solution. When oxidised with permanganate, it yields benzoic acid. On the addition of sodium hydroxide solution to an alcoholic solution of the ketone, an intensely yellow solution of the sodium derivative of the isomeric enolic compound is formed. The sodium salt can be prepared by the addition of sodium wire to a dry ethereal solution of the ketone, but is readily hydrolysed by water. The corresponding *O*-benzoyl derivative,



forms brilliant, pale yellow crystals, m. p. 128 — 129° . It gives no reaction with ferric chloride, and is insoluble in cold alkalis, but is readily hydrolysed with warm alkalis.

The *oxime*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, forms colourless crystals, m. p. 104 — 106° . The ketone readily condenses with benzaldehyde in the presence of piperidine, yielding *dibenzylidenepropiophenone*, $\text{COPh}\cdot\text{C}(\cdot\text{CHPh})\cdot\text{CH}\cdot\text{CHPh}$, in the form of pale yellow needles, m. p. 117° . The ketone also condenses with amyl nitrite and diazobenzene salts.

J. J. S.

Direct Hydrogenation of Aromatic Diketones. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, 145, 1126—1127).—The study of the direct hydrogenation of diketones in the presence of nickel (Abstr., 1907, i, 587) has been extended to typical aromatic diketones, and the results show that the reaction proceeds as in the case of the simple aromatic ketones, with formation of the corresponding hydrocarbon (compare Darzens, Abstr., 1905, i, 66). *s*-Diphenylethane (dibenzyl) is obtained by the direct hydrogenation in the presence of nickel of benzil at 220 — 230° , or of benzoin at 210 — 220° . When α -diketo- α -phenylbutane (benzoylacetone) is similarly treated at 200° , 80% is converted into butylbenzene, containing traces of the hexahydro-derivative, and the remainder into a mixture of acetone, isopropyl alcohol, and toluene.

M. A. W.

Morindin. OTTO A. OESTERLE and EDUARD TISZA (*Arch. Pharm.*, 1907, 245, 534—553. Compare Thorpe and Smith, *Trans.*, 1888, 53, 171; Perkin and Hummel, *Trans.*, 1894, 65, 851).—A pyridine solution of morindin when heated with acetic anhydride yields the

acetate, $C_{27}H_{21}O_6(OAc)_9$, crystallising in thick, light lemon-yellow needles, m. p. 236° . The *benzoate*, $C_{27}H_{21}O_6(OBz)_9$, obtained by the action of benzoyl chloride on morindin in pyridine, crystallises in short, pale yellow needles, m. p. 186° . From the analytical results and the formation of the above derivatives, the authors conclude that morindin has the formula $C_{27}H_{30}O_{15}$, and not $C_{26}H_{28}O_{14}$ as assigned to it by Thorpe. The sugar obtained by the hydrolysis of morindin with dilute sulphuric acid reduces Fehling's solution and ammoniacal silver nitrate solution, has $[\alpha]_D^{20} - 2.18^\circ$, and is not fermented by yeast. The presence of a pentose could not be detected. The sugar yields a *phenylosazone*, yellow needles, m. p. 197° , and *α -phenylbenzylhydrazone*, brilliant yellow needles, m. p. $140-141^\circ$.

Morindone trimethyl ether, $C_{15}H_7O_2(OMe)_3$, corresponding with the triacetyl derivative described by Perkin and Hummel (*loc. cit.*), results from the action of methyl sulphate on morindone in alkaline solution; it forms a glistening, golden-yellow, fine crystalline powder, m. p. 229° . It is considered probable that morindin has the formula: $OH \cdot C_{15}H_7O_2[O \cdot C_6H_7O(OH)_4]_2$ or $C_{15}H_7O_2(OH)_2 \cdot O \cdot C_{12}H_{14}O_3(OH)_7$.

W. H. G.

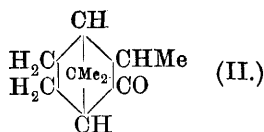
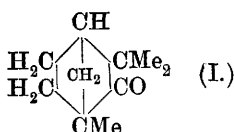
Syntheses of Optically Active *p*-Menthone. ARTHUR KÖTZ and ADOLF SCHWARZ (*Annalen*, 1907, 357, 209—213).—By a series of transformations, Kötz and Hesse (*Abstr.*, 1906, i, 88) synthesised *d-p*-menthone, starting from a hydroaromatic compound, 1-methylcyclohexane-3-one. Optically active menthone has now been synthesised from an aliphatic compound, ethyl δ -methyl- α -isopropylpimelate (this vol., i, 24). This is heated with sodium at 100° and finally at 140° , and the resulting mass is treated with ice-cold dilute sulphuric acid under ether. The ethyl menthonicarboxylate so formed is purified by solution in aqueous sodium carbonate and reprecipitation with sulphuric acid; on distillation, it is obtained as a slightly yellow oil, b. p. $145-149^\circ/14$ mm., has a slight odour of peppermint, gives a deep violet coloration with ferric chloride, and on hydrolysis by means of boiling dilute sulphuric acid yields *p*-menthone. *d-p*-Menthone, $[\alpha]_D + 30.20^\circ$, is formed also by distilling calcium δ -methyl- α -isopropylpimelate.

G. Y.

Constituents of Ethereal Oils. I. Separation of Camphor from Fenchone containing Camphor. II. Santene. FRIEDRICH W. SEMMLER (*Ber.*, 1907, 40, 4591—4598. Compare *Abstr.*, 1907, i, 1062).—The author describes a simple method of separating fenchone from camphor, no convenient method of effecting this separation having hitherto been described.

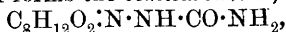
Fenchone and camphor may be separated by their entirely different behaviour towards sodium, camphor being very readily attacked, whilst fenchone may be distilled from sodium without undergoing decomposition.

This behaviour is adduced in favour of the author's formula for fenchone (I) in preference to Wallach's formula (II):



The author has also studied santene, C_9H_{14} , obtained by fractionating East Indian sandal-wood oil. The specimen used was optically inactive, had b. p. $31-33^\circ/9$ mm., D^{20} 0.863, and n_D 1.46658. The author considers that santene is an unsaturated dicyclic hydrocarbon. When dissolved in benzene and oxidised by ozone, it is converted into the *diketone*, $\text{C}_9\text{H}_{14}\text{O}_2$, b. p. $124-127^\circ/9$ mm., D^{20} 1.024, and n_D 1.46658; the *dioxime*, $\text{C}_9\text{H}_{16}\text{O}_2\text{N}_2$, has m. p. 129° ; the *disemicarbazone*, $\text{C}_9\text{H}_{14}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, has m. p. 216° .

When the ketone, $\text{C}_9\text{H}_{14}\text{O}_2$, is oxidised by sodium hydroxide and bromine, it is converted into the *ketonic acid*, $\text{C}_8\text{H}_{12}\text{O}_3$, which has b. p. $175-205^\circ/9$ mm., and forms the *semicarbazone*,

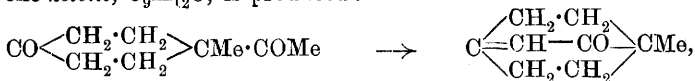


m. p. 168° .

The formation of santene from the tricyclic teresantallic acid, $\text{C}_{10}\text{H}_{14}\text{O}_2$, involves the disruption of the rings; it is not a simple process, but probably takes place in successive phases, as quoted by the author.

A. McK.

Constituents of Ethereal Oils. Further Derivatives of Santalene and the Formation of a New Dicyclic Saturated System—*dicyclo-2:2:2-Octane*. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 4844—4849. Compare Abstr., 1907, i, 781, and preceding abstract).—When the diketone, $\text{C}_9\text{H}_{14}\text{O}_2$, obtained by oxidising santene with ozone, is boiled for ten minutes with a dilute alcoholic solution of sodium ethoxide, condensation occurs between the methyl group and the ring carbonyl group, and a dicyclic ketone, $\text{C}_9\text{H}_{12}\text{O}$, is produced:

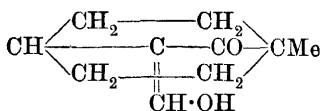


with b. p. $100-105^\circ/9$ mm., D^{20} 1.01, n_D 1.50387. The *semicarbazone* has m. p. 205° . When the diketone is reduced with sodium and alcohol, 1-methyldicyclo-2:2:2-octane-7-ol is formed, b. p.

98— $100^\circ/9$ mm., D^{20} 1.001, n_D 1.49668. It is stable towards permanganate. The acetate, $\text{C}_{11}\text{H}_{18}\text{O}_2$, has b. p. $104-106^\circ/9$ mm., D^{20} 1.011, and n_D 1.47151; the chloride, $\text{C}_9\text{H}_{15}\text{Cl}$, has b. p. $82-84^\circ/9$ mm., D^{20} 1.019, and n_D 1.49097. When reduced, the chloride yields the corresponding hydrocarbon, 1-methyldicyclo-2:2:2-octane, b. p. $149-151^\circ$, D^{20} 0.875, and n_D 1.46900.

When oxidised, the alcohol, $\text{C}_9\text{H}_{16}\text{O}$, yields the saturated ketone, $\text{C}_9\text{H}_{14}\text{O}$, b. p. $91-94^\circ/9$ mm., D^{20} 1.002, n_D 1.48950; the *semicarbazone* of which, $\text{C}_{10}\text{H}_{17}\text{ON}_3$, has m. p.

214°, and the *oxime*, b. p. 132—135°/10 mm., D^{20} 1.051, n_D 1.52058.



When reduced, the *oxime* yields an *amine*, $\text{C}_9\text{H}_{15}\cdot\text{NH}_2$, 7-*amino-1-methyl 2:2:2-dicyclooctane*, b. p. 76—77°/9 mm., D^{20} 0.940, n_D 1.49097; the *picric acid* has m. p. 206°. The *hydroxymethylene* derivative of the ketone (annexed formula) has b. p. 114—116°/11 mm., D^{20} 1.098, n_D 1.5263, and yields an intense coloration with ferric chloride.

J. J. S.

Action of Nitrogen Trioxide on Caoutchouc. CARL D. HARRIES (*Zeitsch. angew. Chem.*, 1907, 20, 1969—1970. Compare Abstr., 1905, i, 223).—Polemical. A criticism of Alexander's recent investigations (Abstr., 1907, i, 433).

W. H. G.

Lupeol. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 10, 292—295; *Compt. rend.*, 1907, 45, 926—929. Compare Abstr., 1904, i, 905; 1906, i, 20).—Lupeol, obtained from bresk, is not converted into lupeylene under the conditions mentioned by Jungfleisch and Leroux (Abstr., 1907, i, 783). It does not lose water when heated in a tube at 190°, and the acetate and benzoate obtained from fused lupeol are identical with those obtained from lupeol which has not been heated. The behaviour of lupeol on melting has been studied, and it is found that this compound exists in two modifications.

W. H. G.

Solubility of "half-hard" African Copals. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1907, [iv], 1, 1131—1143).—The author is making a systematic investigation of the chief analytical constants of the copals of commerce, and has already recorded these for the East African and American resins (Abstr., 1906, i, 870; 1907, i, 67). The present paper gives constants for West African copals.

Benguela copal has D^{16} 1.058, m. p. 165°, acid number 123.1, and Köttstorfer number 157.1. Angola white copal has D^{17} 1.055, m. p. 95°, acid number 127, and Köttstorfer number 159.9. Angola red copal has D^{17} 1.066, m. p. >300°, acid number 128.3, and Köttstorfer number 131.8. Congo copal has D^{17} 1.061, m. p. 195°, acid number 132.3, and Köttstorfer number 131.8. Sierra Leone copal has D^{19} 1.072, m. p. 130°, acid number 110.2, and Köttstorfer number 123.4.

The solubilities of these resins, under various conditions, in a number of organic solvents have been determined, and are given in the original.

T. A. H.

Alcohols and Resinous Acids in the Varnish from the Leaves of *Alnus Glutinosa*. HANS EULER and ASTRID EULER (*Ber.*, 1907, 40, 4760—4764).—From the varnish which covers the leaves of *Alnus glutinosa*, the authors have isolated two crystalline saturated alcohols which do not give the cholesterol reaction, and also two amorphous unsaturated resinous acids which give a marked cholesterol reaction.

Glutinol, $C_{14}H_{26}O$, separates from alcohol in leaflets, m. p. 70—71°. *Glutanol*, $C_{14}H_{26}O_2$ (?), m. p. 76°, differs from glutinol in being soluble in ether with difficulty. *Glutinic acid*, $(C_{28}H_{48}O_5)_x$, softens at 80°, and is possibly a mixture of isomerides. *Glutinic acid*, $C_{28}H_{44}O_7$, also does not melt sharply. A. McK.

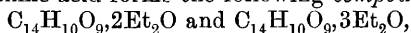
Transformation of Barbaloin into an Isomeride, β -Barbaloin ; Existence of this Latter in Several Aloes. EUGÈNE LÉGER (*Compt. rend.*, 1907, 145, 1179—1181. Compare Abstr., 1907, i, 631).—When barbaloin is heated at 160—165° for three hours, it loses its water of crystallisation, and is partially converted into an optical isomeride, β -barbaloin, which is obtained as an amorphous residue after the barbaloin has been removed by successive crystallisations of an alcoholic extract of the fused mass. β -Barbaloin yields the *chloro*-derivative, $C_{21}H_{16}O_9Cl_4 \cdot 5H_2O$, crystallising in prismatic needles, and a *bromo*-derivative, $C_{21}H_{16}O_9Br_4$. A chloride, $C_{21}H_{16}O_9Cl_4 \cdot 4H_2O$, crystallising in prismatic needles, is obtained by treating with hydrochloric acid and potassium chlorate the mixture obtained by heating barbaloin at 160—165°; this is a mixture of the chlorides of barbaloin and the β -isomeride, and the same mixture is obtained to the extent of 20—22% by the direct chlorination of Cape aloes, whereas they yield only 5% to 6% of crystalline barbaloin; it follows therefore that Cape aloes are richer in aloins than is generally admitted, but that part is present as the amorphous β -barbaloin. Similar results were obtained with Uganda and Socotra aloes. These yielded 20·10% and 23·35% respectively of the *chloro*-derivative, crystallising in needles, or the β -barbaloin can be isolated from the aloes by evaporating the mother liquors from which the barbaloin has been crystallised.

By the direct chlorination of Cape or Uganda aloes, in addition to the compound mentioned above, a *compound*, $C_{14}H_4O_3Cl_4$, is obtained as yellowish-white needles. This is probably methoxytetrachloronaphthaquinone. M. A. W.

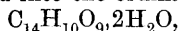
Tannin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1907, 40, 4575—4576).—Quebracho-tannin is oxidised by potassium persulphate in acetic acid containing a little concentrated sulphuric acid to a dark red substance, *rufiquebrachic acid*, which yields anthracene when distilled with zinc dust. C. S.

Tannic Acid in Toxicological Investigations. PIETRO BIGNELLI (*Gazzetta*, 1907, 37, ii, 506—520).—When tannic acid is employed as a precipitant for alkaloids, it must be borne in mind that it also forms insoluble compounds with other substances, such as certain solvents and mineral acids. Some of these compounds have been studied by the author.

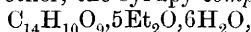
With ether, tannic acid forms the following *compounds* :



both of which are converted into the ordinary dihydrate,



on exposure to the air. When the dihydrate or its aqueous solution is treated with aqueous ether, the syrupy *compound*,



is obtained. With alcohol, the *compounds*:

$C_{14}H_{10}O_9, 2EtOH$ and $C_{14}H_{10}O_9, 3EtOH$ are formed, whilst chloroform, benzene, and light petroleum form no such compounds on treatment with aqueous 10% tannic acid solution.

With mineral acids, the following *compounds* are formed:

$C_{14}H_{10}O_9, H_2SO_4, 12H_2O$; $C_{14}H_{10}O_9, H_2SO_4, 14H_2O$, and $3C_{14}H_{10}O_9, 2HCl, 20H_2O$. The fact that these compounds are precipitated from relatively dilute mineral acid solutions, for example, 5% hydrochloric acid, renders it necessary to employ sufficiently diluted solutions when tannic acid is used as a precipitant for the alkaloids.

The formation of tannates of quinine is also discussed (compare Abstr., 1907, i, 955). T. H. P.

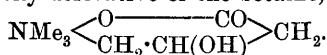
Action of Carbamide, Thiocarbamide, Urethane, and some Amides on Xanthhydrol. ROBERT FOSSE (*Compt. rend.*, 1907, 145, 813—815).—Xanthhydrol condenses with certain primary amides and with unsubstituted diamides, forming xanthyl amides and dixanthyl diamides respectively, which are very easily split up by the halogen acids, regenerating the amide, and forming unstable xanthyl halide salts. *Dixanthylcarbamide* is probably the symmetrical compound: $CO[NH \cdot CH : (C_6H_4)_2 : O]_2$. It forms faintly rose-coloured, silky needles, m. p. varying from 250° to 257 — 258° , according to the rapidity of heating, which are not altered by boiling aqueous alkali hydroxides. *Dixanthylthiocarbamide*, $CS[NH \cdot CH : (C_6H_4)_2 : O]_2$, forms small needles, having m. p. about 200° (decomp.), but varies with the time of heating. *Phenylxanthylthiocarbamide*, $NHPh \cdot CS \cdot NH \cdot CH : (C_6H_4)_2 : O$, crystallises in white, silky needles, which become green at 170° , then melt to a blue liquid, rapidly becoming maroon-coloured. *Xanthylurethane*, $O : (C_6H_4)_2 : CH \cdot NH \cdot CO_2Et$, forms fine needles, m. p. 168 — 169° ; *xanthylacetamide*, $O : (C_6H_4)_2 : CH \cdot NH \cdot COMe$, white needles, m. p. 238 — 244° ; *xanthylpropionamide*, $O : (C_6H_4)_2 : CH \cdot NH \cdot COEt$, colourless needles, m. p. 211 — 214° ; *xanthylbutyramide*, $O : (C_6H_4)_2 : CH \cdot NH \cdot COPr$, colourless needles, m. p. 186 — 187° ; *xanthylisovaleramide*,

$O : (C_6H_4)_2 : CH \cdot NH \cdot CH_2 \cdot CHMe_2$, white, silky needles, m. p. 182 — 184° ; *xanthylphenylacetamide*, $O : (C_6H_4)_2 : CH \cdot NH \cdot CO \cdot CH_2Ph$,

silky needles, m. p. 196 — 197° . E. H.

Extractives of Muscle. IX. Constitution of Carnitine. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1907, 53, 514—525. Compare Abstr., 1905, i, 726; 1907, i, 264).—The acid obtained by the decomposition of carnitine appears to be crotonic acid or an isomeric.

When the base is heated with hydriodic acid and red phosphorus at 130° for six hours, it yields a product identical with Willstätter's γ -trimethylbutyrobetaine (Abstr., 1902, i, 268). Carnitine is therefore undoubtedly a hydroxy-derivative of the betaine, probably



J. J. S.

Morphine. XVI. New Chlorocodide. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 4883—4889. Compare Abstr., 1907, i, 789, 956).—The β -chloromorphide (Ach and Steinbock, Abstr., 1907,

i, 1069), an intermediate product in the formation of *apomorphine*, which is an isomeride of chloromorphide (Schryver and Lees, *Trans.*, 1900, 77, 1029), yields, when methylated, a new *chlorocodide*; which, since it gives deoxycodine on reduction, contains the carbon-nitrogen skeleton of morphine. The isomerism between the two chloromorphides or the two chlorocodides is regarded as optical or position isomerism. In confirmation, β -chlorocodide, on hydrolysis, yields other products than the α -isomeride, namely, *isocodeine* (Lees, *Proc.*, 1906, 22, 253; 1907, 23, 200; *Trans.*, 1907, 91, 1408) and *allo- ψ -codeine* (Abstr., 1907, i, 956; Lees, *loc. cit.*).

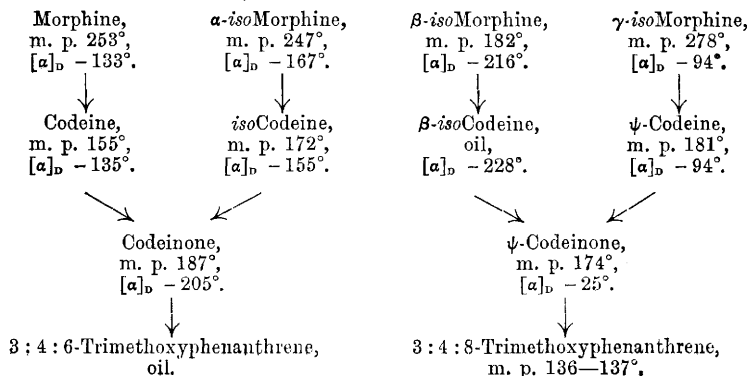
β -Chloromorphide has $[\alpha]_D^{15} - 5^\circ$ in methyl alcohol. When methylated with diazomethane, it forms β -*chlorocodide*, separating in well-formed, right-angled plates, m. p. $152-153^\circ$ (the same as α -chlorocodide, but a mixture of the two melted 30° lower); it has $[\alpha]_D^{15} - 10^\circ$.

β -Chlorocodide is obtained from codeine or ψ -codeine by heating with fuming hydrogen chloride in sealed tubes at $60-70^\circ$, or from α -chlorocodide in a similar manner; it yields deoxycodine when reduced with zinc dust and alcohol. When hydrolysed by boiling with dilute acetic acid, it yields a product, m. p. $140-150^\circ$, $[\alpha]_D^{15} - 170^\circ$, which, on crystallisation, proved to be identical with the A-base of Lees and Tutin (*loc. cit.*); this Lees (*loc. cit.*) has recognised as a molecular compound of *isocodeine* and β -*isocodeine*. Separation was effected by means of the acid oxalate, and the pure *isocodeine* obtained.

E. F. A.

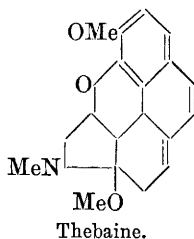
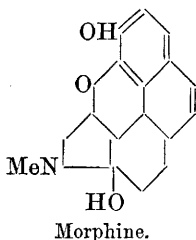
Morphine. XVII. Relationship of *iso*Codeine to Codeine. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, 40, 4889—4892).—*iso*Codeine, when oxidised with chromic acid in sulphuric acid solution, forms codeinone, identified by means of the oxime. Codeine and *isocodeine* are therefore identical in structure, and only differ with respect to the configuration of the groups attached to the asymmetric carbon atom in position 6.

The genetic relationship of the four isomeric morphines and codeines is therefore established, as shown in the following table (compare Schryver and Lees, *Trans.*, 1901, 79, 579; Lees and Tutin, *Proc.*, 1906, 22, 253; Oppé, *Abstr.*, 1907, i, 547; Lees, *Proc.*, 1907, 23, 200, *Trans.*, 1907, 91, 1408):



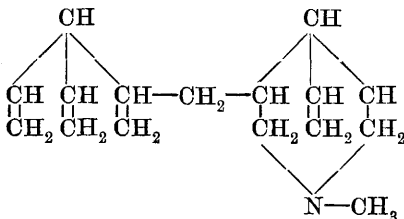
These facts are discussed in relation to the bridged-ring formula proposed for morphine (see Abstr., 1907, i, 789), according to which it contains four asymmetric carbon atoms. The configuration of three of these (positions 5, 9, and 13) is fixed by the bridge. But two optically active isomerides corresponding with position 6 are therefore possible. These are represented by morphine and *isomorphine*, and by their methyl ethers, codeine and *isocodeine*. The β - and γ -*isomorphines* and their methyl ethers differ from the above bases in the position of the alcohol hydroxyl group; in these, attached to position 8. In the ketones, codeinone and ψ -codeinone, the structural isomerism is due to the same difference in the position of the keto-group. E. F. A.

Constitution of Morphine and Thebaine. HANS TH. BUCHERER (*J. pr. Chem.*, 1907, [ii], 76, 428—432).—The results obtained in the investigation of the action of sulphites on pyridine and its derivatives, and consequently on morphine and thebaine, which will be published in detail later, have led the author to suggest for these two alkaloids the following structural formulæ, which are discussed shortly :



G. Y.

Sparteine. Application of Hofmann's Reaction to Sparteine Methylhemisparteilene. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1907, 145, 815—817. Compare Abstr., 1905, i, 716).—Crude methylsparteine ($\alpha_D - 25.2^\circ$ in alcohol), obtained by distilling methylsparteinium hydroxide in a vacuum, when treated with methyl iodide is methylated to the extent of 66%. From the methiodide formed, crude dimethylsparteine ($\alpha_D + 0.61^\circ$) is obtained, which on treatment with excess of methyl iodide gives a *dimethiodide*, $C_{15}H_{24}Me_2N_2 \cdot 2MeI \cdot H_2O$. The latter by the action of moist silver oxide (2 mols.) gives *tetramethylsparteinium dihydroxide*, $C_{15}H_{24}Me_2N_2(MeOH)_2$, which on distillation gives *methylhemisparteilene*, $C_{16}H_{25}N$, a liquid, b. p. $160-161^\circ/16$ mm., and $\alpha_D + 156.5^\circ$ (in alcoholic solution).



From its mode of formation, methylhemisparteilene should contain methyl attached to nitrogen, and four ethylenic linkings. These deductions are confirmed by analysis and by the molecular refractive power respectively. Thus the degradation of sparteine by Hofmann's reaction is more

profound than was at first considered, involving five instead of three piperidine nuclei. Only one of the latter remains in methylhemisparteilene.
E. H.

Two Isomeric Methylsparteines. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1907, 145, 929—930).—The crude methylsparteine, obtained by decomposing α -methylsparteinium hydroxide (preceding abstract), has $\alpha_D - 25^\circ$, and is a mixture of 10% of sparteine and 90% of α - and β -methylsparteine. The three bases can be separated by warming the mixture with a slight excess of normal sulphuric acid, whereby the α -methylsparteine sulphate is converted into the methosulphate; the sparteine and β -methylsparteine sulphates do not undergo this isomeric change, and the bases are separated by fractional crystallisation of the hydriodides.

α -Methylsparteine, $C_{15}H_{25}N_2Me$, m. p. $30-31^\circ$, b. p. $178-179^\circ$ (corr.)/11 mm., has a faint odour, and has $\alpha_D - 55.4^\circ$ in absolute alcoholic solution. The dihydrochloride is very deliquescent; the platinichloride, $C_{15}H_{25}N_2Me, H_2PtCl_6, 3H_2O$, is microcrystalline, and decomposes at 247° ; the dihydriodide, $C_{15}H_{25}N_2Me, 2HI$, crystallises in needles, and has $\alpha_D - 38.3^\circ$, and the picrate, $C_{15}H_{25}N_2Me, C_6H_3O_7N_3$, is amorphous.

β -Methylsparteine, $C_{15}H_{25}N_2Me$, a colourless liquid, b. p. $181-183^\circ$ (corr.)/16.5 mm., $\alpha_D + 9.9^\circ$, has an odour of onions, and is less stable in air than its isomeride. The hydriodide, $C_{15}H_{25}N_2Me, HI, 2H_2O$, is crystalline; the anhydrous salt has m. p. $77-78^\circ$, and $\alpha_D - 32.2^\circ$ in aqueous, or -28.2° in methyl-alcoholic, solution; the dihydriodide, $C_{15}H_{25}N_2Me, 2HI$, is crystalline, and has $\alpha_D - 13.5^\circ$ in methyl-alcoholic solution; the platinichloride, $C_{15}H_{25}N_2Me, H_2PtCl_6, 3H_2O$, has m. p. 230° , and the picrate, $C_{15}H_{25}N_2Me, 2C_6H_3O_7N_3$, has m. p. $94-95^\circ$.

α - and β -Methylsparteines are unsaturated bases, and in each compound the methyl group is attached to a nitrogen atom (compare Herzog and Meyer, *Abstr.*, 1896, i, 68).
M. A. W.

Sparteine. Isomerisation of α -Methylsparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1907, 145, 1184—1185. Compare preceding abstracts).—When α -methylsparteine dihydriodide, $C_{15}H_{25}N_2Me, 2HI$, is heated in a sealed tube at 125° with twice its weight of water, it is partially converted into isosparteine methiodide, $C_{15}H_{26}N_2, MeI$, $\alpha_D - 16.8^\circ$. The same compound is also obtained by treating α -methylsparteine dihydriodide with alkalis, but the yield is poor, and the best results are obtained by heating α -methylsparteine on the water-bath with a slight excess of *N*-sulphuric acid until the solution no longer reduces permanganate solution. The solution is then neutralised with barium hydroxide solution, and, on the addition of barium iodide, the hydriodide of isosparteine methiodide,

$C_{15}H_{26}N_2, MeI, HI, H_2O$, separates. isoSparteine hydriodide, $C_{15}H_{26}N_2, HI$, is obtained in a crystalline form by heating the hydriodide of isosparteine methiodide at $220-225^\circ$, and extracting the residue with hot water; it is also obtained by heating, at $225-230^\circ$, α -methylsparteine dihydriodide.

M. A. W.

Xanthine Bases. ERNST SCHMIDT (*Arch. Pharm.*, 1907, 245, 389—398).—In addition to the alkyltheobromines obtained from potassiotheobromine and alkyl iodides (which melt at a lower temperature and are more soluble in water than theobromine itself, in proportion, as the alkyl group contains more carbon atoms), corresponding alkyltheobromines with comparatively high melting points have been described as formed in a similar manner from silver theobromine. It is now shown that the ethyltheobromine of high melting point is really regenerated theobromine; a little ethyltheobromine is formed, but it has the lower melting point. Silver theobromine thus does not react with ethyl iodide to form an alkyl derivative by any means so readily as with methyl iodide. C. F. B.

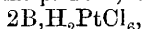
ψ -Theobromine. ERNST SCHMIDT and WILLMAR SCHWABE, jun. (*Arch. Pharm.*, 1907, 245, 398—405. Compare Pommerehne, *Abstr.*, 1897, i, 129; 1898, i, 539).— ψ -Theobromine is best prepared by heating silver xanthine with methyl sulphate at 150°; by taking suitable precautions, a yield can be obtained equal to 35—40% of the xanthine employed. The *sulphate*, $B, H_2SO_4, 2H_2O$; *aurichloride*, $B, HAuCl_4$, m. p. 251°, and *platinichloride*, $2B, H_2PtCl_6, 4H_2O$, are described [$B = C_7H_8O_2N_4$]. When ψ -theobromine is boiled with potassium dichromate and dilute sulphuric acid, it is oxidised to methylparabanic acid, methylamine, ammonia, and carbon dioxide; hence, it can only contain one methyl group in the carbamide residue. C. F. B.

Some Alkyl Derivatives of Theophylline. WILLMAR SCHWABE, jun. (*Arch. Pharm.*, 1907, 245, 312—325. Compare *Abstr.*, 1907, i, 449).—Ethyltheophylline, $C_9H_{12}O_2N_4$, was prepared by boiling dry potassiotheophylline with ethyl iodide and a little ethyl alcohol for six hours, or by digesting the same substance with ethyl sulphate for three days at the ordinary temperature; from it were prepared crystalline salts of the following composition: $B, HCl, 2H_2O$ ($2H_2O + HCl$ lost at 100°); B, HBr (stable at 100°); B, H_2SO_4 ; $B, HAuCl_4$, m. p. 224°; $2B, H_2PtCl_6$; $B, HgCl_2$; $B, Hg(CN)_2$; $B, AgNO_3, H_2O$; B, MeI , 182°; $[B, Me]AuCl_4$, 190°; $[B, Me]_2PtCl_6$, 250°. When ethyltheophylline is added to bromine, *bromoethyltheophylline*, $C_9H_{11}O_2N_4Br$, m. p. 170°, is formed, and, when this is boiled with alcoholic potassium hydroxide, it is converted into *ethoxyethyltheophylline*, $C_{11}H_{16}O_3N_4$, m. p. 78°. When ethyltheophylline is boiled with potassium dichromate and dilute sulphuric acid, it yields dimethylparabanic acid (cholestrophan), $C_5H_6O_2N_3$, m. p. 151° (not 145°, as stated usually), ethylamine, ammonia, and carbon dioxide. Ethyltheophylline is to be regarded as a 1:3-dimethyl-7-ethyl derivative.

n-Propyltheophylline, $C_{10}H_{14}O_2N_4$, was obtained by heating potassiotheophylline with *n*-propyl iodide and a little alcohol in a sealed tube in the water-bath. Salts: *aurichloride*, $B, HAuCl_4, 2H_2O$, m. p. 214°; *platinichloride*, $2B, H_2PtCl_6, 2H_2O$, crystalline.

*iso*Propyltheophylline was prepared by heating potassiotheophylline with *isopropyl* iodide and a little alcohol at 150°. Salts: *aurichloride*, $B, HAuCl_4, H_2O$, m. p. 183°; *platinichloride*, $2B, H_2PtCl_6, 2H_2O$, m. p. (anhydrous) 201°.

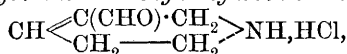
Benzyltheophylline, $C_{14}H_{14}O_2N_4$, was obtained by heating potassiumtheophylline with benzyl chloride in a sealed tube in the water-bath. The *aurichloride*, B_2HAuCl_4 , m. p. 104° , and *platinichloride*,



crystalline, are only stable in the presence of excess of the corresponding acids; they are decomposed by water with separation of benzyltheophylline. C. F. B.

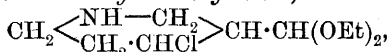
Aminoacetals and Aminoaldehydes. ALFRED WOHL (*Ber.*, 1907, 40, 4679—4684).—A discussion of the results contained in the following five abstracts and this vol., i, 17. W. H. G.

Tetrahydropyridine-3-aldehyde and Piperidine-3-aldehyde. ALFRED WOHL and M. S. LOSANITSCH, jun. (*Ber.*, 1907, 40, 4685—4698).— β -Iminodipropaldehyde tetraethylacetal (compare Abstr., 1906, i, 106) is converted by concentrated hydrochloric acid into Δ^3 -tetrahydropyridine-3-aldehyde hydrochloride,

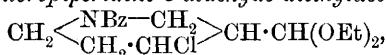


crystallising in needles, m. p. 144 — 145° (decomp.). The *free aldehyde*, C_6H_9ON , cannot be prepared from the hydrochloride by the action of potassium carbonate or sodium ethoxide, but is obtained in a polymerised form by dissolving the hydrochloride in cold diethylamine; it is a pale yellow, amorphous substance. The *oxime hydrochloride*, $C_6H_{10}ON_2 \cdot HCl$, forms colourless crystals, decomposing at 252° (corr.); treatment with potassium carbonate liberates the free *oxime*, $C_6H_{10}ON_2$; it forms groups of colourless crystals, softens at 142° , m. p. 144.5 — 145.5° (corr.).

4-Chloropiperidine-3-aldehyde diethylacetal,



prepared by the action of hydrogen chloride on the hydrochloride of Δ^3 -tetrahydropyridine-3-aldehyde dissolved in ethyl alcohol, is a colourless oil, b. p. $74^\circ/0.15$ mm. It readily loses hydrogen chloride, and consequently, on hydrolysis, is converted, not into the chloroaldehyde, but into Δ^3 -tetrahydropyridine-3-aldehyde hydrochloride. It is converted on treatment with benzoyl chloride and sodium hydroxide into 1-benzoyl-4-chloropiperidine-3-aldehyde diethylacetal,



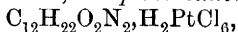
obtained as a soft, pale yellow mass, m. p. 35 — 40° . It does not give off hydrogen chloride so readily as the parent substance.

4-Chloropiperidine-3-aldehyde dimethylacetal, $C_8H_{16}O_2NCl$, is a colourless oil, b. p. 68 — $69^\circ/0.15$ mm.

1-Benzoyl- Δ^3 -tetrahydropyridine-3-aldehyde, $C_{13}H_{13}O_2N$, prepared by acting on β -iminodipropaldehyde tetraethylacetal in pyridine with benzoyl chloride and treating the product so formed with concentrated hydrochloric acid, forms colourless crystals, m. p. 90.5 — 91.5° (corr.). The corresponding *m*-nitrobenzoyl derivative, prepared in a similar manner, crystallises in colourless prisms, sinters at 160° , m. p.

161—162° (corr.). An acetal derivative of this compound could not be prepared.

4-Chloropiperidine-3-aldehyde diethylacetal is reduced by sodium and ethyl alcohol to *piperidine-3-aldehyde diethylacetal*, $C_{10}H_{21}O_2N$, a colourless liquid, b. p. 55°/0.15 mm., 104.5—105°/8.5 mm. It is hydrolysed by concentrated hydrochloric acid with the production of *piperidine-3-aldehyde hydrochloride*, but, since this could not be obtained in a crystalline form, the *platinichloride*,

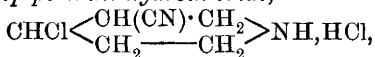


orange needles or rhombohedra, decomposing at 168—178°, and the *m-nitrophenylhydrazone hydrochloride*, $C_{12}H_{16}O_2N_4 \cdot HCl$, golden-yellow crystals, decomposing at 232—233° (corr.), were prepared. Piperidine-3-aldehyde hydrochloride, on treatment with diethylamine, yields the free *piperidine-3-aldehyde*, but, as is shown by mol. wt. determinations, only in the bimolecular form, $(C_6H_{11}ON)_2$; it is obtained as a pale yellow, amorphous mass.

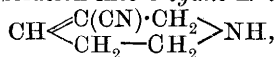
W. H. G.

Synthesis of the Racemic Cincholeuponic Acids. ALFRED WOHL and M. S. LOSANITSCH, jun. (*Ber.*, 1907, 40, 4698—4711).—Two stereoisomeric 4-pipecoline-3:ω-dicarboxylic acids, representing the two racemic forms of the cincholeuponic acids (compare Königs, *Abstr.*, 1896, i, 264; 1897, i, 497), have been synthesised from β-iminodipropaldehyde tetraethylacetal by way of Δ³-tetrahydropyridine-3-aldoxime (compare preceding abstract) and 3-cyano-Δ³-tetrahydropyridine. The acid, m. p. 211°, is named α- and the other acid, m. p. 229°, is named β-r-cincholeuponic acid; they have not yet been resolved into the active forms.

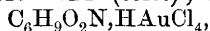
4-Chloro-3-cyanopiperidine hydrochloride,



obtained by the action of thionyl chloride on Δ³-tetrahydropyridine-3-aldoxime hydrochloride, crystallises in colourless plates and long, blunt prisms, decomposing at 192—193° (corr.). It is converted by sodium hydroxide in aqueous solution into 3-cyano-Δ³-tetrahydropyridine,



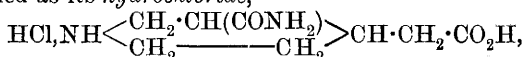
a colourless liquid, b. p. 48°/0.2 mm., 107.5°/12 mm.; the *platinichloride*, $C_{12}H_{16}N_4 \cdot H_2PtCl_6$, crystallises in long, golden-yellow needles, decomposing at 208—209° (corr.). Δ³-Tetrahydropyridine-3-carboxylic acid hydrochloride, $C_6H_9O_2N \cdot HCl$, is prepared by treating 4-chloro-3-cyanopiperidine hydrochloride successively with concentrated hydrochloric acid, barium hydroxide, and sulphuric acid; it crystallises in colourless prisms and needles, decomposing at 309—314° (corr.); the *platinichloride*, $(C_6H_9O_2N)_2 \cdot H_2PtCl_6$, crystallises in golden-yellow needles, decomposing at 215—224° (corr.); the *aurichloride*,



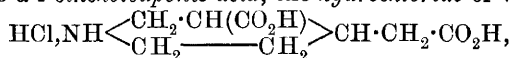
forms lemon-yellow prisms, m. p. 190° (decomp.); heated quickly, m. p. 196° (decomp.).

3-Cyano-Δ³-tetrahydropyridine condenses with ethyl malonate in the presence of sodium ethoxide in alcoholic solution with the formation of a "crude product," which, when heated for a short time with

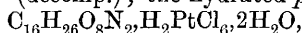
barium hydroxide and water, yields α -r-3-carboxylamido-4-piperidylacetic acid, obtained as its *hydrochloride*,



crystallising in long, colourless needles or prisms, which sinter at 242° and decompose at $244\text{--}245^\circ$ (corr.); heated quickly, at 251° (corr.). It is converted by concentrated hydrochloric acid into α -r-cincholeuponic acid *hydrochloride*. α -r-3-Cyano-4-piperidylacetic acid results on heating the above "crude product" for one to one and a-half hours with barium hydroxide and water; the *hydrochloride*, $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_2 \cdot \text{HCl}$, forms long, spear-shaped, colourless crystals, decomposing at 330° (corr.); it yields α -r-cincholeuponic acid when hydrolysed with concentrated hydrochloric acid. The "crude product," when heated from six to twelve hours with barium hydroxide and water, is converted almost entirely into α -r-cincholeuponic acid, the *hydrochloride* of which,



crystallises in colourless prisms or plates with rough faces; it softens at 210° , decomposes at $212\text{--}213^\circ$ (corr.). The free acid is obtained from the *hydrochloride* by treating it with slight excess of silver carbonate; it crystallises with 1 mol. of water in large, colourless prisms, decomposing at 145° ; the *anhydrous* acid decomposes at $208\text{--}209^\circ$. The *hydrobromide*, $\text{C}_8\text{H}_{13}\text{O}_4\text{N} \cdot \text{HBr}$, crystallises in prisms, softens at 218° , m. p. $224\text{--}225^\circ$ (decomp.); the hydrated *platinichloride*,



crystallises in orange-coloured plates or flat prisms, decomposing at $160\text{--}170^\circ$; the *anhydrous*, golden-yellow salt sinters at 205° and decomposes at 210° (corr.). A cold aqueous solution of α -r-cincholeuponic acid *hydrochloride*, when treated with sodium nitrite, yields 1-nitroso- α -r-cincholeuponic acid, $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_2$, crystallising in almost colourless prisms, m. p. $152\text{--}153^\circ$ (decomp. corr.). α -r-Cincholeuponic acid is decomposed by concentrated sulphuric acid at $270\text{--}280^\circ$ with the formation of 4-methylpyridine (compare Skraup, Abstr., 1897, i, 98), the *platinichloride* of which does not melt at 237° as given by Skraup, but decomposes at $244\text{--}245^\circ$; heated rapidly, at 258° (corr.).

β -r-Cincholeuponic acid *hydrochloride* is the chief product resulting from the action of concentrated hydrochloric acid on the above "crude product"; it crystallises in flat prisms, decomposing at $223\text{--}224^\circ$ (corr.), or, when heated quickly, at 229° . When heated with potassium hydroxide solution for six hours at $180\text{--}190^\circ$, it is converted into the α -acid. β -r-Cincholeuponic acid, $\text{C}_8\text{H}_{13}\text{O}_4\text{N}$, crystallises in colourless prisms, decomposing at $248\text{--}249^\circ$ (corr.); heated slowly, at 242° (corr.); the *hydrobromide*, $\text{C}_8\text{H}_{13}\text{O}_4\text{N} \cdot \text{HBr}$, forms large, granular crystals, decomposing at 226° (corr.); the *platinichloride*, $\text{C}_{16}\text{H}_{26}\text{O}_8\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, crystallises in orange-coloured, rhombic plates or prisms, decomposing at $218\text{--}225^\circ$ (corr.). 1-Nitroso- β -r-cincholeuponic acid, $\text{C}_8\text{H}_{12}\text{O}_5\text{N}_2$, is not so stable as the α -compound; it softens at 156° , m. p. $157\text{--}158^\circ$ (decomp.). The β -acid is converted under the same conditions as the α -acid into 4-methylpyridine.

W. H. G.

Arecaidine and Arecoline. ALFRED WOHL and A. JOHNSON (*Ber.*, 1907, 40, 4712—4719. Compare preceding abstract).—Arecaidine was first synthesised by Jahns (*Abstr.*, 1892, 737), who showed that it was a methyltetrahydronicotinic acid and assigned to it the formula : $\text{CH} \begin{smallmatrix} \text{CH} - \text{CH}_2 \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CO}_2\text{H}$. The authors show in the present paper how arecaidine may be synthesised from β -methyliminodipropaldehyde tetraethylacetal by way of 1-methyl- Δ^3 -tetrahydropyridine-3-aldehyde and 3-cyano-1-methyl- Δ^3 -tetrahydropyridine. From its mode of formation, it follows that the position of the ethylene-linking in Jahns' formula is incorrect, and that arecaidine has the constitution : $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{CO}_2\text{H}$; arecoline must consequently be represented by the formula : $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{CO}_2\text{Me}$.

β -Methyliminodipropaldehyde tetraethylacetal,
 $\text{NMe}[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$,

is prepared by heating under pressure a benzene solution of methylamine (three mols.) and β -chloropropaldehyde acetal (two mols.) at 125—135°; it is an almost colourless oil, b. p. 112°/0.48 mm. At the same time is formed small quantities of *β -methylaminopropaldehyde diethylacetal*, $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, a colourless oil.

1-Methyl- Δ^3 -tetrahydropyridine-3-aldehyde hydrochloride,
 $\text{C}_7\text{H}_{11}\text{ON}, \text{HCl}$,

results on treating the above tertiary base with cold concentrated hydrochloric acid; it forms long, white crystals, m. p. 194.5° (corr.). The *oxime hydrochloride*, $\text{C}_7\text{H}_{12}\text{ON}_2, \text{HCl}$, crystallises in long, colourless needles, m. p. 249.5° (corr.). Thionyl chloride converts the latter compound into *3-cyano-1-methyl- Δ^3 -tetrahydropyridine hydrochloride*, $\text{CH} \begin{smallmatrix} \text{C}(\text{CN}) \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > \text{NMe}, \text{HCl}$, colourless needles, m. p. 230.5° (corr.).

This substance on hydrolysis with concentrated hydrochloric acid yields arecaidine (1-methyl- Δ^3 -tetrahydronicotinic acid) hydrochloride, identical in all respects with that obtained from the betel-nut; the platinichloride, heated quickly, gives m. p. 225—226° (corr.); Jahns (*loc. cit.*) gives m. p. 208—209°. The arecoline prepared by the methylation of arecaidine, obtained as above, yields a methiodide identical with that described by Willstätter (*Abstr.*, 1897, i, 385). *Arecoline hydrobromide*, $\text{C}_8\text{H}_{13}\text{O}_2\text{N}, \text{HBr}$, crystallises in slender prisms, m. p. 167—169° (corr.); the *hydrochloride* forms deliquescent, slender needles, m. p. 157—158° (corr.).

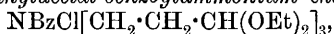
W. H. G.

A Tertiary Triacetal Base and Arecaidinealdehyde. ALFRED WOHL and E. GROSSE (*Ber.*, 1907, 40, 4719—4722. Compare preceding abstract).—An investigation on tripropaldehydehexaethylacetalamine, $\text{N}[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_3$; the chemical properties of such tertiary triacetal bases have not hitherto been studied.

Tripropaldehydehexaethylacetalamine is formed together with β -iminodipropaldehyde tetraethylacetal by the action of ammonia on β -chloropropaldehyde diethylacetal (compare Wohl, Hertzberg, and Losanitsch, *Abstr.*, 1906, i, 106). It is a lemon-yellow, viscous oil,

b. p. 209—210°/11 mm., 127—128°/0.06 mm., and combines with methyl iodide, yielding *tripropaldehydehexaethylacetal-methylammonium iodide*, $\text{NMeI}[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_3$, colourless crystals, m. p. 93.5°. An aqueous solution of this compound, treated with silver chloride, yields the corresponding *chloride*, an exceedingly deliquescent substance; the *aurichloride*, $\text{C}_{22}\text{H}_{47}\text{O}_6\text{N} \cdot \text{HAuCl}_4$, m. p. 57°, is difficultly soluble in water. The chloride, when evaporated with dilute hydrochloric acid in a vacuum at 50°, is decomposed into 1-methyl- Δ^3 -tetrahydropyridine-3-aldehyde (arecaidinealdehyde) hydrochloride (compare preceding abstract) and acraldehyde.

Arecaidinealdehyde, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{NMe} \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CHO}$, may be obtained by acting on an aqueous solution of the hydrochloride with potassium carbonate; it is a colourless oil, b. p. 40—43°/0.17 mm., with a pungent, basic odour, and changes into a dark brown solid when kept a short time. It combines readily with benzoyl chloride, forming *tripropaldehydehexaethylacetal-benzoylammonium chloride*,

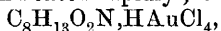


a green, crystalline substance, m. p. 60°.

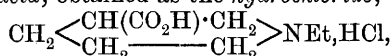
W. H. G.

1-Ethylnipecotinic Acid and ω -Amino-1-ethyl- β -pipecoline.
ALFRED WOHL and M. S. LOSANITSCH, jun. (*Ber.*, 1907, 40, 4723—4727. Compare Abstr., 1906, i, 106, and preceding abstracts).

—3-Cyano-1-ethyl- Δ^3 -tetrahydropyridine, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{NEt} \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CN}$, is obtained from its hydrochloride (compare Abstr., 1906, i, 106) on treatment with potassium carbonate; it is a colourless oil, b. p. 51—53°/0.04 mm.; the crystalline *aurichloride*, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{HAuCl}_4$, m. p. 144—145° (decomp.), decomposes slightly at 110°. The nitrile yields, on hydrolysis with concentrated hydrochloric acid, 1-ethyl- Δ^3 -tetrahydropyridine-3-carboxylic acid hydrochloride, $\text{C}_8\text{H}_{13}\text{O}_2\text{N} \cdot \text{HCl}$, crystallising in white needles, which soften at about 225°, m. p. 232—233° (decomp.); the *platinichloride*, $\text{C}_{16}\text{H}_{26}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, decomposes at 229° (corr.) when heated rapidly; the *aurichloride*,

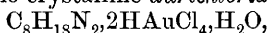


crystallises in short, lemon-yellow prisms, softens at about 205°, m. p. 214—215° (corr.). The above tetrahydro-acid hydrochloride is reduced by sodium and ethyl alcohol to 1-ethylnipecotinic (1-ethylpiperidine-3-carboxylic) acid, obtained as the *hydrochloride*,



white needles, softening at 170°, m. p. 178° (not sharp); the *aurichloride* crystallises in prisms, m. p. 158° (corr.); the *platinichloride* forms crystals, m. p. 214—215° (decomp.).

ω -Amino-1-ethyl- β -pipecoline (3-aminomethyl-1-ethylpiperidine) is obtained by the reduction of 1-ethyl- Δ^3 -tetrahydropyridine-3-aldoxime with sodium and ethyl alcohol; it is a colourless liquid, b. p. 105—110°/20 mm. The crystalline *aurichloride*,

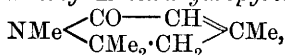


m. p. 184—185° (corr.), and *platinichloride*, $\text{C}_8\text{H}_{18}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$,

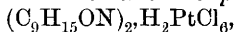
crystallising in orange plates and prisms, m. p. 239° (corr.), were prepared.
W. H. G.

Hydrolysis of Oxyhydropyridine Nitriles. I. GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1907, 42, 1004—1017).—The monocarboxylic acids corresponding with 3-cyano-2-keto-4:6:6-trimethyl- Δ^3 -tetrahydropyridine and 3-cyano-2-keto-1:4:6:6-tetramethyl- Δ^3 -tetrahydropyridine are unstable, so that, when these cyano-derivatives are hydrolysed, compounds are obtained in which the cyanogen group is replaced by hydrogen.

2-Keto-1:4:6:6-tetramethyl- Δ^3 -tetrahydropyridine,

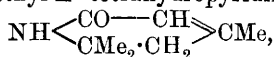


prepared by hydrolysing its 3-cyano-derivative by the action of an excess of concentrated hydrochloric acid at 140—150°, solidifies in somewhat hygroscopic, hard, colourless crystals, m. p. 49·5°, b. p. 250°/745 mm.; has the normal molecular weight in freezing benzene, and reduces permanganate in the cold. Its *platinichloride*,



m. p. 205·5°, *picrate*, $\text{C}_9\text{H}_{15}\text{ON}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 126°, and *aurichloride*, $(\text{C}_9\text{H}_{15}\text{ON})_2, \text{HAuCl}_4$, m. p. 122—123°, were prepared.

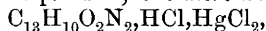
2-Keto-4:6:6-trimethyl- Δ^3 -tetrahydropyridine,



obtained by the action of hydrochloric acid on the corresponding 3-cyano-compound, separates in white crystals, m. p. 120—121° [Benedicenti and Quenda (*R. Acc. Med. Torino*, 51, iv) gave m. p. 115—116°]. Its *hydrochloride*, $\text{C}_8\text{H}_{13}\text{ON}, \text{HCl}, \text{H}_2\text{O}$, m. p. 79—80°, or, in the anhydrous condition, 110—115°, *picrate*, $\text{C}_8\text{H}_{13}\text{ON}, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 123°, and *platinichloride*, $(\text{C}_8\text{H}_{13}\text{ON})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$, m. p. 118—120°, or, in the anhydrous state, 177°, were prepared.

T. H. P.

Condensation of γ -Picoline with *o*-Nitrobenzaldehyde. MARTIN LÖWENSOHN (*Ber.*, 1907, 40, 4860—4863).— γ -Picoline (4-methylpyridine) and *o*-nitrobenzaldehyde condense when heated with zinc chloride under pressure at 170—180° for nine to ten hours, yielding 2'-nitro-4-stilbazole, $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$, m. p. 98—100°. The *hydrochloride*, $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2, \text{HCl}$, has m. p. 191—192°; the *nitrate*, m. p. 95°; the *sulphate*, $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2, \text{H}_2\text{SO}_4$, m. p. 110°; the *platinichloride*, m. p. 206°; the *aurichloride*, m. p. 215°; the *mercurichloride*,



m. p. 175—176°, and the *picrate*, m. p. 198°.

2'-Amino-4-stilbazole, $\text{C}_{13}\text{H}_{12}\text{N}_2$, immediately forms the carbonate, $(\text{C}_{13}\text{H}_{12}\text{N}_2)_2\text{H}_2\text{CO}_3$, m. p. 76°. The *hydrochloride* has m. p. 205°; the *sulphate*, m. p. 140°; the *stannichloride*, m. p. 155°, and the *platinichloride*, m. p. 238°.

When reduced with hydriodic acid and red phosphorus at 150°, the amine yields 2'-aminodihydro-4-stilbazole, $\text{C}_{13}\text{H}_{14}\text{N}_2$, in the form of small, colourless needles, m. p. 76°. The *hydrochloride* has m. p. 247°, and the *picrate* melts above 300°.

The diazo-salts obtained from 2'-amino-4-stilbazole couple with

alkaline solutions of phenols, yielding dyes. 4-*Stilbazole-2'-azo-β-naphthol hydrochloride*, $C_{23}H_{14}ON_3Cl$, separates from alcohol in red needles. Dyes have also been obtained by coupling the diazo-solution with β-naphtholdisulphonic acid, for example, *sodium 4-stilbazole-2'-azo-β-naphtholdisulphonate*, $C_{23}H_{15}O_7N_3S_2Na_2$. Also, 4-*stilbazole-2'-azo-resorcinol hydrochloride*, $C_{19}H_{16}O_2N_3Cl$ (yellow); *sodium salt of 4-stilbazole-2'-azonitro-α-naphthol*, $C_{23}H_{15}O_3N_4Na$ (dark yellow); *sodium 4-stilbazole-2'-azo-β-naphtholsulphonate*, $C_{23}H_{16}O_4N_3SNa$ (red); *sodium salt of 4-stilbazole-2'-azo-α-naphthol*, $C_{23}H_{17}ON_3Na$ (pale yellow), and the corresponding *sulphonate*, $C_{23}H_{16}O_4N_3SNa$ (yellow.) J. J. S.

Conversion of Acridone into Phenylacridine Derivatives. FRITZ ULLMANN, WALTER BADER, and HANS LABHARDT (*Ber.*, 1907, 40, 4795—4799).—Acridones and dimethylaniline condense in the presence of phosphoryl chloride at 100° to form acridines, in which the dimethylaniline radicle is in the para-position to the acridine carbon atom, as shown by colour reactions. The reaction is a general one.

4-*Dimethylamino-9-phenylacridine*, $C_6H_4 \begin{smallmatrix} \diagup C \\ \diagdown N \end{smallmatrix} \begin{smallmatrix} C_6H_4 \cdot NMe_2 \\ C_6H_4 \end{smallmatrix}$, is ob-

tained in 92% yield, and crystallises from amyl alcohol in yellow aggregates of needles, m. p. 279°; the corresponding *diethyl* compound, $C_{23}H_{22}N_2$, crystallises from petroleum in glistening, yellowish-brown needles, m. p. 197°. 2-*Nitroacridone*, $C_{13}H_8O_3N_2$, prepared by heating anhydrous aluminium chloride with the chloride of *m*-nitrodiphenylaminocarboxylic acid in benzene solution, crystallises from nitrobenzene in yellow leaflets, m. p. above 360°, and is converted into 2-*nitro-4'-dimethylamino-9-phenylacridine*, $NO_2 \cdot C_{13}NH_6 \cdot C_6H_4 \cdot NMe_2$, a large excess of dimethylaniline being required. It forms red plates from a mixture of benzene and petroleum; m. p. 255°.

2:4-*Dinitroacridone*, $C_{13}H_7O_5N_3$, forming orange leaflets, m. p. above 360°, gives a 50% yield of 2:4-*dinitro-4'-dimethylamino-9-phenylacridine*, $C_{21}H_{16}O_4N_3$, which crystallises in dark brownish-violet leaflets. W. R.

Condensation of *p*-Phenylenediamine, β-Naphthylamine, and β-Naphthylhydrazine with Aldehydes and Ketones. S. ROTHENFUSSER (*Arch. Pharm.*, 1907, 245, 360—376).—The condensation is effected by warming the substances together in aqueous-alcoholic solution in the case of the first two bases, and in alcoholic solution in the case of β-naphthylhydrazine; each amino-group condenses with a carbonyl group, water being eliminated. The products are crystalline, and yellow to white in colour; a list of them with their m. p.'s is given below. These reactions might be used as a means of detecting the respective aldehydes or ketones in essential oils.

p-Phenylenediamine: with cinnamaldehyde, yellow, 223—224°.

β-Naphthylamine: with cinnamaldehyde, yellow, 125°.

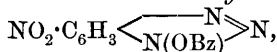
β-Naphthylhydrazine: with citral, white (turns yellow in daylight), 122°; with cinnamaldehyde, yellow, 188°; with anisaldehyde, nearly white, 187°; with piperonal; flesh-coloured, 186°; with vanillin, flesh-coloured, 187°; with carvone, white, 147°.

C. F. B.

Action of Hydrazine Hydrate on Nitro-compounds. V. Action of Hydrazine Hydrate on 2:4-Dinitrophenylhydrazine. THEODOR CURTIUS and MAX MAYER (*J. pr. Chem.*, 1907, [ii], 76, 369—400. Compare Abstr., 1907, i, 969, 970, 1078, 1079).—The action of acid chlorides on 2:4-dinitrophenylhydrazine (Curtius and Dedichen, Abstr., 1895, i, 29) in boiling alcoholic solution leads to the formation of *s*-monohydrazides. In this manner have been prepared: *s*-benzoyl-2:4-dinitrophenylhydrazide, $C_6H_3(NO_2)_2 \cdot NH \cdot NHBz$, orange-red leaflets, m. p. 206—207°; *s*-2:4:6:2':4'-pentanitrohydrazobenzene (Ciusa, Abstr., 1907, i, 874), and *s*-acetyl-2:4-dinitrophenylhydrazide, m. p. 196—197° (193—194°: Purgotti, Abstr., 1895, i, 27).

2:4-Dinitrophenylhydrazine reacts with dilute alkalis only when heated, but with concentrated alkalis at the ordinary temperature, evolving nitrogen and yielding a brown *product* which is not 2:4-dinitrophenol (compare Curtius and Dedichen, *loc. cit.*).

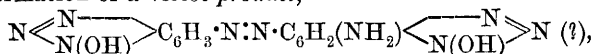
When heated with alcoholic hydrazine hydrate, 2:4-dinitrophenylhydrazine evolves small amounts of nitrogen and ammonia, and forms, as the chief product, the *hydrazine* salt, $NO_2 \cdot C_6H_3 \cdot \overleftarrow{N(OH)}^N \cdot N_2H_4$ which crystallises on cooling in small, yellow needles, m. p. 205—206° (decomp.), and dissolves in water to a dark red solution if concentrated, or a yellowish-red if very dilute. 6-Nitro-1-hydroxy-1:2:3-benzotriazole, $C_6H_4O_3N_4$ (Abstr., 1907, i, 969), formed by the action of hydrochloric or acetic acid on the hydrazine salt, crystallises from water in yellow needles or prisms, or from nitrobenzene in leaflets, detonates at 190—192°, dissolves in aqueous alkalis or alkali carbonates, and is reprecipitated unchanged on dilution of its solution in concentrated sulphuric acid. The *sodium*, $C_6H_5O_3N_4Na$, *potassium*, and *ammonium* salts are described. The solution of the sodium salt gives precipitates with salts of the alkaline earths and heavy metals. The *aniline* salt, $C_6H_4O_3N_4 \cdot NH_2Ph$, crystallises in yellow needles, m. p. 159—160°. The *ethyl ether*, $NO_2 \cdot C_6H_3 \cdot \overleftarrow{N(OEt)}^N \cdot N$, prepared by boiling the sodium salt with alcoholic ethyl iodide, crystallises in yellow needles, m. p. 79—80°. The *methyl ether*, $C_7H_6O_3N_4$, crystallises in white needles, m. p. 129—130°. The *benzyl ether*, $C_{13}H_{10}O_3N_4$, forms prisms, m. p. 115—116°. The *benzoyl* derivative,



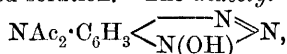
prepared by boiling the sodium salt with ethereal benzoyl chloride, crystallises in white needles, m. p. 160—161°. The *acetyl* derivative is obtained as a white substance, which decomposes on recrystallisation from alcohol. Oxidation of the benzotriazole with permanganate in dilute potassium hydroxide solution leads to the formation of 1-hydroxy-1:2:3-triazole-4:5-dicarboxylic acid, m. p. 152—153° (150°: Zincke and Schwarz, Abstr., 1900, i, 527).

Whilst reduction of the benzotriazole with hydriodic acid at 140—150° leads to the formation of a black, carbonaceous mass from which a definite product cannot be isolated, 6-amino-1-hydroxy-1:2:3-benzotriazole hydrochloride, $NH_2 \cdot C_6H_3 \cdot \overleftarrow{N(OH)}^N \cdot N \cdot HCl$, m. p.

220° (decomp.), is prepared by treatment of the nitro-compound or its ethyl ether with tin and hydrochloric acid. This is obtained as a rose-coloured substance, which with silver nitrate forms silver chloride and a gelatinous mass, and when neutralised with sodium hydroxide or ammonia and treated with sodium acetate forms a red solution which slowly deposits a dark, flocculent precipitate. The action of aqueous sodium nitrite on the hydrochloride in neutral solution leads to the formation of a violet product,



which dissolves in alkalis to a red solution and is reprecipitated by acids, but in strongly acid solution to the formation of the *diazo*-salt, which with resorcinol gives a brownish-red precipitate dissolving in acids to a Bordeaux-red solution. The *diacetyl* derivative,



m. p. about 202° (decomp.), prepared by boiling the hydrochloride with acetic anhydride, decomposes when dissolved in acetic acid, forming 6-amino-1-hydroxy-1 : 2 : 3-benzotriazole acetate, $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_4$, which crystallises in prisms, detonating at 235—236°.

When treated with aqueous alkalis or ammonia, or hydrazine hydrate, under varying conditions, 2 : 4 : 6-trinitrophenylhydrazine (Curtius and Dedichen, *loc. cit.*) yields only products which are insoluble in alkalis or indifferent solvents, are not explosive, and hence cannot be dinitro-1-hydroxy-1 : 2 : 3-benzotriazole. G. Y.

The Amino-groups Attached to the Nitrogen Atom of Heterocyclic Compounds. CARL BÜLOW and EMIL KLEMANN (*Ber.*, 1907, 40, 4749—4760).—The present research is concerned with the investigation of the *N*-amino-group in ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate (Abstr., 1903, i, 196). The amino-group is replaced by hydrogen when the compound is acted on by nitrous acid, Knorr's ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate being formed. Whilst the amino-group attached to the *ring carbon* of carboxylic or heterocyclic compounds is transformed in acid solution by means of sodium nitrite into the diazonium group, the amino-group attached to the *ring nitrogen* of heterocyclic compounds is eliminated under similar conditions as nitrous oxide, and is replaced by a hydrogen atom. The reactivity of the *N*-amino-group of the pyrrole derivative under consideration is much less than that of a primary *C*-amine or of a secondary hydrazine. Whilst, for example, secondary hydrazines, as a class, easily interact with aromatic aldehydes and ketones, ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate couples with aldehydes only after boiling for several hours in ethyl-alcoholic solution, whilst it reacts with ketones even with greater difficulty.

Ethyl benzylideneamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, $\text{C}_{19}\text{H}_{22}\text{O}_4\text{N}_2$, obtained by boiling ethyl amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate for eight hours with a mixture of benzaldehyde and ethyl alcohol, separates from dilute alcohol in prisms, m. p. 49°; when boiled with dilute acetic acid, benzaldehyde is eliminated.

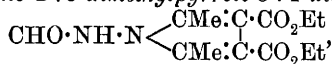
Ethyl p-hydroxybenzylideneamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate

oxylate, $C_{19}H_{22}O_5N$, obtained in a similar manner from *p*-hydroxybenzaldehyde, has m. p. 154°.

Ethyl 1-propylideneamino-2:5-dimethylpyrrole-3:4-dicarboxylate, $CM_e_3:N \cdot CNMe_2(CO_2Et)_2$, obtained by heating ethyl 1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate with acetone for ten hours at 100° in a sealed tube, is an oil, b. p. 247—253°/60 mm.

Ethyl 1- α -phenylethylideneamino-2:5-dimethylpyrrole-3:4-dicarboxylate, $CM_ePh:N \cdot N \begin{smallmatrix} \text{CMe:C} \cdot CO_2Et \\ \text{CMe:C} \cdot CO_2Et \end{smallmatrix}$, obtained from acetophenone, separates from light petroleum in glistening plates, m. p. 111—112°.

Ethyl 1-formylamino-2:5-dimethylpyrrole-3:4-dicarboxylate,



obtained by heating ethyl 1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate with anhydrous formic acid, crystallises in needles, m. p. 139°. The same compound is obtained when formylhydrazide acts on ethyl diacetylsuccinate. When partially saponified at the ordinary temperature, the operation may be conducted so that only one of the oxyethyl-groups is eliminated with the formation of *monoethyl 1-formylamino-2:5-dimethylpyrrole-3:4-dicarboxylate*, $C_{11}H_{14}O_5N_2$, which decomposes at 150°.

Ethyl 1-phenylacetylmethylamino-2:5-dimethylpyrrole-3:4-dicarboxylate, $CH_2Ph \cdot CO \cdot NMe \cdot N \begin{smallmatrix} \text{CMe:C} \cdot CO_2Et \\ \text{CMe:C} \cdot CO_2Et \end{smallmatrix}$, obtained by the methylation of ethyl 1-phenylacetylaminodimethylpyrroledicarboxylate by means of methyl sulphate, is insoluble in dilute alkali, and separates from light petroleum in prisms or plates, m. p. 82°.

Ethyl 1-methylthiocarbamido-2:5-dimethylpyrrole-3:4-dicarboxylate, $NHMe \cdot CS \cdot NH \cdot N \begin{smallmatrix} \text{CMe:C} \cdot CO_2Et \\ \text{CMe:C} \cdot CO_2Et \end{smallmatrix}$, obtained from methylthiocarbimide and ethyl *N*-aminodimethylpyrroledicarboxylate, has m. p. 193—194°.

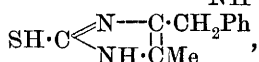
Ethyl 1-allylthiocarbamido-2:5-dimethylpyrrole-3:4-dicarboxylate, $CH_2:CH \cdot CH_2 \cdot NH \cdot CS \cdot NH \cdot N \begin{smallmatrix} \text{CMe:C} \cdot CO_2Et \\ \text{CMe:C} \cdot CO_2Et \end{smallmatrix}$, obtained from allylthiocarbimide in a similar manner, has m. p. 192°.

Ethyl α -naphthylthiocarbamido-2:5-dimethylpyrrole-3:4-dicarboxylate, $C_{10}H_7 \cdot NH \cdot CS \cdot NH \cdot N \begin{smallmatrix} \text{CMe:C} \cdot CO_2Et \\ \text{CMe:C} \cdot CO_2Et \end{smallmatrix}$, obtained from naphthylthiocarbimide, has m. p. 183°.

A. McK.

α -Amino- α -benzylacetone. ADOLF SONN (*Ber.*, 1907, 40, 4666—4670).— *α -Amino- α -benzylacetone* is obtained in the form of its *hydrochloride*, $COMe \cdot CH(CH_2Ph) \cdot NH_2 \cdot HCl$, white leaflets, m. p. 126—127°, after sintering at 124°, by the reduction of *α -isonitroso- α -benzylacetone* with tin and hydrochloric acid; the *platinichloride*, $(C_{10}H_{13}ON)_2 \cdot H_2PtCl_6$, small, orange, spear-shaped crystals, m. p. 185—186° (decomp.); the crystalline *aurichloride*, $C_{10}H_{13}ON \cdot HAuCl_4$, m. p. 136°, and *picrate*, $C_{10}H_{13}ON \cdot C_6H_2(NO_2)_3OH$, small, yellow

octahedra, m. p. 147°, were prepared. The hydrochloride when warmed with an aqueous solution of potassium thiocyanate yields *benzylmethylglyoxaline mercaptan*, $\text{SH} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{CMe} \\ \text{NH} \cdot \text{C} \cdot \text{CH}_2\text{Ph} \end{smallmatrix}$ or



crystallising in white leaflets, decomposing at 260° (approx.); it has a bitter taste, and evolves sulphur dioxide with concentrated sulphuric acid. Oxidation with hot 10% nitric acid converts it into a compound which is either 4-*benzyl-5-methylglyoxaline*, $\text{CH} \begin{smallmatrix} \text{N} - \text{C} \cdot \text{CH}_2\text{Ph} \\ \text{NH} \cdot \text{CMe} \end{smallmatrix}$, or

5-*benzyl-4-methylglyoxaline*, $\text{CH} \begin{smallmatrix} \text{N} - \text{CMe} \\ \text{NH} \cdot \text{C} \cdot \text{CH}_2\text{Ph} \end{smallmatrix}$ (compare Gabriel and Pinkus, Abstr., 1893, i, 734). It crystallises in small tufts of needles, m. p. 132°; the *aurichloride*, $\text{C}_{11}\text{H}_{12}\text{N} \cdot \text{HAuCl}_4$, forms yellow needles, m. p. 157°; the *picrate*, $\text{C}_{11}\text{H}_{12}\text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, crystallises in yellow plates, m. p. 147°.

α -Amino- α -benzylacetone hydrochloride (1 mol.) interacts with potassium cyanate (1 mol.) in aqueous solution with the formation of 4 : 5-*benzylmethylglyoxaline*, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \text{NH} \cdot \text{C} \cdot \text{CH}_2\text{Ph} \end{smallmatrix}$, white leaflets, turning brown at 220° (approx.), m. p. 270°.

3 : 6-*Dibenzyl-2 : 5-dimethylpyrazine*, $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{CH}_2\text{Ph}) \\ \text{C}(\text{CH}_2\text{Ph}) \cdot \text{CMe} \end{smallmatrix} \text{N}$, is formed by the oxidation of α -amino- α -benzylacetone; it crystallises in large, slightly yellow prisms, m. p. 97—98°; the *platinichloride*, $(\text{C}_{20}\text{H}_{20}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, forms reddish-yellow crystals, m. p. 197—198°; the *aurichloride*, $\text{C}_{20}\text{H}_{20}\text{N}_2 \cdot \text{HAuCl}_4$, crystallises in rhombic prisms, m. p. 164—165° (decomp.); the *picrate*, $\text{C}_{20}\text{H}_{20}\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms yellow crystals, m. p. 125—126°. 3 : 6-Dibenzyl-2 : 5-dimethylpyrazine is converted on oxidation with chromic acid into 3 : 6-*dibenzoyl-2 : 5-dimethylpyrazine*, $\text{C}_4\text{N}_2\text{Me}_2\text{Bz}_2$, pale yellow leaflets, m. p. 159—160°; the *dioxime*, $\text{C}_4\text{N}_2\text{Me}_2(\text{CPh} \cdot \text{N} \cdot \text{OH})_2$, forms white needles, decomposing at 233°. W. H. G.

Glyoxalones; Iminazolones. HEINRICH BILTZ [with P. HORRMANN] (*Ber.*, 1907, 40, 4799—4806. Compare Abstr., 1905, i, 674).—Further disubstituted glyoxalones have been prepared and characterised by means of their acetates. With the exception of Rupe's phenylglyoxalone (compare Abstr., 1895, i, 218), it is found that in all the cases in the literature, or in those examined in the present communication, wherever two imino-groups are separated by a carbonyl group, both are acetylated. If, however, an imino-group is situated between two carbonyl groups, then the iminic hydrogen is apparently not replaceable by acetyl.

4 : 5-*Dimethylglyoxalone* $\begin{smallmatrix} \text{CMe} \cdot \text{NH} \\ \text{CMe} \cdot \text{NH} \end{smallmatrix} > \text{CO}$, obtained readily by heating acetyl methylcarbinol with carbamide in anhydrous acetic acid solution, is crystalline, has no m. p., but turns brown at 290° and at

354—355° decomposes. This may or may not be identical with Künne's dimethylglyoxalone (Abstr., 1895, i, 685). The *diacetate*, $C_9H_{12}O_3N_2$, crystallises from alcohol in needles, m. p. 117—118°.

Attempts to condense acetylmethylcarbinol with methylcarbamide and *s*-dimethylcarbamide were unsuccessful.

It is more convenient to use anhydrous glacial acetic acid in the preparation of 4:5-diphenyl-3-methylglyoxalone (compare Anschütz and Müller, Abstr., 1895, i, 305). The *acetate*, $C_{18}H_{16}O_2N_2$, forms needles, m. p. 134°. 4:5-Diphenyl-1:3-dimethylglyoxalone, $\begin{matrix} \text{CPh} \cdot \text{NMe} \\ | \\ \text{CPh} \cdot \text{NMe} \end{matrix} > \text{CO}$, obtained by heating *s*-dimethylcarbamide and benzoin in anhydrous acetic acid solution at 140—150° for four hours, crystallises in prisms, m. p. 185°. There is, therefore, a decrease in the m. p. with the introduction of methyl groups.

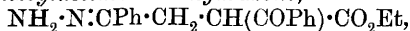
Benzoin and *as*-dimethylcarbamide on heating in acetic acid give diphenylglyoxalone, the two methyl groups being eliminated.

Anschütz and Schwickerath (Abstr., 1895, i, 304) observed that diphenylglyoxalone gives a cherry-red colour with sulphuric acid; this is not characteristic of the substance, as a preparation precipitated from its sulphuric acid solution by water and recrystallisation no longer gave the coloration.

2:4:5-Triphenylglyoxaline does not form an acetate. W. R.

Pyridazine Synthesis. V. Diphenylpyridazine Derivatives. CARL PAAL and GUSTAV KÜHN (*Ber.*, 1907, 40, 4598—4604. Compare Abstr., 1903, i, 289, 290, 722; 1905, i, 91).—In continuation of work on the behaviour of hydrazine hydrate towards γ -diketones and γ -diketonic esters, the authors have studied the formation of some diphenylpyridazine derivatives.

Ethyl phenacylbenzoylacetate monohydrate,

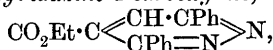


obtained by the addition of hydrazine hydrate to an alcoholic solution of ethyl phenacylbenzoylacetate, separates in yellowish-white needles, m. p. 125—126°. When heated above its melting point, it loses water and is converted into *ethyl 3:6-diphenyl-4:5-dihydropyridazine-4-carboxylate*, $\text{CO}_2\text{Et} \cdot \text{CH} < \begin{matrix} \text{CH}_2 \cdot \text{CPh} \\ \text{CPh} = \text{N} \end{matrix} > \text{N}$; the latter compound may also

be formed directly from ethyl phenacylbenzoylacetate and hydrazine hydrate in glacial acetic acid solution; it crystallises from dilute alcohol in greenish-yellow needles, m. p. 116—117°, and is characterised by conversion into 3:6-diphenylpyridazine.

3:6-Diphenyldihydropyridazine-4-carboxylic acid, $C_{17}H_{14}O_2N_2$, obtained by the action of alcoholic potassium hydroxide either on the preceding ester or on the hydrazone already described, separates from aqueous alcohol in colourless needles, m. p. 205—206°. Attempts to prepare 3:6-diphenyldihydropyridazine by heating this acid were not successful.

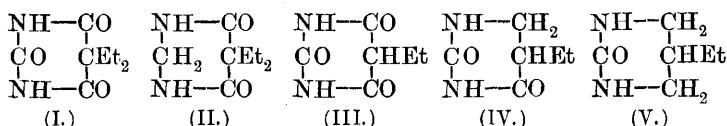
Ethyl 3:6-diphenylpyridazine-4-carboxylate,



obtained by oxidising the dihydro-ester with nitrous acid, crystallises

in needles, m. p. 98—99°. When saponified, it forms 3 : 6-diphenylpyridazine-4-carboxylic acid, $C_{17}H_{12}O_2N_2$, which separates from aqueous alcohol in colourless needles, m. p. 220—221° (decomp.); in contradistinction to the dihydro-acid, this acid readily loses carbon dioxide and forms 3 : 6-diphenylpyridazine. A. McK.

Electrolytic Reduction of Ethylbarbituric Acid. JULIUS TAFEL and HERBERT BRYAN THOMPSON (*Ber.*, 1907, 40, 4489—4497). —Tafel and Weinschenk have shown (*Abstr.*, 1901, i, 72) that electrolytic reduction of barbituric acid leads to the formation of hydro-uracil. It is now found that 5 : 5-diethylbarbituric acid (veronal) (I) on electrolytic reduction yields 4 : 6-diketo-5 : 5-diethylhexahydropyrimidine (2-deoxyveronal) (II), together with a small amount of a yellow resin, whereas, under similar conditions, 5-ethylbarbituric acid (III) yields 5-ethylhydrouracil (IV) and 5-ethyltrimethylenecarbamide (V).



On reduction in 75% sulphuric acid solution with a current density of 30 amperes and lead electrodes at 48—53° for seven hours, veronal yields 90% of its weight of 4 : 6-diketo-5 : 5-diethylhexahydropyrimidine, which crystallises from ethyl acetate in leaflets, m. p. 292°, sublimes when quickly heated, is readily soluble in cold dilute alkalis, and on hydrolysis with baryta at 140° forms a mixture of diethylmalonic and diethylmalonamic acids. When heated with bromine in glacial acetic acid at 100°, diethylhexahydropyrimidine yields ammonium bromide and formic and diethylmalonic acids. Formic and diethylmalonic acids are formed by hydrolysis of the yellow resin obtained on reduction of veronal.

Diethylmalonamic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C} \text{Et}_2 \cdot \text{CO}_2 \text{H}$, separates from water in crystals, m. p. 144°, and yields diethylmalonic acid when treated with sodium nitrite in concentrated sulphuric acid solution at 100°, or on prolonged boiling with concentrated aqueous baryta.

5-Ethylhydrouracil, prepared by reduction of 5-ethylbarbituric acid with a current density of 15 amperes at 7—15° for four hours, crystallises from water in colourless leaflets, m. p. 274°, sublimes when quickly heated, is neutral in aqueous solution, and is only sparingly soluble in dilute sodium hydroxide. On successive treatment with bromine in 15% glacial acetic acid solution at 100° and sodium hydroxide, 5-ethylhydrouracil yields 5-ethyluracil, which separates on acidification of the alkaline solution and crystallises from methyl alcohol in needles, m. p. 303°.

5-Ethyltrimethylenecarbamide, prepared by reduction of 5-ethylbarbituric acid with a current density of 12 amperes at 38—45°, is isolated in the form of its *picrate*, $C_{12}H_{15}O_8N_5$, m. p. 131—133°. The free carbamide crystallises in prisms, m. p. 170°. G. Y.

Pyrimidines. XXVIII. Synthesis of 4-Methyluracil-5-acetic Acid. TREAT B. JOHNSON and FREDERICK W. HEYL (*Amer. Chem. J.*, 1907, 38, 659—670).—It has been shown in a previous paper (Abstr., 1907, i, 1083) that ethyl formylsuccinate condenses readily with ψ -ethylthiocarbamide to form ethyl 6-oxy-2-ethylthiolpyrimidine-5-acetate, which can be converted easily into thymine-5-carboxylic acid. It is now shown that 4-methyluracil-5-acetic acid can be prepared in a quite analogous manner from ψ -ethylthiocarbamide and ethyl acetylsuccinate. 6-Oxy-2-methylthiol-4-methylpyrimidine-5-acetic acid, $\text{SMe} \cdot \text{C} \begin{smallmatrix} \text{N-CMe} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is formed when ψ -methylthiocarbamide hydriodide is treated with ethyl acetylsuccinate in presence of potassium hydroxide solution. It sinters at 260° , decomposes at 270 — 272° , and crystallises from hot water or alcohol in flat prisms.

6-Oxy-2-ethylthiol-4-methylpyrimidine-5-acetic acid, m. p. 255° (decomp.), similarly prepared, crystallises in long prisms from boiling benzonitrile or nitrobenzene. The *potassium* salt is crystalline. The *ethyl* ester, m. p. 163 — 165° , formed in the usual manner with some *ethyl* 4-methyluracil-5-acetate (see below) as a by-product, crystallises from alcohol in hair-like needles. When the acid is heated with ammonia in alcohol at 170 — 180° during four hours, 2-amino-6-oxy-4-methylpyrimidine-5-acetic acid, $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N-CMe} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 322° (decomp.), is produced. It crystallises from water in needles. On digesting the acid at 100° with phosphoryl chloride and pouring the product into cold ammonia in alcohol, 6-chloro-2-ethylthiol-4-methylpyrimidine-5-acetamide, m. p. 167° (decomp.), crystallising from water in sheaves, is formed, but if the reaction mixture be poured on ice there is produced 6-chloro-2-ethylthiol-4-methylpyrimidine-5-acetic acid, $\text{SEt} \cdot \text{C} \begin{smallmatrix} \text{N-CMe} \\ \text{N}=\text{CCl} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 118 — 119° (decomp.), which crystallises from hot water in needles. Alcoholic ammonia only reacts with the latter substance when heated with it at 125 — 135° , and then forms 6-amino-2-ethylthiol-4-methylpyrimidine-5-acetic acid, m. p. 221° , crystallising from alcohol in beautiful needles. When the reaction is conducted at 167 — 180° , the action goes further, and 2:6-diamino-4-methylpyrimidine-5-acetic acid, m. p. 279 — 280° (decomp.), crystallising in small prisms from hot water, is formed.

4-Methyluracil-5-acetic acid, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 340° (decomp.), is formed when 6-oxy-2-ethylthiol-4-methylpyrimidine-5-acetic acid is boiled with hydrochloric acid. It crystallises from hot water in long prisms, sinters at 329° , decomposes at 340° , is soluble in water to the extent of 0.0894% to 0.0901%, and is unaffected by heating with dilute sulphuric acid (20%) during two hours at 153 — 173° . The *lead*, *potassium*, and *barium* salts are crystalline, and the *silver* salt amorphous. The *ethyl* ester, m. p. 221 — 222° , crystallises in needles from alcohol; the *methyl* ester melts at 280 — 282° .

T. A. H.

Formation of Pyrazine Compounds from Quinoxaline Derivatives. SIEGFRIED GABRIEL and ADOLF SONN (*Ber.*, 1907, 40, 4850—4860).—Quinoxaline and its 2:3-dimethyl derivatives are oxidised to pyrazine 2:3-dicarboxylic acid and 5:6-dimethylpyrazine-2:3-dicarboxylic acid when heated with a 2% permanganate solution in the presence of potassium hydroxide.

Pyrazine-2:3-dicarboxylic acid, $\begin{array}{c} \text{CH:N}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ | \\ \text{CH:N}\cdot\text{C}\cdot\text{CO}_2\text{H} \end{array}$, crystallises from water in colourless, glistening prisms containing $2\text{H}_2\text{O}$; when heated, it gives up water and melts and decomposes at 186° , whereas the anhydrous acid has m. p. 193° (decomp.). The *barium*, *lead*, *cupric*, and *silver* salts are sparingly soluble. When heated with glacial acetic acid at 180° , the acid yields pyrazine.

2:3-Dimethylquinoxaline, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N}\cdot\text{CMe} \\ | \\ \text{N}\cdot\text{CMe} \end{array}$, is readily prepared by the condensation of *o*-phenylenediamine acetate with diacetylmonoxime in warm aqueous solution. It crystallises from water in slender, glistening needles containing water of crystallisation, which it loses on exposure to the air. When rapidly heated, the crystals melt at 85° , resolidify, and melt a second time at $104\text{--}106^\circ$. The *platinichloride*, $(\text{C}_{10}\text{H}_{10}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$, forms orange-red prisms; the *aurichloride*, a yellow precipitate, which sinters at $90\text{--}95^\circ$ and decomposes at 130° ; the *picrate* has m. p. 189° .

2:3-Dimethylpyrazine-5:6-dicarboxylic acid, $\begin{array}{c} \text{CMe}\cdot\text{N}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ | \\ \text{CMe}\cdot\text{N}\cdot\text{C}\cdot\text{CO}_2\text{H} \end{array}$, crystallises from hot water in glistening, rhombic prisms containing $2\text{H}_2\text{O}$. When anhydrous, it melts and decomposes at 200° . The *barium* salt forms sparingly soluble needles. The *cupric*, *lead*, and *silver* salts are also sparingly soluble. When heated with acetic acid at 180° , the acid yields 2:3-dimethylpyrazine (Jorre, *Inaug. Diss.*, Kiel, 1897), the *picrate* of which has m. p. 150° . When the dicarboxylic acids are distilled, the chief products are the monobasic acids. Pyrazinecarboxylic acid has m. p. 222° (Stöhr gives 229°). 2:3-Dimethylpyrazine-5-carboxylic acid crystallises in slender needles, m. p. 182° , and produces an orange coloration with ferric chloride.

The *anhydride*, $\begin{array}{c} \text{CH:N}\cdot\text{C}\cdot\text{CO} \\ | \\ \text{CH:N}\cdot\text{C}\cdot\text{CO} \end{array} > \text{O}$, prepared by the action of thionyl chloride or acetic anhydride on the dicarboxylic acid, crystallises in slender needles and decomposes at about 170° . The *methyl ester*, $\text{C}_4\text{H}_2\text{N}_2(\text{CO}_2\text{Me})_2$, forms colourless needles, which sinter at 47° and melt at 50° . The *diamide*, $\text{C}_4\text{H}_2\text{N}_2(\text{CO}\cdot\text{NH}_2)_2$, obtained by the action of a methyl-alcoholic solution of ammonia on the ester, crystallises from hot water in minute octahedra, m. p. 240° (decomp.).

The *imide*, $\begin{array}{c} \text{CH:N}\cdot\text{C}\cdot\text{CO} \\ | \\ \text{CH:N}\cdot\text{C}\cdot\text{CO} \end{array} > \text{NH}$, crystallises from hot alcohol in flat prisms, m. p. 245° , and is soluble in dilute alkalis or ammonia. When the diamide is warmed with bromine and potassium hydroxide solution, the *compound*, $\begin{array}{c} \text{CH:N}\cdot\text{C}\cdot\text{CO}\cdot\text{NH} \\ | \\ \text{CH:N}\cdot\text{C}\cdot\text{NH}\cdot\text{CO} \end{array}$

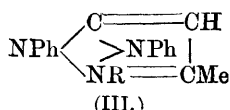
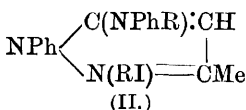
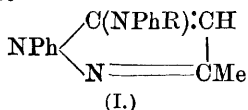
is obtained. It crystallises from hot water in long prisms, which are not molten at 300° , and possesses acidic properties. When the diamide is warmed with 1 gram-molecule of hypobromite, 2-aminopyrazine-3-carboxylic acid, $\text{NH}_2 \cdot \text{C}_4\text{H}_2\text{N}_2 \cdot \text{CO}_2\text{H}$, is obtained. This crystallises from hot water in felted needles, m. p. $209-210^{\circ}$ (decomp.). When heated slightly above its melting point, the amino-acid yields 2-aminopyrazine, $\text{C}_4\text{H}_3\text{N}_2 \cdot \text{NH}_2$, in the form of yellow crystals, which sinter at 110° , and melt to a clear liquid at 117° . The *picrate* is sparingly soluble and has no definite m. p. The *hydrochloride* forms pointed needles, sparingly soluble in concentrated hydrochloric acid; the *hydriodide*, dark brown prisms; the *aurichloride*, sparingly soluble, short prisms, and the *mercurichloride*, colourless needles.

J. J. S.

Nitroso-compounds of ψ -Pyrines, and 2-Alkylanilopyrines.
 AUGUST MICHAELIS and GEORG MIELECKE (*Ber.*, 1907, 40, 4482—4488).—Whilst in the pyrine series nitroso-derivatives have been obtained from antipyrines but not from thio-, seleno-, or anilo-pyrines, nitroso-derivatives of ψ -thiopyrines have been described by Michaelis and Dorn (*Abstr.*, 1907, i, 246), and of ψ -selenopyrines by Michaelis and von der Hagen (*ibid.*, 249). In continuation of this work, it is now found that ψ -antipyrines and ψ -anilopyrines yield similar, intensely green nitroso-derivatives. Thus 5-ethoxy-1-phenyl-3-methylpyrazole (ψ -ethylantipyrine), when treated with sodium nitrite in glacial acetic acid, yields an intensely green solution, depositing on addition of water a green oil which rapidly darkens. It has not yet been found possible to obtain such nitroso- ψ -antipyrines in the crystalline state. Nitroso- ψ -anilopyrines, on the other hand, readily crystallise, and with phenol in sulphuric acid solution give a red coloration, becoming green on addition of water and excess of sodium hydroxide.

4-Nitroso- ψ -anilopyrine, $\text{NPh} \begin{array}{l} \diagup \text{C}(\text{NMePh}) : \text{C} \cdot \text{NO} \\ \diagdown \text{N} = \text{CMe} \end{array}$, prepared by addition of concentrated aqueous sodium nitrite to a glacial acetic acid solution of ψ -anilopyrine, crystallises in dark green leaflets, m. p. 89° . The *hydrochloride*, $\text{C}_{17}\text{H}_{16}\text{N}_8 \cdot \text{NO} \cdot \text{HCl}$, m. p. 156° (decomp.), loses HCl becoming green, slowly on exposure to air or rapidly on treatment with water.

The homologues of ψ -anilopyrine (I) are prepared by distillation of the corresponding alkylidides (II) of the 2-alkylanilopyrines (III), which are obtained by successive action of phosphoryl chloride and aniline on the 2-alkylantipyrines (*Abstr.*, 1904, i, 112), or of the alkylidide and sodium hydroxide on 5-anilino-1-phenyl-3-methylpyrazole.



2-Ethylanilopyrine, $\text{C}_{18}\text{H}_{19}\text{N}_3$, forms strongly refracting, monoclinic crystals, m. p. 69.5° , b. p. $230/22$ mm. (slight decomp.), and has an alkaline reaction to alcoholic litmus. The *hydrochloride* crystallises in

hygroscopic needles; the *platinichloride*, $(C_{18}H_{19}N_3)_2, H_2PtCl_6$, yellow leaflets, m. p. 199° ; the *hydriodide*, white needles, m. p. 182° ; the *picrate*, yellow leaflets, m. p. 131° ; the *chromate*, golden leaflets, m. p. 178° ; the *methiodide*, white needles, m. p. 159° ; the *ethiodide*, $C_{18}H_{19}N_3, EtI$, large, transparent crystals, m. p. 146° ; the *propiodide*, white leaflets, m. p. 107° ; the *benzoyl iodide*, m. p. 187° ; the *acetyl iodide*, m. p. 180.5° .

ψ -*Ethylanilopyrine*, $C_{18}H_{19}N_3$, is obtained as a yellow oil, b. p. $235^\circ/20$ mm., is neutral, dissolves in dilute hydrochloric acid, but is reprecipitated on addition of water, and when heated with ethyl iodide yields 2-ethylanilopyrine ethiodide. The *platinichloride*,

$(C_{18}H_{19}N_3)_2, H_2PtCl_6$, forms yellow leaflets, m. p. 189° . The 4-*nitroso*-derivative is obtained in dark green crystals, m. p. 98° , and forms a *hydrochloride* crystallising in yellow needles, m. p. 140° (decomp.).

2-*n*-*Propylanilopyrine*, $C_{19}H_{21}N_3$, crystallises in yellow needles, m. p. 50° , and is strongly alkaline. The *platinichloride*, m. p. 197° , *hydriodide*, m. p. 173.5° , *methiodide*, m. p. 179° , *ethiodide*, m. p. 118° , and *propiodide*, m. p. 154 — 155° , are described.

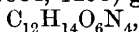
ψ -*n*-*Propylanilopyrine* forms monoclinic crystals, m. p. 74° ; the *platinichloride*, m. p. 156° . The 4-*nitroso*-derivative, $C_{19}H_{20}N_3 \cdot NO$, is obtained in green crystals, m. p. 73° , and forms a yellow *hydrochloride*, m. p. 129° .

2-*Benzylanilopyrine*, $C_{23}H_{21}N_3$, obtained in small yields by heating 5-anilino-1-phenyl-3-methylpyrazole with benzyl chloride at 150° and treatment of the product with sodium hydroxide, crystallises in yellow needles, m. p. 84° , and has a strong alkaline reaction. The *hydrochloride*, $C_{23}H_{21}N_3 \cdot HCl$, m. p. 99° , *platinichloride*, m. p. 206° , *hydriodide*, m. p. 169° , *chromate*, m. p. 172° , *methiodide*, m. p. 137° , *ethiodide*, m. p. 149° , *propiodide*, m. p. 159° , and *benzoylchloride* ($+ 2H_2O$), m. p. 75° , are described.

ψ -*Benzylanilopyrine*, $C_{23}H_{21}N_3$, crystallises in yellow leaflets, m. p. 83° , b. p. $260^\circ/18$ mm., and is neutral. The *platinichloride* crystallises in golden needles, m. p. 171° . The 4-*nitroso*-derivative, $C_{23}H_{20}N_3 \cdot NO$, crystallises in green needles, m. p. 70° , and forms a *hydrochloride*, $C_{23}H_{20}N_3 \cdot NO, HCl$, crystallising in yellow needles, m. p. 134° .

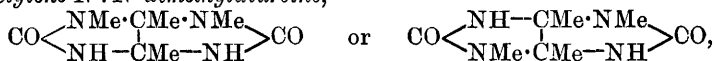
[With LUTZE.]— ψ -*Iminopyrine*, $NPh \begin{smallmatrix} C(NHMe):CH \\ \diagdown \quad \diagup \\ N \quad \quad CMe \end{smallmatrix}$, prepared by distillation of iminopyrine methiodide (Stolz, Abstr., 1904, i, 113), is obtained as a colourless oil, and forms a 4-*nitroso*-derivative which separates from ether in green crystals, m. p. 139° . G. Y.

Diureines. HEINRICH BILTZ [with P. HORRMANN] (*Ber.*, 1907, 40, 4806—4816).—A study of the behaviour of diureines towards acetic anhydride, as diureines may be considered to be diglyoxalones (compare this vol., i, 56). Acetylenecarbamide (Schiff, Abstr., 1878, 287; Pinner, Abstr., 1884, 1298) gives a *tetra-acetate*,



which crystallises from alcohol in needles, m. p. 236 — 238° . Dimethylacetylenediureine (Franchimont and Klobbe, Abstr., 1888, 1180; 1889, 126), however, does not yield an acetate.

The condensation of methylcarbamide and diacetyl gives *dimethylacetylene-N : N'-dimethyldiureine*,

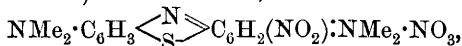


crystallising in prisms or needles, decomp. 305—306°. It gives a *monoacetate*, $\text{C}_{10}\text{H}_{16}\text{O}_3\text{N}_4$, needles, m. p. 174—175°. *s*-Dimethylcarbamide and diacetyl gives rise to a product, decomp. 165°, which has not yet been identified.

Diphenylacetylenediureine (Angeli, Abstr., 1890, 1290; Anschütz and Geldermann, 1891, 725) gives a *diacetate*, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_4$, crystallising from acetic acid in flat prisms, m. p. 299—301° (Angeli, *loc. cit.*, gives 266°). W. R.

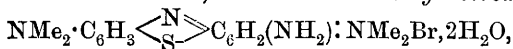
Thiazines. I. Derivatives of Methylene-blue. ROBERT GNEHM [and EMIL WALDER] (*J. pr. Chem.*, 1907, [ii], 76, 401—427. Compare Abstr., 1904, i, 687, 935; 1906, i, 211, 389, 390; Kehrman, Abstr., 1902, i, 566).—The preparation of disulphides of the thiazine series has been undertaken with the object of throwing light on the relation of the thiazines to certain blue sulphur dyes. The method of preparation adopted consists of the nitration of thiazines, reduction of the nitro-compounds to amines, and conversion of these into the corresponding halogen substitution products and mercaptothiazines, which yield disulphides on oxidation.

Details are now given of the preparation of methylene-green (nitromethylene-blue) and its nitrate,

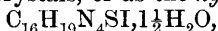


and hydrobromide from methylene-blue (Gnehm and Walder, Abstr., 1906, i, 390). The dye does not give the nitroso-reactions and must be a nitro-compound, as the hydrobromide requires 4 mols. of hydrogen for complete reduction by means of tin and hydrochloric acid.

Aminomethylene-blue, prepared by reduction of the nitro-compound by means of zinc dust and acetic acid and oxidation of the resulting *leuco-base* with ferric chloride, is isolated as the *hydrobromide*,



which forms olive-green crystals, or as the *hydriodide*,



which crystallises in microscopic, olive-green needles, violet by transmitted light. The free base dissolves in water, alcohols, or glacial acetic acid, forming a blue, or if concentrated a violet-blue, solution with a slight fluorescence, and dyes silk and cotton mordanted with tannin with a stronger and more violet shade than methylene-blue.

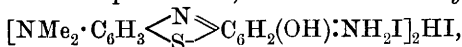
On diazotisation, the amino-dye yields an unstable, greyish-violet solution, which slowly evolves nitrogen, becoming blue. When coupled with *R*-salt in ammoniacal solution, the diazotised dye yields a mixture of a violet *azo-dye*, which dyes silk and wool in a sulphuric acid bath, and a blue dye (hydroxymethylene-blue†), which dyes mordanted cotton and silk in an ammoniacal, or silk in an acetic acid, bath. With β -naphthol in ammoniacal solution, the diazotised

dye forms a violet-blue, or with dimethylaniline in an acetic acid solution a greenish-blue, *azo-dye*.

Iodomethylene-blue iodide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \langle \text{N} \rangle_{\text{S}} \text{C}_6\text{H}_2\text{I} : \text{NMe}_2\text{I} \cdot \frac{1}{2}\text{H}_2\text{O}$, prepared by the action of potassium iodide on diazotised aminomethylene-blue, crystallises in microscopic, brownish-violet needles; the *chromate* and *mercurichloride* are precipitated quantitatively even from the most dilute solutions.

Attempts to prepare bromomethylene-blue from the diazotised amino-dye led to the formation of a product containing only traces of halogen. The action of potassium xanthate, alcoholic potassium sulphide, and cuprous sodium thiosulphate on diazotised aminomethylene-blue leads to the formation of *dyes* which differ from the typical sulphur dyes in that they are readily reduced by sodium sulphide in the cold.

Hydroxymethylene-blue, formed when diazotised aminomethylene-blue is heated with sulphuric acid, is isolated as the *hydriodide*,



which is obtained as an olive-green, crystalline powder. It forms blue solutions with a slight red fluorescence, dyes silk and mordanted cotton a more violet shade than methylene-blue, is decolorised by stannous chloride, and forms precipitates with ammonia, mercuric chloride, and potassium dichromate.

The action of bromine on methylene-blue hydrochloride in glacial acetic acid solution leads to the formation of a *product* which crystallises in brownish-violet needles, and has solubilities and gives colorations resembling those of methylene-blue.

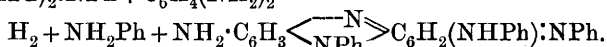
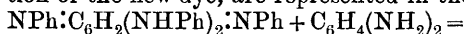
Dinitromethylthionine, formed by the action of nitric acid on methylene-blue or methylene-green in hot acetic acid solution, is isolated as the *nitrate*, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \langle \text{N} \rangle_{\text{S}} \text{C}_6\text{H}(\text{NO}_2)_2 : \text{NH}_2 \cdot \text{NO}_3$, which crystallises in olive-brown needles, and detonates at about 240° . The *hydrobromide* crystallises in olive-brown needles. The dye-salts form bluish-red, dichroic solutions in methyl or ethyl alcohol, acetic acid, or acetone with scarlet fluorescence; the similarly coloured aqueous solution is not fluorescent. Addition of ammonia to the aqueous solution precipitates the brown, amorphous base, which detonates when heated, and remains partly unchanged when boiled with acetic acid. The dinitro-compound dyes silk or mordanted cotton a brownish-violet.

Reduction of the dinitro-nitrate with zinc dust and glacial acetic acid leads to the formation of a soluble *leuco-base*, which is readily oxidised by ferric chloride, forming *diaminodimethylthionine*. The *hydrobromide* of this is a bluish-black, amorphous powder, forms bluish-green solutions, and dyes silk and mordanted cotton green.

The absorption spectra of the various compounds are described, and also the colorations given with strong acids. G. Y.

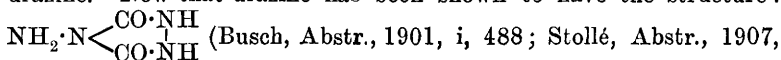
Synthesis of Phenylated *s*-Anilinophenosafranine. PHILIPPE BARBIER and PAUL SISLEY (*Compt. rend.*, 1907, 145, 1185—1187. Compare Abstr., 1905, i, 840; 1906, i, 51, 989; 1907, i, 160, 563).—

When a mixture of azophenine (Fischer and Hepp, Abstr., 1903, i, 134) and *p*-phenylenediamine in molecular proportions is heated in alcohol at 165° during six to seven hours, aniline is produced together with a *phenylated s-anilinophenosafranine*, which can be separated as its *hydrochloride*, $C_{30}H_{23}N_5 \cdot 2HCl$, a dark crystalline powder with a feeble metallic reflex; the *platinichloride*, $C_{30}H_{23}N_5 \cdot H_2PtCl_6$, is a reddish-brown powder. It dyes mordanted silk or cotton a beautiful violet-blue shade. The mechanism of the reaction, and the constitution of the new dye, are represented in the following scheme:



If in the above reaction the *p*-phenylenediamine is replaced by *as*-dimethyl- or diethyl-*p*-phenylenediamine, soluble dyes are obtained in which the NH_2 -group of the original compound is replaced by NMe_2 or NEt_2 , and these dye in a bluer shade. M. A. W.

Action of Cyanogen Bromide on Hydrazine. *N*-Aminoguanazole (Guanazine). III. GUIDO PELLIZZARI and ANGELO REPETTO (*Gazzetta*, 1907, 37, ii, 317—326. Compare Abstr., 1907, i, 833).—The hexagonal formula for guanazine (Abstr., 1905, i, 577) was based on the analogy of this compound with urazine and thio-urazine. Now that urazine has been shown to have the structure:



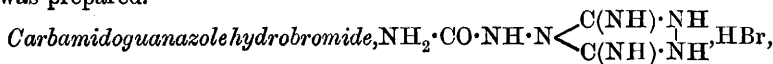
guanazine must be 4-aminoguanazole, $NH_2 \cdot N \begin{array}{c} C(NH) \cdot NH \\ C(NH) \cdot NH \end{array}$,

or $NH_2 \cdot N \begin{array}{c} C(NH_2) : N \\ C(NH_2) : N \end{array}$. This structure is in accord with the properties and reactions of the compound (compare Pellizzari and Roncagliolo, Abstr., 1901, i, 772).

4-Aminoguanazole (guanazine), $C_2N_6H_6$, separated from its hydrobromide, separates from water in large, faintly yellow crystals, or from alcohol in minute, almost white crystals, m. p. 257° (decomp.), has a marked alkaline reaction, and reduces ammoniacal silver nitrate and Fehling's solution on heating. Its *nitrate*, $C_2N_6H_6 \cdot HNO_3$, m. p. 210°; *sulphate*, $(C_2N_6H_6)_2 \cdot H_2SO_4 \cdot H_2O$, m. p. 275°, and *acetate*, $C_2N_6H_6 \cdot C_2H_4O_2 \cdot \frac{1}{2}H_2O$, m. p. 175°, were prepared.

Triacetylaminoguanazole, $NHAc \cdot N \begin{array}{c} C(NH) \cdot NAc \\ C(NH) \cdot NAc \end{array}$, crystallises from alcohol in shining, white needles, m. p. 240°.

Dibenzylideneaminoguanazole, $CHPh \cdot N \cdot N \begin{array}{c} C(NH) \cdot N \\ C(NH) \cdot N \end{array} \text{---} CHPh$, prepared by the interaction of aminoguanazole and benzaldehyde in alcoholic solution in presence of piperidine, separates from alcohol in intensely yellow crystals, m. p. 196°. Its *hydrochloride*, $C_{16}N_6H_{14} \cdot HCl$, was prepared.



prepared by the interaction of aminoguanazole hydrobromide, potassium cyanate, and hydrobromic acid, has m. p. 221° . The free base decomposes readily, and could not be isolated. T. H. P.

Formation of Pyrimidine Derivatives from Purine Bases. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 53, 508—513).—Several of Burian's experiments on heating guanine and adenine with sulphuric acid and sucrose (Abstr., 1907, i, 735) have been repeated, but in no case has any pyrimidine derivative been obtained.

J. J. S.

The Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. IV. Condensation of Nitro-derivatives of Phenylhydrazine with Quinones and Quinoneoximes of the Benzene Series. WALTHER BORSCHKE (*Annalen*, 1907, 357, 171—191. Compare Abstr., 1904, i, 1056; 1905, i, 719; 1906, i, 319).—Attempts to prepare *p*-hydroxyazo-compounds of the benzene series by the method employed by Zincke in the naphthalene series have hitherto been unsuccessful. The results obtained (Abstr., 1905, i, 719) with acylhydrazides suggested that phenylhydrazines containing negative substituting groups might react with benzoquinones. This has now been found to be the case with *o*-nitrophenylhydrazine, which reacts with benzoquinones and their oximes, forming *p*-hydroxyazo-compounds of the type: $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, which are identical with the substances obtained by coupling diazotised *o*-nitroaniline with phenols, and quinoneoximehydrazones, which are considered to be of the type: $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NOH}$, respectively. *p*-Nitrophenylhydrazine, on the other hand, reacts only with the quinoneoximes, whilst *m*-nitrophenylhydrazine does not form either hydroxyazo-compounds or quinoneoximehydrazones. 2:4-Dinitrophenylhydrazine reacts with quinones and quinoneoximes more readily than does *o*-nitrophenylhydrazine, but attempts to form hydroxyazo-compounds from 2:4:6-trinitrophenylhydrazine have so far been unsuccessful.

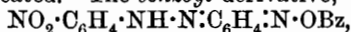
1:3-Bis-2'-nitrobenzeneazo-4-hydroxybenzene, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, is formed together with 4-hydroxybenzeneazo-2'-nitrobenzene by Elb's and Keiper's method (Abstr., 1903, i, 662); it crystallises from glacial acetic acid in dark brown needles, m. p. 203° .

2'-Nitro-4-hydroxy-3-methylazobenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$, obtained in orange-red, crystalline nodules, m. p. 111 — 112° , prepared from toluquinone and *o*-nitrophenylhydrazine hydrochloride, or, together with bis-*o*-nitrobenzeneazo-*o*-cresol, crystallising in dark brown needles, m. p. 258 — 260° evolving gas, by the action of diazotised *o*-nitroaniline on *o*-cresol.

2'-Nitro-4-hydroxy-2-methyl-5-isopropylazobenzene,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_2\text{MePr}^s \cdot \text{OH}$,
 crystallising in long needles, m. p. 144 — 145° , is prepared from thymoquinone and *o*-nitrophenylhydrazine, or, together with a small amount of the corresponding bisazo-compound, crystallising in blackish-brown needles, m. p. 179 — 180° (decomp.), from diazotised *o*-nitroaniline and thymol.

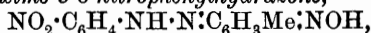
2':4'-Dinitro-4-hydroxyazobenzene, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, crystallising in brown needles, m. p. 185—186°; 2':4'-dinitro-4-hydroxy-3-methylazobenzene, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, forming an orange powder, m. p. 127—128°, and 2':4'-dinitro-4-hydroxy-2-methyl-5-isopropylazobenzene, $\text{OH}\cdot\text{C}_6\text{H}_2\text{MePr}^\beta\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, crystallising in dark red needles, m. p. 179—180°, are prepared by the action of 2:4-dinitrophenylhydrazine on quinone, toluquinone, and thymoquinone respectively, and form bluish-red to violet-blue solutions in dilute alkalis.

Benzoquinoneoxime-o-nitrophenylhydrazine, $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_4$, prepared by the action of *o*-nitrophenylhydrazine on benzoquinoneoxime in cooled alcoholic solution, crystallises in dark red needles, and gradually decomposes when heated. The *benzoyl* derivative,



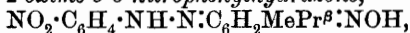
formed from benzoquinoneoxime benzoate, is obtained as an insoluble, scarlet precipitate, and does not melt in a sulphuric acid bath. When heated with glacial acetic acid, or more rapidly when treated with chromic or concentrated nitric acid in glacial acetic acid solution, benzoquinoneoxime-2-nitrophenylhydrazine is converted into 4:4'-bis-*o*-nitrobenzeneazooxybenzene, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, which is formed also as a by-product in the preparation of the hydrazone, or by the action of benzaldehyde on the hydrazone. It crystallises in dark yellow needles, m. p. 258° (decomp.). The action of nitric acid on benzoquinoneoxime-*o*-nitrophenylhydrazine in boiling glacial acetic acid solution, or of hydrogen peroxide on the hydrazone in dilute sodium hydroxide solution, leads to the formation of 2:4'-dinitroazobenzene, $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_4$, which crystallises in iridescent leaflets, m. p. 131—132°.

Toluquinone-2-oxime-5-o-nitrophenylhydrazine,



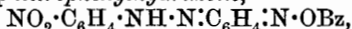
prepared from nitroso-*m*-cresol and *o*-nitrophenylhydrazine hydrochloride, is obtained as a dark brown, flocculent precipitate, m. p. 206—207° (decomp.), and when treated with nitric acid in boiling glacial acetic acid solution yields 2:4'-dinitro-3'-methylazobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$, crystallising in dark yellow leaflets, m. p. 128°.

Thymoquinone-2-oxime-5-o-nitrophenylhydrazine,



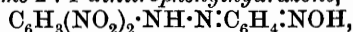
prepared from nitrosothymol, crystallises in dark red needles, m. p. 218—220° (decomp.).

The condensation products of *p*-nitrophenylhydrazine and quinone-oximes are unstable. Only the more easily isolated *benzoyl*-benzoquinoneoxime-*p*-nitrophenylhydrazine,



is described. It is formed from benzoquinoneoxime benzoate, crystallises in small, reddish-brown leaflets, does not melt at 260°, and is insoluble in the usual organic solvents.

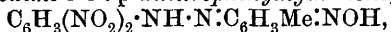
Benzoquinoneoxime-2:4-dinitrophenylhydrazine,



forms a dark red, crystalline powder, m. p. 214—215° (decomp.), dissolves to a reddish-blue solution in dilute sodium hydroxide, and

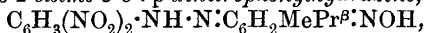
when boiled with glacial acetic acid yields 2:4:4'-trinitroazobenzene.

Toluquinone-2-oxime-5-o : p-dinitrophenylhydrazine,



forms a glistening, bluish-red powder, decomp. 222—223°, and when treated with nitric acid in hot glacial acetic acid solution yields 4 : 2' : 4'-trinitro-3-methylazobenzene, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$, crystallising in reddish-brown needles, m. p. 164—165°.

Thymoquinone-2-oxime-5-o : p-dinitrophenylhydrazine,



crystallises in dark red needles, decomp. 249—250°. 4 : 2' : 4'-Trinitro-3-methyl-6-isopropylazobenzene, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{MePr}^\beta \cdot \text{NO}_2$, crystallises in yellowish-red needles, m. p. 198°. G. Y.

Azo-derivatives of Guaiacol. AMEDEO COLOMBANO and BATTISTA LEONARDI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 639—648; *Gazzetta*, 1907, 37, 461—471. Compare Colombano, *Abstr.*, 1907, i, 1091).—The compounds not already described (*loc. cit.*) are as follows.

The *acetyl* derivative of *benzeneazoguaiacol*, $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2$, separates from light petroleum in reddish-brown, acicular crystals, m. p. 61°.

The *ethyl ether* of *benzeneazoguaiacol*, $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$, crystallises from alcohol or water in tufts of long, silky needles, m. p. 86—89°.

o-Nitrobenzeneazoguaiacol, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OMe}$, separates from aqueous alcohol in red, acicular crystals, m. p. 144°.

m-Nitrobenzeneazoguaiacol, $\text{C}_{13}\text{H}_{11}\text{O}_4\text{N}_3$, crystallises from aqueous alcohol in yellowish-red needles, m. p. 124°. Its *acetyl* derivative, $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}_3$, has m. p. 95—97°.

p-Nitrobenzeneazoguaiacol, $\text{C}_{13}\text{H}_{11}\text{O}_4\text{N}_3$, separates from aqueous alcohol in chocolate-brown needles, m. p. 125—135°.

o-Tolueneazoguaiacol, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OMe}$, separates in reddish-brown, acicular crystals, m. p. 85°. Its *acetyl* derivative, $\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_2$, forms orange-red rhombohedra, m. p. 87°.

α -Naphthylazoguaiacol, $\text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OMe}$, forms brownish-black needles, m. p. 125°. Its *acetyl* derivative, $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$, forms dark orange-red, acicular crystals, m. p. 105—110°.

β -Naphthylazoguaiacol, $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$, separates from aqueous alcohol in pale yellow, flocculent crystals, m. p. 92—94°. T. H. P.

Action of Thorium Nitrate and of Uranyl Nitrate on Albumins. BÉLA SZILARD (*J. Chim. phys.*, 1907, 5, 495—496).—When the albumin of white of egg, coagulated by boiling, is added in small quantities at a time to a boiling 2% aqueous solution of thorium or uranyl nitrate, a considerable amount of it goes into solution, leaving only a slight insoluble residue. The filtered thorium solution is colourless and slightly opalescent, and does not give the ordinary reactions for thorium or for albumin; the latter seems to be present as an albumose or peptone. The uranyl solution is yellow in colour. Keratin is dissolved by these salt solutions in a similar way. G. S.

Conditions of Hydrolysis of Protoplasmides. ALEXANDRE ETARD and ANTONY VILA (*Compt. rend.*, 1907, 145, 1217—1219. Compare *Abstr.*, 1901, i, 490; ii, 563; 1902, i, 110, 589).—The author

discusses the unsatisfactory nature of the present methods of hydrolysing protoplasmides and the impossibility of obtaining quantitative results. The hydrolysis is usually effected by means of excess of acids or bases, and the salts formed when they are neutralised carry down a large proportion of the products of hydrolysis. Thus 1 kilo. of beef muscle after removal of the fat and drying at 100° yielded 240 grams of dry muscular tissue; this was hydrolysed by means of 650 grams of sulphuric acid in 1200 grams of water, and neutralised with baryta; it yielded 171 grams of dry hydrolytic products, 15 grams being retained by the barium sulphate.

M. A. W.

Hydrolysis of Hordein. A. KLEINSCHMITT (*Zeitsch. physiol. Chem.*, 1907, 54, 110—118).—By hydrolysis of hordein (from barley) by concentrated hydrochloric acid, the following percentage yields were obtained: alanine 1.34, aminovaleric acid 1.40, leucine 7.00, pyrrolidine-2-carboxylic acid (α -proline) 5.88, phenylalanine 5.48, glutamic acid 41.32, aspartic acid 1.32, serine 0.10, histidine 0.51, arginine 3.14, tyrosine 4.00, ammonia 4.34, leucineimide 0.58. Like zein and gliadin (the other alcohol-soluble vegetable proteins), hordein contains no glycine and no lysine. As shown by the results of hydrolysis, gliadin and hordein are not identical, as has sometimes been supposed.

G. B.

Urochrome. OTTORINO BOCCHI (*Beitr. chem. Physiol. Path.*, 1907, 11, 79—80).—A method for preparing urochrome is given, and is said to yield a purer product than that obtained according to Garrod's method. The urochrome is obtained free from indican and urea.

G. B.

Nucleo-protein of the Placenta. M. SAVARÈ (*Beitr. chem. Physiol. Path.*, 1907, 11, 73—75).—The nucleo-protein of the placenta contains C, 50%; H, 7.3%; N, 15%; S, 1%, and P, 0.45%. In its composition, and especially in its low phosphorus content, it shows a certain analogy to the nucleo-protein of the lacteal gland; this is possibly connected with the fact that both organs are concerned in infantile nutrition.

G. B.

Polypeptidephosphoric Acid (Paranucleic Acid) from Caseinogen. ALFRED REH (*Beitr. chem. Physiol. Path.*, 1907, 11, 1—18).—The paranucleic acid of Salkowski was prepared from a caseinogen solution which had undergone peptic digestion for two days by precipitation with uranyl acetate in the presence of acetic acid. The uranyl compound is readily soluble in hydrochloric acid; its phosphorus is removed quantitatively by boiling baryta, and it does not contain sulphur; phosphorus and uranium are present in atomic proportions. The free acid contains P 6.9%, or eight times as much as that of the caseinogen employed (Salkowski's preparation contained 4.3% P).

The uranyl compound was hydrolysed by boiling with 25% sulphuric acid, and yielded arginine, histidine, lysine, alanine, proline, aminovaleric acid, leucine, *isoleucine*, phenylalanine, tyrosine, aspartic acid, and glutamic acid.

G. B.

Nucleic Acids in Animals. OSWALD SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1907, 57, 309—337).—The empirical formula for nucleic acid reckoned from elementary analysis is $C_{40}H_{56}N_{14}O_{16}, 2P_2O_5$. A distinction is drawn between this, the anhydrous form of the acid, and the hydrated form, which has $2H_2O$ (or, in a few cases, $5H_2O$) in addition. The anhydrous form possesses the property of gelatinising. The preparations were made from salmon-roe, thymus, pancreas, and thyroid. The bulk of the paper relates to the method used in preparing the substance; the separation by means of its copper salt was mainly used.

W. D. H.

Guanylic Acid from the Pancreas. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 53, 539—544).—It is shown that guanylic acid can be prepared from the nucleo-protein of the pancreas by Bang's method (Abstr., 1899, i, 179; 1901, i, 299; Fürth and Jerusalem, Abstr., 1907, i, 993), and a nucleic acid by Neumann's method. Guanylic acid does not yield glycerol on hydrolysis.

J. J. S.

Guanylic Acid. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1907, 11, 76—78).—A reply to von Fürth and Jerusalem (Abstr., 1907, i, 993), who refuse to place this acid apart from other nucleic acids. These authors did not work with pure material. The large nitrogen deficit in their determination of the purine bases was due to faulty application of the method, and led to great loss, especially as regards the guanine. Further work is promised.

G. B.

The Compound of Uric Acid with Nucleic Acid. Y. SEO (*Arch. exp. Path. Pharm.*, 1907, 58, 75—92).—This compound, described by Minkowski and by Goto (Abstr., 1900, ii, 421, 740), was prepared by dissolving nucleic acid and uric acid in dilute sodium hydroxide, acidifying with acetic acid, filtering off the excess of uric acid, which separated after a time, and finally precipitating the compound by adding concentrated hydrochloric acid to the filtrate. The amorphous, colourless precipitate gives the murexide reaction; its solution in water does not yield a precipitate with acetic acid or with silver nitrate. When boiled with acetic acid, or treated with excess of ammonia in the cold, it is decomposed into its two components. Analysis of the copper compound indicates that 2 molecules of nucleic acid are combined with 1 of uric acid.

Egg-albumin precipitates nucleic acid from the combination of the two acids, thus setting the uric acid free; the latter can be obtained crystalline from the albumin filtrate. Hence uric acid may occur as a nucleic acid compound in the blood, despite the fact that free uric acid is obtained after removal of the proteins by acidification and boiling.

After the injection of uric acid + nucleic acid, much more uric acid is found in the urine than when the two substances are injected at separate times (compare Abstr., 1906, ii, 109).

G. B.

Neurokeratin. ALFRED ARGIRIS (*Zeitsch. physiol. Chem.*, 1907, 54, 86—94).—The method of preparation (from human brains) is

described in detail, and is a modification of that used by Kühne and Chittenden. The composition of the substance agrees closely with that found by the latter authors as regard C, H, and N, but somewhat higher values for S were found (2.24—2.31%, instead of 1.75%). On hydrolysis, by boiling with 33% sulphuric acid, neurokeratin yielded: lysine, 2.72%; arginine, 2.28%; histidine, 0.76%; tyrosine, 4.60%, and cystine, 1.50%, besides other amino-acids. G. B.

Separation of Proteins. II. Deutero-albumose. HENRY C. HASLAM (*J. Physiol.*, 1907, 36, 164—176. Compare Abstr., 1905, i, 495).—Deutero-albumose is resolved by alcohol into two substances differing in solubility, but it is not decomposed by ammonium or zinc sulphate. The total number of the albumoses of Witte's peptone is reduced to five, namely, hetero-proteose, two varieties of proto-proteose, and two of deutero-proteose. W. D. H.

Compounds of Protamines with other Proteins. ANDREW HUNTER (*Zeitsch. physiol. Chem.*, 1907, 53, 526—538. Compare Kossel, *Deut. Med. Woch.*, 1894, No. 7).—Clupein yields precipitates with faintly ammoniacal solutions of crystallised egg-albumin, casein, hemielastin, gelatin, edestin, hetero-albumose, and proto-albumose. Precipitates are not obtained with elastin, peptone, deutero-albumose, histopeptone, and various polypeptides. A solution of metaprotein in a slight excess of sodium hydroxide and a solution of histone sulphate in sodium carbonate yield precipitates.

The following figures give the number of parts by weight of the protein which unite with one part by weight of clupein: ovalbumin, 4.1; gelatin, 4.8; hemielastin, 5.2; casein, 2.5; edestin, 8.5.

J. J. S.

Pepsin and Chymosin (Rennin). J. W. A. GEWIN (*Zeitsch. physiol. Chem.*, 1907, 54, 32—79).—Bang's parachymosin, obtained from the pig's stomach, is not essentially different from the chymosin from the calf. Such differences as exist between the two preparations are due to admixed impurities.

Attempts to separate rennin from pepsin by means of dialysis, the addition of much protein, &c., were unsuccessful. In the researches of those observers (Bang, Schmidt-Nielsen) who obtained enzyme solutions having only a peptic or only a rennitic action, the action of the other enzyme was only inhibited, and could be restored by removal of the inhibiting substance. Pepsin and rennin are one and the same ferment. The rennet action is the first stage in the digestion of caseinogen; if hydrogen ions are absent and calcium ions are present, the digestion stops and a curd separates; if a sufficient number of hydrogen ions are present, ordinary peptic digestion proceeds.

G. B.

Method for the Determination of the Accelerating Action of Sodium and Potassium Salts on the Coagulation of Milk by Ferments. C. GERBER (*Compt. rend.*, 1907, 145, 831—833. Compare Abstr., 1907, i, 1100).—The author recommends that the milk

used in the determination of the accelerating influence of certain salts on coagulation should be treated previously with sodium oxalate, in order to eliminate the action of the calcium compounds present naturally in the milk. These compounds interfere with the action of such salts as fluorides, the calcium combining with the fluorine and causing untrustworthy results to be obtained.

W. P. S.

Peroxydases from Beetroot. ADOLF ERNEST and HEINRICH BERGER (*Ber.*, 1907, 40, 4671—4679. Compare Bach and Chodat, *Abstr.*, 1902, ii, 344, 522; 1903, i, 377, 378; 1904, i, 542).—The beetroot is extracted with diluted alcohol, and an aqueous solution of the raw material so obtained treated with a mixture of absolute alcohol and ether. The precipitated material consists of peroxydases only, and does not contain any oxydase, catalase, amylase, invertase, emulsin, or proteolytic enzyme.

The quantity of purpurogallin produced by the action of the peroxydases on a mixture of pyrogallol and hydrogen peroxide increases with an increase in the proportion of hydrogen peroxide or peroxydase, but decreases with an increase in the proportion of pyrogallol.

W. H. G.

Philothion. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1907, [iv], 1, 1051—1053. Compare *Abstr.*, 1907, i, 372).—It is shown that the white of a duck's egg furnishes but little hydrogen sulphide when mixed with sulphur, and cannot therefore be used as a source of philothion.

The reciprocal action of oxidising ferments and philothion, simultaneously present in muscular tissue, has been examined by extracting finely-divided cock's muscle with a dilute aqueous solution of sodium fluoride and potassium iodide, the latter being a solvent for oxydases. This solution contains philothion when freshly made, but after being kept at 40—45° during five hours it no longer gives the characteristic philothion reaction, although it still contains albumin. This disappearance of philothion (albumin hydride) it is suggested is due to dehydrogenation by the action of the oxydases (*loc. cit.*).

Since the soluble albumin of the circulatory system is free from philothion whilst that of muscular tissue contains it, it must be assumed that the living cell has the property of hydrogenating albumin, which can then be reoxidised to simple albumin by other constituents of muscular tissue. Philothion therefore plays the part of a hydrogenating enzyme.

T. A. H.

Organic Chemistry.

Viscosity of Ethyl Alcohol. L. GAILLARD (*J. Pharm. Chim.*, 1907, [vi], 26, 481—487).—The relative viscosities (compared with that of water taken as unity) of absolute ethyl alcohol and of mixtures containing from 1 to 10 molecules of water per molecule of alcohol are 1.45, 2.53, 2.96, 3.10, 3.10, 2.95, 2.84, 2.67, 2.55, 2.43, and 2.23 respectively, whilst those of mixtures containing 95%, 20%, 15%, 11%, 10%, and 5% of alcohol are 1.78, 1.96, 1.65, 1.45, 1.35, and 1.21, all the values having been obtained at 15°. Examination of these values shows that the viscosity of ethyl alcohol increases with dilution until a maximum value of 3.1 is reached for the two mixtures of the composition $\text{EtOH}, 3\text{H}_2\text{O}$ and $\text{EtOH}, 4\text{H}_2\text{O}$, and then diminishes, and that absolute alcohol and a mixture containing 11% of alcohol have the same viscosity. This confirms the existence of the trihydrate, the formation of which is accompanied by the maximum contraction, and renders probable the existence of the tetrahydrate. Mixtures of the two alcohols $\text{EtOH}, 3\text{H}_2\text{O}$ and $\text{EtOH}, 4\text{H}_2\text{O}$ in any proportion whatever all have the viscosity 3.1, indicating that intermediate hydrates are not formed. E. H.

Action of Zinc Allyl Iodide on the Anhydrides of Monobasic Acids. ALEXANDER M. SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1232—1239).—When an anhydride of a monobasic acid reacts with allyl iodide in the presence of zinc, the following reactions most probably occur: $\text{O}(\text{CO}\cdot\text{R})_2 + \text{C}_3\text{H}_5\cdot\text{ZnI} = \text{C}_3\text{H}_5\cdot\text{CR}(\text{OZnI})\cdot\text{O}\cdot\text{COR} \rightarrow \text{CR}(\text{C}_3\text{H}_5)_2\cdot\text{OH}$, and, as a side reaction, $\text{CR}(\text{C}_3\text{H}_5)_2\cdot\text{OZnI} \rightarrow \text{C}_3\text{H}_5\cdot\text{CR}\cdot\text{O}\cdot\text{COR}$.

The yield and purity of the alcohol are much superior to that obtained when the ester is employed instead of the anhydride. The following substances have been obtained. Methylallylcarbinol, yield 36.5% of the theoretical, having b. p. 157—159°, D_0^0 0.87747, D_{20}^{20} 0.86314, D_{20}^{20} 0.86258 (Sorokin gives D_0^0 0.8640, D_0^{15} 0.8524). Ethylallylcarbinol, yield 37—39%, b. p. 175—176°/755.6 mm., D_0^0 0.88603, D_{20}^{20} 0.86877, D_{20}^{20} 0.87002 (Smirensky: D_0^0 0.8776, D_0^{17} 0.8637). Propylallylcarbinol, yield nearly 41%, b. p. 192—194°, D_0^0 0.87939, D_{20}^{20} 0.86286, D_{20}^{20} 0.86412 (P. and A. Saytzeff: D_0^0 0.8707, D_{20}^{20} 0.8564). *iso*Propylallylcarbinol, yield 37%, b. p. 187—188°, D_0^0 0.88859, D_{20}^{20} 0.87133, D_{20}^{20} 0.87259 (Rjabinin and Saytzeff: D_0^0 0.8647, D_0^0 0.8512). Z. K.

Alkylene Glycol-chlorohydrin Ethers and their Changes. JOSEF HOUBEN and KARL FÜHRER (*Ber.*, 1907, 40, 4990—5000).—Ethylene glycol-chlorohydrin ether [α -chloro- β -ethoxybutane], $\text{CH}_2\text{Cl}\cdot\text{CHEt}\cdot\text{OEt}$, originally obtained by Lieben, using zinc ethyl, is more conveniently prepared by the interaction of dichloro-ether and magnesium ethyl bromide. It is not converted into methyl ethyl ketone or, indeed, changed by heating in boiling methyl alcohol with sodium hydroxide. *α -Chloro- β -ethoxyisohexane*, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{OEt}$, is a colourless liquid, b. p. 60—61°/8 mm.

iso- α -Chloro- β -ethoxy-isoeptane, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{C}_5\text{H}_{11})\cdot\text{OEt}$, is a colourless liquid of unpleasant odour, b. p. $77-78^\circ/9$ mm. β -Chloro- α -ethoxyethylbenzene, $\text{CH}_2\text{Cl}\cdot\text{CHPh}\cdot\text{OEt}$, is a colourless, pleasant smelling liquid, b. p. $107-108^\circ/9$ mm.; when heated with sodium hydroxide, it is converted almost quantitatively into acetophenone, and for the preparation of this from bromobenzene it is not necessary to first purify the hydrin ether. By the action of sodium iodide on the above chlorohydrin ether, the chlorine is to a large extent replaced by iodine; the product obtained has b. p. $110-111^\circ/9.5$ mm., and distils as a dark red oil without much decomposition at $226^\circ/760$ mm. γ -Chloro- α -ethoxypropylbenzene, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{OEt}$, is a colourless liquid of agreeable odour, b. p. $125-126^\circ/9.5$ mm., which, like the aliphatic compounds, is not altered on boiling with sodium hydroxide. 1- β -Chloro- α -ethoxyethylnaphthalene, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{C}_{10}\text{H}_7)\cdot\text{OEt}$, has b. p. $178-179^\circ/9$ mm., and forms a yellow liquid of faint odour. Heated with sodium hydroxide, it forms α -naphthyl methyl ketone.

E. F. A.

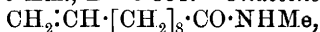
Oxidation of Butyric Acid by Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 77-89).—Ammonium butyrate is readily oxidised by hydrogen peroxide at 37° , but the reaction is accelerated by warming. The products obtained were: acetoacetic acid, acetone, propaldehyde, acetaldehyde, acetic and formic acids, and carbon dioxide; propionic acid was probably also present. It is probable that α - and β -hydroxybutyric acids are the initial products. All products except acetone are on further treatment converted eventually with carbon dioxide and water. Acetone is very resistant to hydrogen peroxide. There is no need to assume that acetone is formed as an intermediate substance in the oxidation of all the butyric acid formed in the body. It is probable that β -hydroxybutyric acid may be decomposed so as to give acetic acid and its oxidation products. It is much less probable that the α -acid is an alternative initial product in tissue oxidation; this, however, may be further oxidised through propionic acid.

W. D. H.

Mercuric Heptoate. J. TH. BORNWATER (*Rec. trav. chim.*, 1907, 26, 413).—When yellow mercuric oxide is shaken with an aqueous solution of *n*-heptoic acid, at the end of some days the oxide is completely transformed into a white precipitate of mercuric heptoate, $(\text{CH}_2\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CO}_2)_2\text{Hg}$. It crystallises from methyl alcohol in nacreous plates, m. p. 106.5° . Solutions of the salt decompose after a time, mercuric oxide being deposited; they are rendered more stable by addition of heptoic acid. Mercuric heptoate does not form a double salt with mercuric chloride.

E. H.

Derivatives of Undecenoic Acid. J. TH. BORNWATER (*Rec. trav. chim.*, 1907, 26, 409-412).—Methyl undecenoate (Noerdlinger, Abstr., 1890, 1237), prepared according to Perkin's method for the ethyl ester (*Trans.*, 1886, 49, 206), has b. p. $249.5-250^\circ/780$ mm., m. p. -27.5° , D^{15}_D 0.889. As the temperature rises from 11.2° to 25° , the n_D falls from 1.44301 to 1.43727. Ethyl undecenoate has m. p. -37.5° , b. p. $263-263.5^\circ/780$ mm., D^{15}_D 0.881. Undecenomethylamide,



prepared by the action of an aqueous solution of methylamine on the crude chloride, forms fine, crystalline plates, m. p. 46° (below that of the amide, Franchimont, Abstr., 1897, ii, 542). *Undecenodimethylamide*, $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_8\cdot\text{CO}\cdot\text{NMe}_2$, obtained by shaking an ethereal solution of the chloride with an aqueous solution of dimethylamine hydrochloride, is a liquid, b. p. $186.5^{\circ}/20$ mm., D_4^{25} 0.89278, which solidifies when cooled in ice and salt to a solid, m. p. -16.5° .

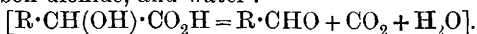
E. H.

Action of Ozone on Compounds containing Triple Linkings.

CARL D. HARRIES (*Ber.*, 1907, 40, 4905—4908).—The author disputes Molinari's statement (Abstr., 1907, i, 1039) that ozone does not react with substances containing a triple linking or a benzene double linking. Stearolic acid and phenylpropionic acid yield with ozone unstable substances which exhibit the typical reactions of ozonides.

C. S.

Oxidation of Ammonium Salts of Hydroxy-fatty Acids with Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 91—100).—The ammonium salts of glycollic, lactic, α - and β -hydroxybutyric, α -hydroxyisobutyric, and α -hydroxyisovaleric acids were oxidised with hydrogen peroxide. With the exception of glycollic and β -hydroxybutyric acids, the primary products are an aldehyde, carbon dioxide, and water:



In the case of α -hydroxyisobutyric acid, acetone is formed. More or less of the aldehyde is further oxidised to the corresponding acid, and in some cases oxidation goes on still further; thus lactic acid yields acetaldehyde, acetic acid, and carbon dioxide. Leucic acid undergoes oxidation like other hydroxy-acids. Glycollic acid yields first glyoxylic acid and formaldehyde, then formic acid, and, finally, carbon dioxide and water. β -Hydroxybutyric acid yields numerous products, including acetoacetic acid, acetone, acetaldehyde, acetic and formic acids, and carbon dioxide.

W. D. H.

The Reduction of Ethyl Oxalate. WILHELM TRAUBE (*Ber.*, 1907, 40, 4942—4956. Compare Löwig, *J. pr. Chem.*, 1861, [i], 83, 129, and 84, 1; Debus, this Journ., 1872, 25, 365; Eghis, *ibid.*, 1871, 24, 820).—A solution of ethyl oxalate in absolute alcohol was reduced with sodium amalgam, and, in order to avoid hydrolysis of the esters, the product was mixed with an excess of alcoholic hydrogen chloride and fractionally distilled. In the first fraction, ethyl alcohol, hydrogen chloride, and a small amount of ethyl carbonate passed over, and then a small amount of ethyl glyoxalate alcoholate and ethyl glycollate. A fraction, distilling between 170° and 220° , consisted mainly of ethyl diethylglyoxylate, $\text{CH}(\text{OEt})_2\cdot\text{CO}_2\text{Et}$, and ethyl oxomalonate, $\text{CO}(\text{CO}_2\text{Et})_2$, together with a little ethyl oxalate. The residue when distilled under reduced pressure gave a fraction 160 — $200^{\circ}/20$ mm., consisting mainly of ethyl deoxalate (Klein, Abstr., 1880, 36) (crystals) and ethyl tartrate (liquid). The diethylglyoxylic ester, which is formed in considerable amounts, is not a primary reduction product,

but is formed by the action of the alcohol and hydrogen chloride on the ethyl glyoxylate alcoholate. The formation of the acetal can be prevented by using just sufficient hydrogen chloride to neutralise the alkali formed during the reduction, or by using an alcoholic solution of oxalic acid. Under these conditions, the chief product is the alcoholate (20—25 grams from 100 of ethyl oxalate), which appears to be the first product of reduction: $\text{EtO} \cdot \text{CO} \cdot \text{CO} \cdot \text{OEt} \rightarrow \text{EtO} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{OEt}$. *Ethyl glyoxalate alcoholate*, $\text{CO}_2\text{Et} \cdot \text{CH}(\text{OH}) \cdot \text{OEt}$, may be separated from the mixture of reduction products by fractional distillation, and forms a colourless liquid, b. p. 136—138°. When heated, it gives rise to an extremely strong odour, and, when mixed with the theoretical amount of phosphoric oxide, decanted, and distilled, it yields ethyl glyoxalate, b. p. 130°, which readily polymerises. When warmed with barium hydroxide, the alcoholate and also glyoxylic acid yield gaseous hydrogen. The alcoholate condenses with ethyl malonate in the presence of acetic anhydride, yielding Perkin and Bishop's ethyl ethylenetricarboxylate (*Proc.*, 1891, 7, 41), which is hydrolysed with 25% hydrochloric acid to fumaric and malic acids. The ethyl ethylenetricarboxylate reacts with ethyl malonate and sodium ethoxide, forming ethyl propanepentacarboxylate, from which tricarballic acid is produced on hydrolysis.

Attention is drawn to the fact that many of the products formed by the reduction of ethyl oxalate occur in plant structures (compare Koenigs, *Ber.*, 1892, 25, 800). J. J. S.

Simple Ester Anhydrides of Saturated Dibasic Organic Acids. D. MOL (*Rec. trav. chim.*, 1907, 26, 373—408. Compare Abstr., 1906, i, 4).—The ester anhydrides of the dibasic acids are obtained by (1) the action of the monoalkyl chloride on the mixed alkali alkyl salt; (2) the interaction of phosphoryl chloride and a slight excess of the alkali alkyl salt (compare Gerhardt, *Annalen*, 1853, 87, 237; Geuther, *ibid.*, 1862, 123, 113), or (3) the action of acetyl chloride on the alkali alkyl salt (compare Bouveault, Abstr., 1900, i, 474).

Ethyl anhydro-oxalate, $\text{O}(\text{CO} \cdot \text{CO}_2\text{Et})_2$, can be prepared by either of the three methods. It is a colourless liquid with a faint odour, b. p. 139°/15 mm., 140°/16 mm., which in a freezing mixture solidifies to crystals, m. p. 8°. The liquid has D_4^{25} 1.2480, n_D^{20} 1.42762, n_D^{25} 1.42592. Its ethereal solution reacts with dry ammonia gas, forming ethyl oxamate and ammonium ethyl oxalate. When very rapidly heated at 240°, ethyl anhydro-oxalate decomposes, evolving carbon dioxide, and forming anhydrous ethyl mesoxalate and a liquid having the same empirical formula as the latter, but double its molecular weight. At 150°, the ester anhydride forms carbon monoxide and dioxide, and ethyl formate. Attempts to prepare ethyl anhydromalonate by the second and third methods give no definite result, probably owing to the reactivity of the hydrogen atoms of the CH_2 group. The action of potassium ethyl malonate on ethyl malonic chloride has not been studied.

Ethyl anhydrosuccinate, $\text{O}(\text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, is prepared either by the interaction of sodium ethyl succinate (Blaise, Abstr., 1899, i,

793) and ethyl succinic chloride, obtained by a modification of Michaelis and Hermens' method (Abstr., 1892, 1494), or by the action of phosphoryl chloride on the former salt. It forms colourless crystals, m. p. 28° . In ethereal solution, it is attacked by dry ammonia, forming *ethyl succinamate*, $C_6H_{11}O_3N$, as colourless needles, m. p. 75° , and an extremely deliquescent solid, identified from its reactions as *ammonium ethyl succinate*. When boiled under the ordinary pressure, ethyl anhydrosuccinate carbonises, and after four distillations a mixture of much succinic anhydride and a little ethyl succinate is obtained.

By the action of phosphoryl chloride on sodium ethyl glutarate (obtained by Blaise's method), *ethylanhydroglutarate*, $O(CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Et)_2$, is formed as a colourless liquid, which, when strongly cooled, solidifies to crystals, m. p. $7-8^{\circ}$. The liquid has b. p. $150^{\circ}/15$ mm., $D_4^{13.5} 1.1245$, $n_D^{20} 1.44466$, and $n_D^{25} 1.44275$.

The author points out that the customary method of preparing acid chlorides by addition of phosphoryl chloride to the salt of the acid is contrary to the original directions of Gerhardt, who added the powdered salt to the oxychloride. This would account for the poor yields obtained by some workers.

A vacuum distillation apparatus, based on Dewar's absorption of gases by charcoal cooled in liquid air, is described. E. H.

Synthesis of Methyleneethylmalic Acid. M. L. SHDANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1411—1414).—Ethyl α -bromobutyrate reacts with pyruvic acid in the presence of zinc, forming ethyl methyleneethylmalate, $CO_2Et \cdot CHEt \cdot CMe(OH) \cdot CO_2Et$, the yield being 81—84% of the theoretical; when hydrolysed, crystals are formed which could not be purified.

The ammonium salt has m. p. $172.5-174^{\circ}$; at 179° , it resolidifies and then melts at $180-181^{\circ}$ (Michael: m. p. 179°); the silver salt has also been obtained. Z. K.

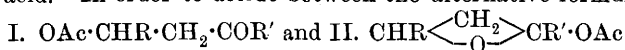
Conversion of Methyl Alcohol into Formaldehyde and the Preparation of Formalin. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1414—1439. Compare Abstr., 1907, i, 892, 1008).—The conversion of methyl alcohol into formaldehyde is not a reversible reaction, and is accompanied by secondary reactions, such as $CH_3O \rightarrow CO + H_2$ and $2H_2 + O_2 = 2H_2O$, &c. The yield of formaldehyde is a maximum when the following relations are observed. The quantity of oxygen: the total quantity of alcohol vapour = $0.4:1$; oxygen: total quantity of the gaseous mixture = $0.1375:1$; total quantity of alcohol vapour: total quantity of gaseous mixture = $0.342:1$. When, in these circumstances, the action proceeds without the application of external energy, $C^2C_1/V^2 = 0.00103$ (where C and C_1 = concentration of the methyl alcohol and oxygen respectively, and V = the mean velocity of the gaseous mixture through the catalyst).

The function of the catalyst is discussed at length, the above relations being true when the catalyst consists of a roll of copper gauze 12 cm. in length, 16 mm. transverse section, in which there are 15×15 threads in each cubic centimetre.

The ordinary thermodynamic equation for the energy of a reaction is not applicable here. An equation is deduced by which it is possible to calculate the total quantity of gas which should be obtained in any experiment, but it was observed that the quantity actually obtained was always more than that required by this equation, this being due to the absorption of the unknown gas, $(\text{CH}_2)_2\text{O}$, by the palladium chloride contained in the palladium employed for the absorption of hydrogen. The mixture of gases in the various experiments contains 2% to 18% of this gas, which has an odour resembling slowly oxidising phosphorus and is decomposed at a red-heat. Z. K.

The Ammonia Reaction for Distinguishing between Enolic and Ketonic Derivatives. II. ARTHUR MICHAEL and HAROLD HIBBERT (*Ber.*, 1907, 40, 4916—4918. Compare Abstr., 1907, i, 1010).—The untrustworthiness of this reaction is further borne out by the behaviour of enolic ethyl diacetosuccinate in solution. From a light petroleum solution, the ketone is precipitated; from ethyl bromide, the ammonium salt of the enol, and from chloroform a mixture of ketone and enolic salt. Where the enol reacts more readily than the ketone, an almost quantitative separation of the tautomeric substances can be effected with aqueous ammonia. Ketonic dibenzoylacetylmethane and enolic tribenzoylmethane with ammonia in organic solvents both give precipitates. W. R.

Synthesis by Means of Mixed Organo-metallic Compounds of Zinc. Constitution of the β -Acetoxy-ketones. EDMOND E. BLAISE (*Compt. rend.*, 1907, 145, 1285—1287).—The β -acetoxy-ketones, prepared by the condensation of the chlorides of β -acetoxy-aliphatic acids with mixed organo-metallic derivatives of zinc (Abstr., 1907, i, 749), do not form crystalline derivatives with either phenylhydrazine, *p*-nitrophenylhydrazine, phenylbenzylhydrazine, or semicarbazide. The only reaction for ketones giving a positive result is obtained with sodium nitro-prusside, which in the presence of a trace of potash produces the characteristic yellowish-red coloration, stable in acetic acid. In order to decide between the alternative formulæ



for the β -acetoxy-ketones, the author has determined their molecular volumes and those of compounds in which a closed lactonic or oxide-chain is known to exist. Whilst in the latter case there are considerable differences between the calculated and observed values due to the closure of the chain, in the former only the normal differences characteristic of open-chain compounds are found. The conclusion is drawn that the β -acetoxy-ketones have the ketonic constitution (I).

E. H.

Behaviour of Cellulose with Sodium Hydroxide. O. MILLER (*Ber.*, 1907, 40, 4903—4905. Compare Vieweg, Abstr., 1907, i, 893).—Gladstone's formula for mercerised cellulose, $\text{C}_{12}\text{H}_{20}\text{O}_{10}, \text{NaOH}$, is not substantiated by the experiments of the author, who finds that the percentage of sodium hydroxide in mercerised cotton increases with the concentration of the alkaline solution. C. S.

Stereochemistry of Chromium. III. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1907, **56**, 261—278).—The paper contains a summary of the mutual relationships of the stereoisomeric chromium salts, and the methods for determining their constitution. Part of the experimental material has already been published (Abstr., 1905, i, 33; 1906, i, 71, ii, 614; 1907, i, 895), and the remainder will be published in detail later (compare next abstract). The more important methods used in determining the constitution of the compounds have already been dealt with (*loc. cit.*). G. S.

Stereochemistry of Chromium. IV. The Isomeric Dibromosalts. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1907, **56**, 279—295. Compare previous abstract).—It has been shown in earlier papers that the diacidodiethylenediaminechromium salts, $[\text{En}_2\text{CrX}_2]\text{X}$ (where En = ethylenediamine, and X = acid group), exist in two stereoisomeric modifications, distinguished as the *cis*-form, $\left[\begin{smallmatrix} \text{En} \\ \text{En} \end{smallmatrix} \right] \text{Cr} \begin{smallmatrix} < \text{X} \\ < \text{X} \end{smallmatrix}$ (violet salts), and the *trans*-form, $\left[\begin{smallmatrix} \text{En} \\ \text{X} \end{smallmatrix} \right] \text{Cr} \begin{smallmatrix} < \text{En} \\ < \text{X} \end{smallmatrix}$ (green salts), respectively.

In the present paper, the dibromo-salts and certain of their derivatives are described. Their constitution has been established mainly from their relationship to the dioxalato-salts already described.

cis-Dibromodiethylenediaminechromium bromide, $[\text{En}_2\text{CrBr}_2]\text{Br}, \text{H}_2\text{O}$, and the corresponding iodide and dithionate, described in a previous paper (Abstr., 1907, i, 895), have been more fully investigated.

trans-Dibromodiethylenediaminechromium bromide, $[\text{En}_2\text{CrBr}_2]\text{Br}, \text{H}_2\text{O}$ (microscopic, green plates), is prepared by evaporating an aqueous solution of the diaquo-salt, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{Br}]\text{Br}_2$, with hydrobromic acid in the presence of mercuric bromide. A double salt, $[\text{En}_2\text{CrBr}_2]\text{Br}, \text{HgBr}_2$, separates as a green, lustrous, crystalline powder; on the removal of the mercury by means of hydrogen sulphide, a green solution containing the *trans*-salt is obtained.

The corresponding salts described below are obtained from the green solution by double decomposition with the alkali salt of the corresponding acid. All, including the bromide itself, are soluble in water, but the solutions are very unstable, the intraradicle bromine is eliminated, and the colour changes simultaneously from green to yellowish-brown.

With concentrated hydrobromic acid, the compound, $[\text{En}_2\text{CrBr}_2]\text{Br}$, gives a double salt, $[\text{En}_2\text{CrBr}_2]\text{Br}, \text{HBr}, 2\text{H}_2\text{O}$, which occurs in grass-green, transparent plates, and is very unstable.

trans-Dibromodiethylenediaminechromium dithionate, $[\text{En}_2\text{CrBr}_2]\text{S}_2\text{O}_6$, occurs in lustrous, flat, green needles; the corresponding iodide, nitrate, and thiocyanate also form lustrous, green needles.

The compound, $[\text{En}_2\text{CrI}_2]\text{I}, \text{HgI}_2$, obtained by the action of hydriodic acid on a solution of the bromobis-aquobromide and mercuric iodide, occurs in lustrous, deep green leaflets, almost insoluble in water.

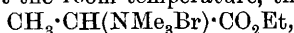
trans-Dichlorodiethylenediaminechromium dithionate, $[\text{En}_2\text{CrCl}_2]\text{S}_2\text{O}_6$, prepared by the general method, occurs in lustrous, red needles, which turn green on rubbing.

trans-Dichlorodiethylenediaminechromium platinichloride,
 $[\text{En}_2\text{CrCl}_2]\text{PtCl}_6, 12\text{H}_2\text{O}$,

obtained by the action of chloroplatinic acid on the corresponding chloride, forms small, yellowish-green needles. G. S.

Optically Active Trimethyl- α -propiobetaine (α -Homobetaine). EMIL FISCHER (*Ber.*, 1907, 40, 5000—5008. Compare Abstr., 1907, i, 192).—1-Trimethylpropiobetaine, $\text{CHMe} \begin{smallmatrix} \text{---CO---} \\ \text{NMe}_3 \end{smallmatrix} \text{O}$ (compare Brühl, this Journ., 1876, i, 698), prepared by the interaction of *d*-bromopropionic acid with trimethylamine in the cold, forms colourless plates, decomp. 242° (corr.), $[\alpha]_D^{20} - 19.7^\circ$. It forms two dimorphous aurichlorides (compare the behaviour of betaine, Fischer, Abstr., 1902, i, 428, and Willstätter, *loc. cit.*, 266), the one crystallising in lustrous, gold-coloured, thin crystals, m. p. 259° (decomp., corr.), from the acid solution, and the other forming a yellow powder consisting of microscopic, short needles, aggregated in crosses or six-armed stars, m. p. 226° (corr.), obtained on crystallisation from warm water. They give the unchanged active betaine when decomposed with hydrogen sulphide. An identical trimethylpropiobetaine is obtained by the action of methyl iodide on *d*-alanine. The action of ammonia and of trimethylamine on *d*- α -bromopropionic acid takes place accordingly in the same stereochemical sense, whilst it has already been shown that no Walden rearrangement takes place in the case of ammonia.

By the interaction of trimethylamine and ethyl *d*- α -bromopropionate in alcoholic solution at the room temperature, the compound,



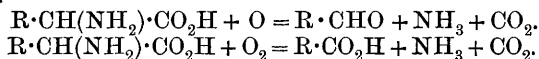
is formed quantitatively in large, colourless needles, m. p. 150 — 151° (corr.), but is quite optically inactive, and is identical with that formed from inactive ethyl α -bromopropionate. The aurichloride separates in very thin, characteristic, yellow plates, m. p. 96 — 97° (corr.). The compound yields inactive trimethyl α -propiobetaine when treated with silver oxide. It is possible by interrupting the reaction at an early stage to obtain a product having $[\alpha]_D - 8.1^\circ$, which yields a propiobetaine, $[\alpha]_D - 3.2^\circ$, that is about five-sixths racemised. Excess of trimethylamine rapidly racemises salts of ethyl trimethylaminopropionate, but is without action on salts of ethyl *d*-alanine ester. It would appear that the mere presence of a quaternary ammonium group is sufficient greatly to increase the tendency of the betaine to racemise, autoracemisation at a low temperature being characteristic of optically active quinquivalent nitrogen derivatives. E. F. A.

Oxidation of Leucine, α -Aminoisovaleric Acid, and α -Amino-*n*-valeric Acid with Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 63—76).—Leucine on oxidation with hydrogen peroxide yields isovaleraldehyde, isovaleric acid, ammonia, and carbon dioxide. On further oxidation, acetone is formed from the isovaleric acid. The reaction closely resembles several biochemical changes in which leucine takes part. Breinl and Baudisch's statement as to the formation of isobutaldehyde is incorrect, and the product Liebig described when lead peroxide is used is not butaldehyde, but isovaleraldehyde. α -Aminoisovaleric acid, under similar conditions, yields isobutaldehyde, isobutyric acid, ammonia, and carbon dioxide.

Part of the *isobutyric* acid is further oxidised with acetone and carbon dioxide. With lead peroxide, α -amino*isovaleric* acid yields *isobut*-aldehyde.

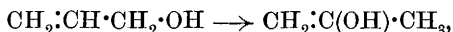
α -Amino-*n*-valeric acid on oxidation yields *n*-butaldehyde, butyric acid, ammonia, and carbon dioxide. On further oxidation, the butyric acid is, in part, decomposed with formation of acetone, aldehydes, lower fatty acids, and carbon dioxide.

The first steps in the oxidation of each of the above amino-acids are analogous to those observed in other amino-acids, and may be expressed as follows:



W. D. H.

Action of Nitrous Acid on Allylamine. LOUIS HENRY (*Compt. rend.*, 1907, 145, 1247—1249).—When an aqueous solution of allylamine neutralised by hydrochloric acid is treated with sodium nitrite, allyl alcohol is the sole product. This shows that at the moment of formation the allyl alcohol does not undergo the isomeric change:



which occurs in the saturated propyl alcohol, since the unsaturated alcohol, $\text{CH}_2\text{:C}(\text{OH})\cdot\text{CH}_3$, would be immediately transformed into acetone, and this is not formed. Thus allylamine behaves differently from propylamine towards nitrous acid. The action of nitrous acid on allylamine may be compared with that on trimethyleneamine, which

gives, not *iso*allyl alcohol, $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CH}\cdot\text{OH}$, but allyl alcohol (Kijner, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 377).

The action of sodium nitrite on dibromopropylamine hydrochloride, $\text{CH}_2\cdot\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{NH}_2\cdot\text{HCl}$ (Henry, *Ann. Soc. Sci. Brussels*, 1880, 4, 317), appears to be more complicated than the reaction with allylamine.

E. H.

Preparation of Methyl and Ethyl Cyanides. VICTOR AUGER (*Compt. rend.*, 1907, 145, 1287—1290).—Potassium cyanide in concentrated aqueous solution acts on (1) methyl sulphate, giving 92% of the theoretical yield of acetonitrile; (2) ethyl sulphate, 90% of propionitrile; (3) sodium methyl sulphate (which, contrary to Beilstein, is not anhydrous, but contains $1\text{H}_2\text{O}$), 92% of acetonitrile and 0.2—0.8% of methylcarbylamine; (4) potassium ethyl sulphate, 75% propionitrile and 0.45% of ethylcarbylamine (using the dry salts only, 55% of propionitrile is obtained); (5) methyl iodide, 95% acetonitrile, and (6) ethyl iodide in the presence of methyl alcohol, 97% of propionitrile in the form of its constant boiling mixture with methyl alcohol.

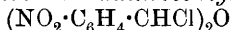
In the last two cases, the carbylamine if formed would be destroyed by the alkyl iodide. Thus, whilst Guillemard's results (*Abstr.*, 1907, i, 300) lead to the conclusion that potassium cyanide has the *isocyanide* constitution when in the solid state, those of the author assign to it a normal structure when in aqueous solution.

E. H.

Preparation of cycloPropane. GABRIEL GUSTAVSON (*J. pr. Chem.*, 1907, [ii], 76, 512. Compare Willstätter and Bruce, *Abstr.*, 1907, i, 1018).—In the author's method of preparing cyclopropane (*Abstr.*, 1888, 240; 1899, i, 421) by the action of zinc dust on trimethylene dibromide, the reaction is carried out in 75% alcohol, and the temperature is raised above 60° only towards the end. The first portions of the product are rejected, as the trimethylene dibromide always contains propylene dibromide. G. Y.

Synthesis of o-Nitrotriphenylmethane. ALFRED KIEGL (*Ber.*, 1907, 40, 4937—4942. Compare Baeyer and Löhr, *Abstr.*, 1900, 1141).—*o*-Nitrotriphenylmethane cannot be obtained by condensing *o*-nitrobenzaldehyde with benzene. The product is a colourless resin, which is completely soluble in concentrated sulphuric acid. The desired compound may be prepared readily from *o*-nitrobenzylidene chloride and benzene by Friedel and Crafts' synthesis.

o-Nitrobenzylidene chloride, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHCl}_2$ (70—75%), and a small amount of *o*-*o*-dichloro-2 : 2'-dinitrobenzyl ether,



(5%), are formed by the action of phosphorus pentachloride on a benzene solution of *o*-nitrobenzaldehyde. The benzylidene chloride is a lemon-yellow liquid, b. p. 143—144°/12 mm., and solidifies in a freezing mixture. It decomposes on exposure to light, or when kept for some time in contact with the atmosphere. When warmed with concentrated sulphuric acid, the aldehyde (40%) is regenerated. The benzyl ether is probably identical with the product obtained by Zimmermann and Müller (*Abstr.*, 1885, 771). A better yield (29%) is obtained by the action of phosphorus pentachloride on a well-cooled chloroform solution of the aldehyde. It is very sparingly soluble in all the ordinary solvents, but may be crystallised from pure ethyl acetate, and decomposes at about 180°. When boiled with acetic acid, it yields the aldehyde, and with alcohol the *diethylacetal* of the aldehyde, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OEt})_2$, b. p. 154—156°/18 mm.

o-Nitrotriphenylmethane, $\text{C}_{19}\text{H}_{15}\text{O}_2\text{N}$, is best obtained when the reaction mixture, with an excess of benzene, is kept at the ordinary temperature for several days, and then decomposed with dilute hydrochloric acid. It crystallises from alcohol in pale yellow, glistening plates, or from light petroleum (100—140°) in compact prisms, m. p. 93—94°, and does not give a coloration with alcoholic potassium hydroxide. J. J. S.

Action of Dichloroacetic Acid on Aniline and its Homologues. I. IWAN VON OSTROMISLENSKY (*Ber.*, 1907, 40, 4972—4979).—When *o*-toluidine is treated with dichloroacetic acid, the author was unable to detect the formation of di-*o*-toluidinoacetic acid according to Meyer (*Abstr.*, 1884, 47); the main product of the action was *o*-methylaminophenyl-*o*-toluidinoacetic acid, $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_2$, which separates from alcohol in prismatic needles, m. p. 239—240° (decomp.). *o*-Tolyl-*o*-methylimesatin, $\text{C}_{16}\text{H}_{14}\text{ON}_2$, obtained as a by-product, separates from alcohol in glistening, golden-yellow leaflets, m. p. about 225° (decomp.); when boiled with acids, it forms *o*-methylisatin and the toluidine salt.

The mechanism of the interaction of *o*-toluidine and dichloroacetic acid is discussed, and the results obtained by Meyer from the action of *p*-toluidine on dichloroacetic acid are confirmed.

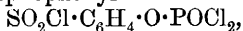
The action of aniline on dichloroacetic acid was also studied.

A. McK.

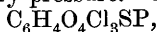
Salts and Ethers of Hexanitrodiphenylamine. D. K. ALEXANDROFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1391—1395).—*s*-Hexanitrodiphenylamine, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_2(NO_2)_3$, is a typical example of a pseudo-acid (compare Hantzsch, *Abstr.*, 1906, i, 576, 651, 833, 856); thus, whilst it is itself a slightly-coloured non-electrolyte, its salts, which are either the *syn*- or *anti*-derivatives, are all brightly coloured. The sodium, lithium, silver, and ammonium salts are red; the potassium and rubidium salts dark violet; they all correspond with the formula $C_{12}H_4O_{12}N_7M$. The crystalline forms of the two series are different, but they all form bright yellow solutions. From the silver salt, red solutions of either the *syn*- or *anti*-methyl and propyl ethers were formed, which could not be isolated. Z. K.

Which Substances Contain a Readily Resolvable Single Carbon-Nitrogen Linking? HERMANN EMDE (*J. pr. Chem.*, 1907, [ii], **76**, 509—511. Compare Mohr, *Abstr.*, 1907, i, 721).—It was shown previously that, on reduction with sodium amalgam, cinnamyl-trimethylammonium chloride, $CHPh:CH \cdot CH_2 \cdot NMe_3Cl$, yields trimethylamine hydrochloride and α -phenylpropylene (Schmidt and Emde, *Abstr.*, 1906, i, 945). On the other hand, the corresponding chlorohydrin, formed by addition of hypochlorous acid to the ethylene linking, when reduced with sodium amalgam yields an amino-alcohol, hydrogen being substituted for the chlorine atom. Hence the C-N linking in the cinnamylamine is rendered unstable by the ethylene linking in the grouping $C:C \cdot C \cdot N$. G. Y.

Action of the Chlorides of Phosphorus on Phenolsulphonic Acids. I. RICHARD ANSCHÜTZ (*Annalen*, 1907, **358**, 92—97).—The action of phosphorus pentachloride on phenol-*p*-sulphonic acid, if analogous to that of the pentachloride on *p*-hydroxybenzoic acid (*Abstr.*, 1906, i, 500), must lead to the formation in the first place of phosphoryl chloride and phenol-*p*-sulphonyl chloride, and thereafter to that of chlorosulphophenyl dichloro-orthophosphate,

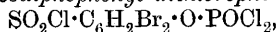


whereas Kekulé obtained *p*-chlorophenylphosphoryl chloride (this *Journ.*, 1873, 1239). On re-investigation of the reaction, it has been found that Kekulé's compound is formed only if the immediate product is distilled under the ordinary pressure. The *dichlorophosphate*,



is obtained if the product of the action of phosphorus pentachloride on potassium phenol-*p*-sulphonate is extracted with light petroleum; it crystallises in colourless needles, m. p. 87—88°, b. p. 203°/13.5 mm.

2 : 6-Dibromo-4-chlorosulphophenyl dichlorophosphate,



prepared in the same manner from potassium 2:6-dibromophenol-4-sulphonate, separates from carbon tetrachloride as a hygroscopic, white, crystalline crust, m. p. 76—78° (compare Zincke and Glahn, Abstr., 1907, i, 698). G. Y.

Oxidation of Thymol by the Oxidising Ferment of Mushrooms. H. COUSIN and HENRI HÉRISSEY (*J. Pharm. Chim.*, 1907, [vi], 26, 487—491. Compare Bougault, Abstr., 1902, i, 638).—When an aqueous solution of thymol is treated with the oxidising ferment of mushrooms in the presence of air, a white precipitate is formed (Bourquelot, Abstr., 1897, ii, 66). The authors have prepared this precipitate by means of the ferment obtained from *Russula delica* and from *Lactarius controversus*. It contains the dithymol, $C_{20}H_{26}O_2 \cdot H_2O$, m. p. 100—101°, described by Dianine (Abstr., 1882, 623), which, after the first melting, resolidifies, and again melts at 164·5° (corr.) (Dianine gives 165·5°), the m. p. of the anhydrous substance. The dithymol so formed is very pure, giving colourless solutions in alkalis instead of the orange solutions obtained by Dianine. The ferment obtained from the second source gives a less pure product. The white precipitate contains other compounds which seem to be of a quinonoid nature, and have not yet been obtained crystalline. The oxidation product of thymol has no antiseptic power, and the authors conclude that in many circumstances thymol is a bad antiseptic agent. E. H.

Sulphoxides and Sulphines. KARL A. HOFMANN and K. OTT (*Ber.*, 1907, 40, 4930—4936).—A solution of ferric chloride in thionyl chloride reacts with heptane from petroleum, yielding a blood-red oil, which gradually solidifies to a black, crystalline mass of *ditolylsulphoxide ferrichloride*, $SO(C_7H_7)_2 \cdot FeCl_3$, m. p. 60·5°. It decomposes when heated with water, yielding ditolylsulphoxide and ferric chloride, and dissolves readily in chloroform to an intense reddish-violet solution, which shows two absorption bands, 660—680 $\mu\mu$ and 520—618 $\mu\mu$, in addition to complete absorption from 440 $\mu\mu$ in the violet end. Toluene yields the same product.

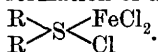
A molecular mixture of benzyl sulphide and benzyl chloride reacts with an ethereal solution of ferric chloride, yielding *tribenzylsulphine chloride ferrichloride*, $S(C_7H_7)_3Cl \cdot FeCl_3$, which crystallises from alcohol in pale yellowish-green, twinned plates, m. p. 98·5°. *Bistribenzylsulphine chloride ferrichloride*, $2S(C_7H_7)_2Cl \cdot FeCl_3$, is formed when excess of benzyl chloride is used, or by the action of thionyl chloride and benzyl chloride on ferric chloride at the ordinary temperature. It forms thick, glistening, crystalline plates, m. p. 97—107° (decomp.). *Tribenzylsulphine platinumchloride*, $[S(C_7H_7)_3]_2PtCl_6$, is insoluble in water, and has m. p. 186°. *Tribenzylsulphine iodide* forms a pale yellow powder, m. p. 75°, and the *ferrocyanide*, $S(C_7H_7)_3 \cdot H_3FeC_6N_6$, a white precipitate which decomposes at 180°.

Benzyl chloride and benzyl sulphide do not appear to react in the absence of ferric chloride. The following mixed sulphine chlorides have been prepared with the aid of ferric chloride, and from the ferrichlorides the ferrocyanides have been obtained by precipitating with

ammonia and adding potassium ferrocyanide solution to the filtrate: dibenzyl-*tert.*-butylsulphine chloride, diethyl-*tert.*-butylsulphine chloride, benzyldiethylsulphine chloride, dibenzyl ethylsulphine chloride, and triethylsulphine chloride.

The ferrocyanides form white precipitates, all of which, with the exception of the last, are insoluble in water.

The accelerating effect of the ferric chloride appears to be due to the formation of an additive compound of the chloride with the sulphide,



J. J. S.

Transformation of the Tetramethylene Ring into the Trimethylene Ring. NICOLAUS J. DEMJANOFF (*Ber.*, 1907, 40, 4961—4963).—Perkin (*Trans.*, 1894, 65, 950) found that when *cyclo*-butylamine, $\text{NH}_2 \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array} \text{CH}_2$, is acted on by nitrous acid, an alcohol, $\text{C}_4\text{H}_8\text{O}$, is formed, to which he assigned the formula $\text{OH} \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array} \text{CH}_2$. The author concludes that, in the action in question, the tetramethylene ring is converted into the trimethylene ring.

The alcohol, $\text{C}_4\text{H}_8\text{O}$, has b. p. 123—124°. It was oxidised by means of a mixture of chromic and sulphuric acids in aqueous solution; the oxidation product exhibited reactions typical of aldehydes, and the semicarbazone prepared from it was by no means uniform, since by treatment with ether it was resolved into *cyclobutanonesemicarbazone*, m. p. 202°, and a semicarbazone, m. p. 126—127°, which has all the properties of *cyclopropaldehydesemicarbazone*. The latter compound is decomposed by dilute acids to form an aldehyde.

It is concluded that the oxidation product of the alcohol, obtained from the amine, $\text{NH}_2 \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array} \text{CH}_2$, is a mixture of *cyclobutanone* and *cyclopropanaldehyde*.

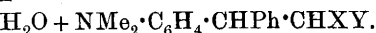
A. McK.

***cyclo*Butylcarbinol and its Isomerisation to Pentamethylene Derivatives.** NICOLAUS J. DEMJANOFF (*Ber.*, 1907, 40, 4959—4961).—*cyclo*Butylcarbinol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \\ \diagdown \text{CH}_2 \end{array} \text{CH}_2$ (compare Perkin, *Trans.*, 1901, 79, 329), may be conveniently prepared by the reduction of ethyl *cyclobutanecarboxylate* by means of sodium and alcohol according to Bouveault and Blanc's method. It is a transparent, thick oil, b. p. 142—142.5°/750 mm., D_{10}^{20} 0.9199, D_{20}^{20} 0.9129, n_D^{19} 1.4449. When warmed with concentrated hydrobromic acid, it is converted into the *bromide*, $\text{C}_5\text{H}_9\text{Br}$, a transparent liquid, b. p. 137—139°, D_{19}^{19} 1.400, n_D^{19} 1.4875. When reduced, a hydrocarbon, C_5H_{10} , is formed with b. p. 49.5—50°; the properties of this hydrocarbon agree with those of *cyclopentane*, but differ from those of *methylcyclobutane*.

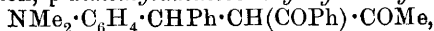
A. McK.

Aromatic Alcohols. New Reactions. ROBERT FOSSE (*Compt. rend.*, 1907, 145, 1290—1293).—Benzhydrol-*p*-dimethylamine similarly to xanthhydrol and dinaphthapyranol (*Abstr.*, 1906, i, 975

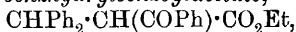
and benzhydrol-*p-p*-tetramethyldiamine (Abstr., 1907, i, 414), condenses with methylenic derivatives with elimination of water, thus :
 $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{OH} + \text{H} \cdot \text{CHXY} =$



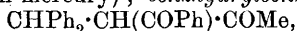
By this reaction, *p*-dimethylaminobenzhydrylbenzoylacetone,



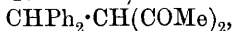
small, faintly sulphur-yellow crystals, m. p. 157—158°, and *p*-dimethylaminobenzhydrylacetylacetone, colourless needles, m. p. 131°, are obtained. In the same way, benzhydrol itself reacts with β -ketonic esters and β -diketones, giving compounds hitherto only obtainable by the action of a halogen derivative of diphenylmethane on the sodium compound of the methylenic derivative. By this new reaction, there were prepared : *ethyl benzhydrylbenzoylacetate*,



needles, m. p. 135° (on mercury) ; *benzhydrylbenzoylacetone*,

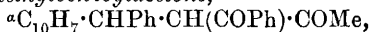


fine, white needles, m. p. 148—150°, and *benzhydrylacetylacetone*,

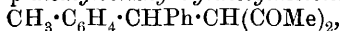


m. p. 116° (on mercury).

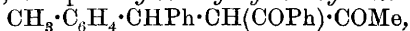
The hydroxyl of different diaryl secondary alcohols will also combine with methylenic hydrogen, forming the compounds : *ethyl phenyl- α -naphthylmethylbenzoylacetate*, $^a\text{C}_{10}\text{H}_7 \cdot \text{CHPh} \cdot \text{CH}(\text{COPh}) \cdot \text{CO}_2\text{Et}$, m. p. 160° (varies with duration of heating) ; *phenyl- α -naphthylmethylacetylacetone*, $^a\text{C}_{10}\text{H}_7 \cdot \text{CHPh} \cdot \text{CH}(\text{COMe})_2$, m. p. 126° (on mercury) ; *phenyl- α -naphthylmethylbenzoylacetone*,



m. p. 185—185.5° ; *p*-methylbenzhydrylacetylacetone,

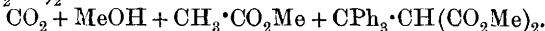


m. p. 104—106°, and *p*-methylbenzhydrylbenzoylacetone,

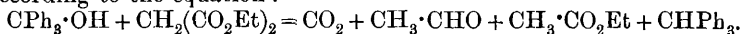


m. p. 130° (on mercury).

By the action of methyl malonate on triphenylcarbinol, carbon dioxide, methyl alcohol, methyl acetate, and *methyl triphenylmethylmalonate*, m. p. 130—131° (on mercury), are formed, thus :



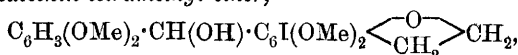
This reaction with ethyl malonate gives Henderson's ethyl triphenylmethylmalonate and, at the same time, triphenylmethane according to the equation :



Hitherto, it has been possible to replace the oxygen in aldehydes by the group :CXY, but not the hydroxyl in alcohols by the group ·CHXY.

E. H.

Catechin. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1907, 40, 4910—4912. Compare Abstr., 1902, i, 553, 637 ; 1907, i, 73).—*Iodocatechin tetramethyl ether*,



m. p. 192—193°, decomp. at 205°, is obtained after a few hours when alcoholic solutions of catechin tetramethyl ether and of iodine

and iodic acid are mixed; it separates from alcohol in long, white needles, forms an *acetate*, $C_{21}H_{23}O_7I$, m. p. 189° , and develops a yellow colour with concentrated sulphuric acid, which after a time becomes violet. The halogen is readily eliminated by zinc dust and alkali, catechin tetramethyl ether being regenerated.

Other halogenated phloroglucinol derivatives in alcoholic solution lose the halogen in a similar manner. Ciamician and Silber's bromomacclurin pentamethyl ether (bromoveratroylphloroglucinol trimethyl ether) is converted into leucomacclurin pentamethyl ether (2:4:6:3'-4'-pentamethoxybenzhydrol), whilst phloroglucinol trimethyl ether is regenerated from *dibromophloroglucinol trimethyl ether*, $C_6HBr_2(OMe)_3$, m. p. $132-133^\circ$, which is obtained by the bromination of the trimethyl ether in glacial acetic acid. C. S.

Ethyl Diazoacetate and *m*-Xylene. EDUARD BUCHNER and KONRAD DELBRÜCK (*Annalen*, 1907, 358, 1—35).—Buchner and his co-workers in a series of investigations (*Abstr.*, 1896, i, 230; 1897, i, 282; 1898, i, 639; 1900, i, 292; 1901, i, 385) have shown that the product of the action of ethyl diazoacetate on benzene is ethyl norcardienecarboxylate, a derivative of a dicyclic system consisting of a three-atom and a six-atom ring, making together a seven-atom ring. Buchner and Feldmann (*Abstr.*, 1904, i, 57) have found the action of ethyl diazoacetate on toluene to lead to the formation of ethyl 3-methylnorcardiene-7-carboxylate or of the products of the conversion of this into derivatives of the methylated seven-atom ring. In the present paper, the substances obtained from ethyl diazoacetate and *m*-xylene are described and their constitutions discussed.

The almost colourless *oil*, b. p. $129^\circ/10$ mm., obtained on fractionally distilling the product of the action of ethyl diazoacetate on *m*-xylene, yields analytical figures corresponding with ethyl dimethylnorcardienecarboxylate, but is a mixture containing comparatively little of this ester. The *oil*, b. p. $115-125^\circ/10$ mm., obtained in the same manner from methyl diazoacetate, when shaken with aqueous ammonia at 0° , yields 3:5-dimethyl- $\Delta^{2,4}$ -norkardiene-7-carboxylamide,

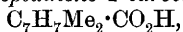
$$\begin{array}{c} \text{CH}:\text{CMe}:\text{CH} \\ \text{CMe}:\text{CH}:\text{CH} \end{array} > \text{CH} \cdot \text{CO} \cdot \text{NH}_2$$
, which crystallises in colourless needles, m. p. 142° , and reduces permanganate in sodium carbonate solution. When boiled with 30% sulphuric acid, the amide is hydrolysed, forming 1:3-dimethylphenyl-4-acetic acid, but, if boiled with 5% sodium hydroxide, it forms 3:5-dimethylcyclo- $\Delta^{3,5,7}$ -heptatriene-1-carboxylic acid,
$$\begin{array}{c} \text{CH}:\text{CMe}:\text{CH}_2 \\ \text{CMe}:\text{CH}:\text{CH} \end{array} > \text{C} \cdot \text{CO}_2\text{H}.$$
 This crystallises in leaflets, m. p. 151° ,

decolorises permanganate in sodium carbonate solution, gives with concentrated sulphuric acid a yellow coloration resembling picric acid, and, when boiled with aqueous sodium hydroxide, yields an acid, m. p. 113° .

The hydr lysis of the crude ethyl dimethylnorcardienecarboxylate with sodium hydroxide leads to the formation of 3:5-dimethylcyclo- $\Delta^{2,5,7}$ -heptatriene-1-carboxylic acid,
$$\begin{array}{c} \text{CH}_2:\text{CMe}:\text{CH} \\ \text{CMe}:\text{CH}:\text{CH} \end{array} > \text{C} \cdot \text{CO}_2\text{H},$$

which crystallises in flat needles, m. p. 148° , decolorises permanganate in sodium carbonate solution, but is stable in air, and gives a yellow coloration with concentrated sulphuric acid. The *magnesium*, *calcium*, and *barium* salts are readily, but the *salts* of the heavy metals only sparingly, soluble; the *silver* salt, $C_{10}H_{11}O_2Ag$, is hygroscopic, and when heated evolves the free acid, m. p. 148° . The *amide*, $C_{10}H_{13}ON$, crystallises in colourless needles, m. p. 107° , becomes yellow and resinous on exposure to air, reduces permanganate in sodium carbonate solution, gives the characteristic yellow coloration with concentrated sulphuric acid, and, on hydrolysis with alkalis, yields the acid, m. p. 148° . On treatment with bromine in glacial acetic acid solution under cooling, the acid forms a *dibromide*, $C_{10}H_{12}O_2Br_2$, which is obtained as a white, crystalline powder, becomes yellow on exposure to light, or at 100° , decomp. 185° , and is only partly soluble in aqueous sodium carbonate. The action of hydrogen bromide on the acid, m. p. 148° , leads to the formation of 1:3-dimethylphenyl-4-acetic acid, m. p. 105° ; the *amide*, $C_{10}H_{13}ON$, crystallises in colourless needles, m. p. 183° . In some cases, the formation of an unstable *product*, intermediate between the dimethylcycloheptatrienecarboxylic acid and the dimethylphenylacetic acid, was observed.

3:5-Dimethylcyclo- $\Delta^{1,5}$ -heptadiene-1-carboxylic acid,



prepared by reduction of the heptatrienecarboxylic acid, m. p. 148° , with sodium amalgam in presence of carbon dioxide, crystallises in colourless needles, m. p. 123° , decolorises permanganate in sodium carbonate solution, is readily oxidised by air, and does not give a coloration with concentrated sulphuric acid. The *amide* crystallises in colourless leaflets, m. p. 101° . The *dibromide*, decomp. 175° , decolorises permanganate.

3:5-Dimethylcyclo- Δ^5 -heptene-1-carboxylic acid, $C_7H_9Me_2 \cdot CO_2H$, prepared by reduction of the cycloheptatriene- or cycloheptadienecarboxylic acid with sodium amalgam in boiling sodium carbonate solution in presence of a current of carbon dioxide, separates from dilute alcohol in crystals, m. p. 80° , decolorises permanganate in sodium carbonate and bromine in glacial acetic acid solution, is not further reduced by sodium amalgam, and does not undergo transformation when boiled with aqueous potassium hydroxide. The *amide* crystallises in leaflets, m. p. 167 – 168° . The acid is converted by the action of hydrogen bromide in glacial acetic acid solution at 100° , or of boiling 50% sulphuric acid, into 3:5-dimethylcycloheptane-

γ -carbolactone, $C_7H_{10}Me_2 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ O \end{smallmatrix}$, which crystallises from light petroleum

in stout prisms, m. p. 76° , and, when boiled with aqueous sodium hydroxide, forms the *sodium* salt of the corresponding hydroxy-acid, which is isolated in the form of its *silver* salt as a white precipitate.

3:5-Dimethylcycloheptanecarboxylic acid, $C_{10}H_{18}O_2N$, prepared by reduction of the three preceding unsaturated acids with sodium in amyl alcoholic solution, is obtained as an oil with an odour resembling that of the fatty acids. The *amide*, $C_{10}H_{19}ON$, crystallises in white

needles, m. p. 157° ; the *silver* salt, $C_{10}H_{17}O_2Ag$, forms yellow leaflets. G. Y.

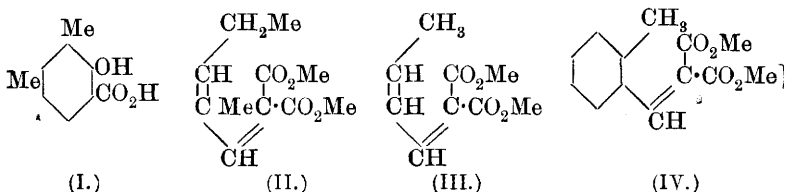
A Case of the Inhibiting Action of the Carboxyl Group. MAXIMILIAN NIERENSTEIN and T. A. WEBSTER (*Ber.*, 1908, 41, 80—81).—The condensation of various phenols and phenolic acids with formaldehyde in the presence of hydrochloric acid to insoluble diphenylmethane derivatives (compare Abstr., 1907, ii, 192) has been studied. With all phenols, the precipitate obtained is completely insoluble in hot water; with hydroxy-acids the amount of precipitate is often less, and only a portion is insoluble in boiling water. The soluble portion consists of hydroxyaurincarboxylic acids. With protocatechuic acid and vanillic acid, precipitates were not obtained.

J. J. S.

Constitution of Phenyl-naphthalenedicarboxylic Acid. A Reply to Stobbe. ARTHUR MICHAEL and JOHN E. BUCHER (*Ber.*, 1908, 41, 70—73. Compare Stobbe, Abstr., 1907, i, 769).—The formation of *o*-benzoylbenzoic acid by the oxidation of 1-phenyl-naphthalene-2:3-dicarboxylic anhydride has been already mentioned by the authors. Most of the differences between Stobbe's results and those obtained previously by the authors (Abstr., 1898, i, 256) are due to the fact that Stobbe did not follow the authors' detailed instructions.

J. J. S.

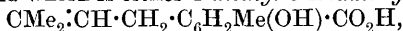
Condensation Reactions of $\alpha\beta$ -Unsaturated Aldehydes; Formation of Benzene Rings. HANS MEERWEIN (*Annalen*, 1907, 358, 71—91).—The formation of aromatic from aliphatic compounds takes place in some cases with great ease, whilst analogously constituted substances may not undergo ring condensation. Thus, whereas the condensation product of methylethylacraldehyde and acetone is readily transformed into ψ -cumene (Barbier and Bouveault, Abstr., 1895, i, 643), Dautwitz (Abstr., 1906, i, 803) was unable to obtain *p*-xylene from the condensation product of tiglic aldehyde and acetone. The present author, who has undertaken a systematic investigation of the factors determining the formation or non-formation of rings in such cases, finds that *o*-hydroxymesitylenic acid (I) is formed from the condensation product (II) of methylethylacraldehyde and methyl malonate, but that the condensation products of crotonaldehyde (III) and tolualdehyde (IV) with methylmalonate do not form aromatic hydroxy-acids:



The ring formation is evidently determined by the presence of

substituting groups, and by their position. Attempts to prepare aromatic hydrocarbons from the condensation products of crotonaldehyde and *o*-tolualdehyde with acetone were unsuccessful.

Condensation of $\alpha\beta$ -Unsaturated Aldehydes with Methyl Malonate: Synthesis of Homologous Salicyclic Acids.—Methyl citralidenemalonate, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Me})_2$, formed in a 63% yield by the action of citral on methyl malonate in presence of piperidine at -10° , is obtained as a viscid oil, b. p. $190-195^\circ/20\text{ mm.}$, D^{15}_D 1.043, n^{15}_D 1.5126; the mol. refraction observed, 76.60, is considerably greater than the calculated, 73.73, as has been found by other authors in the case of compounds containing conjugated ethylene linkings. When boiled with sodium hydroxide in alcoholic solution, the ester is converted into an acid which is either 4-methyl-3-isoamerylsalicylic acid,



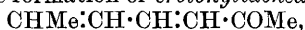
or 4-isohehexenylsalicylic acid, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$. This crystallises in needles, m. p. $166-167^\circ$, sublimes when carefully heated, distils with superheated steam, gives an intense blue coloration with ferric chloride in highly dilute alcoholic or aqueous solution, and forms a dibromide, $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Br}_2$, crystallising in prisms, m. p. $160-161^\circ$.

Methyl crotonylidenemalonate, $\text{C}_9\text{H}_{12}\text{O}_4$, obtained in a 39% yield by the action of crotonaldehyde on methyl malonate in presence of piperidine at -5° , forms a yellow oil with a faint odour, b. p. $130-135^\circ/15\text{ mm.}$, D^{15}_D 1.1105, n^{15}_D 1.48849.

The condensation product of α -methyl- β -ethylacraldehyde and methyl malonate, $\text{C}_{11}\text{H}_{16}\text{O}_4$, b. p. $139-145^\circ/16\text{ mm.}$, is obtained in a 30% yield. When boiled with alcoholic sodium hydroxide, it is converted into *o*-hydroxymesitylenic acid, m. p. 180° (Fittig and Hoogewerff, *Annalen*, 1869, 150, 333).

Methyl *o*-tolylidenemalonate, $\text{C}_{13}\text{H}_{14}\text{O}_4$, forms white crystals, m. p. $59-60^\circ$, b. p. $165-170^\circ/11\text{ mm.}$, and, on hydrolysis, yields *o*-methylcinnamic acid.

Condensation of Crotonaldehyde with Acetone: Crotonylideneacetone.—The action of crotonaldehyde on acetone in aqueous sodium hydroxide leads to the formation of crotonylideneacetone,

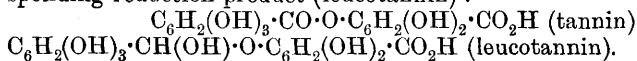


in a 23% yield; it is obtained as a mobile, strongly refracting oil with an aromatic odour, b. p. $78-80^\circ/16\text{ mm.}$, D^{15}_D 0.8990, n^{15}_D 1.51954, is readily oxidised on exposure to air, and forms an additive compound with four atoms of bromine. The oxime, $\text{C}_7\text{H}_{11}\text{ON}$, crystallises in white needles, m. p. $90-92^\circ$, b. p. $124-125^\circ/14\text{ mm.}$; the semicarbazone, $\text{C}_8\text{H}_{13}\text{ON}_3$, crystallises in nacreous leaflets, m. p. $157-158^\circ$; the phenylhydrazone forms yellow leaflets, m. p. $70-71^\circ$. On oxidation with sodium hypochlorite at 70° , the ketone yields chloroform and sorbic acid.

o-Tolylideneacetone, $\text{C}_{11}\text{H}_{12}\text{O}$, solidifies when cooled with ice, and melts about the ordinary temperature, forming a colourless, strongly refracting oil, b. p. $136-138^\circ/10\text{ mm.}$ G. Y.

Constitution of Tannin. III. MAXIMILIAN NIERENSTEIN (*Ber.*, 1908, 41, 77—80. Compare Abstr., 1905, i, 914; 1907, i, 331).—The

penta-acetyl tannin, m. p. 203°, may be reduced to the acetyl derivative, m. p. 166°, by means of zinc dust and glacial acetic acid. The latter acetyl compound, *acetyl-leucotannin*, when further acetylated in the presence of pyridine, yields a *hexa-acetyl-leucotannin*, m. p. 159°. Penta-acetyl-leucotannin is not reduced, and penta-acetyl tannin cannot be further acetylated. These observations support the view that tannin is a mixture of digallic acid (tannin) and the corresponding reduction product (leucotannin):



The formula for leucotannin contains an asymmetric carbon atom which may account for the optical activity of ordinary tannin.

When oxidised, penta-acetyl tannin gives more ellagic acid, but less rufigallic acid, than does triacetylgallic acid. J. J. S.

Glycidic Esters and Aldehydes in the Naphthalene Series.

GEORGES DARZENS (*Compt. rend.*, 1907, 145, 1342—1343. Compare *Abstr.*, 1905, i, 116; 1906, i, 62, 137, 430; 1907, i, 178, 182, 627).—

Ethyl β-1-naphthyl-β-methylglycidate, $\text{O} \begin{array}{l} \text{CMe} \cdot \text{C}_{10}\text{H}_7 \\ \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$, obtained by the

condensation of α -naphthyl methyl ketone with ethyl chloroacetate in the presence of sodium ethoxide, is a colourless, viscous liquid, b. p. 165—170°/4 mm.; the corresponding acid on distillation decomposes into carbon dioxide and α -1-naphthylpropaldehyde, $\text{C}_{10}\text{H}_7 \cdot \text{CHMe} \cdot \text{CHO}$, an amber-coloured liquid with an odour similar to that of hydratropaldehyde, b. p. 131—132°/4 mm.; the *semicarbazone* has m. p. 209—210°.

Ethyl β-2-naphthyl-β-methylglycidate, similarly prepared to the above, is an odourless liquid, b. p. 175—180°/5 mm.; the corresponding acid is solid, and yields on distillation α -2-naphthylpropaldehyde, m. p. 53°; the *semicarbazone* has m. p. 134—135°.

The *semicarbazones* of α - and $\alpha\beta$ -naphthyl methyl ketone have m. p. 232—233° and 235—237° respectively. M. A. W.

Menthazine. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1246—1250. Compare *Abstr.*, 1900, i, 277).—*l*-Menthone, when treated with hydrazine hydrate at the ordinary temperature, forms chiefly *l*-menthazine, m. p. 51°, $[\alpha]_D - 107.68^\circ$; at higher temperatures, or when the mixture is distilled, it forms *d*-menthazine, m. p. 83.5°, $[\alpha]_D + 64.89^\circ$ to $+85.27^\circ$. The latter is also formed when *d*-menthone is employed. The liquid product formed in the action of hydrazine hydrate on *l*-menthone consists of a mixture of *l*- and *d*-menthazines. The production of the *d*-menthazine is due to the isomerisation of *l*-menthazine at higher temperatures. Z. K.

Ketone Derived from β-Hexahydrocarvacrol. LÉON BRUNEL (*Compt. rend.*, 1907, 145, 1427—1429).—When the β -hexahydrocarvacrol (β -carvacromenthol), obtained by the direct hydrogenation

of carvacrol in the presence of reduced nickel (Abstr., 1906, i, 81), is oxidised with chromic acid, it yields the ketone, carvacromenthone, b. p. 221—221·5°, D_D^{20} 0·908. The oxime, amine, and two isomeric semicarbazides were prepared, and were found to be identical with the corresponding derivatives of tetrahydrocarvone described by Baeyer (Abstr., 1893, i, 359) and Wallach (Abstr., 1894, i, 44; 1896, i, 101); it follows therefore that β -carvacromenthol (1-methyl-4-*isopropylcyclohexane*-2-ol) is identical with tetrahydrocarveol.

M. A. W.

Components of Ethereal Oils. Constitution of Umbellulone, $C_{10}H_{14}O$. FRIEDRICH W. SEMMLER (*Ber.*, 1907, 40, 5017—5023).—The physical data for dihydroumbellulone show that it is not a dicyclic derivative belonging to the pinene, camphor, or *dicyclo-octanone* series (compare Tutin, *Trans.*, 1906, 39, 1104; 1907, 91, 271). Umbellulone, $C_{10}H_{14}O$, has b. p. 93—98°/10 mm., D_D^{20} 0·958, n_D 1·4895, α_D -31·5° (100 mm. tube), mol. ref. 45·19. Dihydroumbellulol, $C_{10}H_{18}O$, has b. p. 91—93°/10 mm., D_D^{20} 0·931, n_D 1·47348, α_D -27·5° (100 mm. tube). β -Dihydroumbellulone, $C_{10}H_{16}O$, has b. p. 83—87°/10 mm., D_D^{20} 0·928, n_D 1·45862, α_D -30·5° (100 mm. tube).

Dihydroumbellulone forms oxymethylene and benzylidene compounds, showing that the keto-group is adjacent to a CH_2 group. The *oxymethylene* compound has b. p. 105—107°/10 mm., D_D^{18} 1·001, n_D 1·49097; it yields homotanacetonedicarboxylic acid on oxidation, and gives a violet-red coloration with ferric chloride. The *benzylidene* compound has b. p. 185—188°/9 mm., D_D^{20} 1·03, n_D 1·574, and solidifies to minute needles, m. p. 81—82°.

The molecular refractions of these compounds are all considerably higher than the calculated values, as is also the case in the tanacetone series.

l-Benzylidene- β -dihydroumbellulone yields, on oxidation, *d*-homotanacetonedicarboxylic acid, m. p. 146—147°, α_D +2·5° (20% solution in 100 mm. tube), which unites with the *l*-homotanacetonedicarboxylic acid from *d*-tanacetone (compare Semmler, Abstr., 1904, i, 176) to form *i*-homotanacetonedicarboxylic acid, m. p. 179°, and crystallising in short needles. The *d*-acid forms a neutral *ethyl* ester, b. p. 148—153°/10 mm., and an oily *acid ethyl* ester.

Dihydroumbellulone is regarded as a tanacetone of the methone series, $CH_2 \begin{array}{c} \diagup C(CHMe_2) \cdot CO \\ \diagdown CH - CHMe \end{array} \diagup C$, whereas umbellulone has a double

bond adjacent to the keto-group, $CH_2 \begin{array}{c} \diagup C(CHMe_2) \\ \diagdown CH \cdot CMe : CH \end{array} \diagup CO$.*

E. F. A.

Oxygen Derivatives of Camphene. THADDEUS MILOBENDSKI (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1395—1403).—The camphene prepared from *isoborneol* has m. p. 47·5—48·5°, b. p. 159·5°/755 mm., and is optically inactive; that from *pinene hydrobromide* has m. p. 44—45°, b. p. 159·5°/755 mm., $[\alpha]_D$ -41°46'.

* See also Tutin, *Proc.*, 1908, 24.

The former, when oxidised with permanganate, yielded only a very small quantity of neutral products, containing a glycol, m. p. 197·5—198·5°, and a trace of acid, having the odour of acetic acid. The glycol obtained from the other camphene has m. p. 181—185°, $[\alpha]_D + 21^\circ 40'$; after subliming at 110°, m. p. 156—177°, and when re-sublimed at 96°, m. p. 169—175°. The glycol obtained from diacetylcamphene has m. p. 160—161°. The first glycol, m. p. 197·5—198·5°, when dehydrated, yields camphenilonealdehyde, m. p. 68·5—70°, and a white, resinous substance distilling above 300°/15 mm. When the glycol is oxidised with potassium permanganate, it yields camphenilone, m. p. 36—37°, a small quantity of volatile acids, camphenilic acid, m. p. 170—171° (sodium salt, $C_{10}H_{15}O_3Na \cdot 5H_2O$), and camphenecamphoric acid, m. p. 135—136°. With nitric acid, the glycol yields two acids, $C_{10}H_{16}O_2$, m. p. 93·5—94°, $C_{10}H_{16}O_4$, m. p. 191·5—192·5°, apocamphoric anhydride, $C_9H_{12}O_3$, m. p. 177·5—178°, a ketonic acid, m. p. 235°, the oxime of which has m. p. 195—196·5°, and some other crystalline products which could not be isolated. With chromic acid, the glycol yields camphenilone and camphenecamphoric acid.

Camphenecamphoric acid, obtained from either of the two camphenes mentioned above, is optically inactive, and has m. p. 135·5—136°, and distils at 235—237°/10—11 mm., 250—251°/20 mm., but when it is obtained from camphene prepared from borneol chloride it has m. p. 145—146°. The chloroanhydride of camphenecamphoric acid has b. p. 153·5—154·5°/13 mm., but in estimating the chlorine in alcoholic solution the results are too low. It was not found possible to obtain the pure ethyl ester by Fischer's method. The chromate is also described. An attempt was made to determine the constitution of the acid by bromination, then removing hydrogen bromide by means of potassium hydroxide, and, finally, oxidising the unsaturated acids so obtained with potassium permanganate, but without success. One crystalline unsaturated acid, m. p. 147·5—149°, was thus isolated; it is readily soluble in water, alcohol, and chloroform. Z. K.

Investigations in the Terpene and Camphor Series. LEO A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1324—1343. Compare Abstr., 1905, i, 71, 166).—Since pinene is very unstable, most of its derivatives have a different constitution from the parent substances; consequently, to obtain true derivatives, the xanthogen reaction has been applied, as in this case polymerisation does not occur. Pinocampeol was prepared from pinene by a modification of Wallach's method, and then converted into the xanthogen derivative, $C_{10}H_{17} \cdot O \cdot C \cdot S_2Me$, m. p. 60·5—61°; it forms rhombic crystals $[a:b:c = 1:3747:1:0:97875]$. At 180—190°, it decomposes thus: $C_{10}H_{17} \cdot O \cdot CS_2Me \rightarrow C_{10}H_{16} + MeSH + CSO$, yielding inactive pinene; from this it is evident that pinocamphone and pinocampeol are true derivatives of pinene (compare Wallach and Engelbrecht, Abstr., 1906, i, 683).

l-Dihydrocarveol was converted into the xanthate, $C_{10}H_{17} \cdot O \cdot CS_2Me$, which by the action of ammonia yielded the amide, $C_{10}H_{17} \cdot O \cdot CSNH_2$, m. p. 62—63°, $[\alpha]_D^{21} - 138 \cdot 89^\circ$; it forms rhombic crystals $[a:b:c = 0:6548:1:0:7058]$. The racemic modification of this amide has

m. p. 95·5—96°, crystallises in small needles, and is much less soluble in organic solvents than the active amides. Methyl dihydrocarveol xanthate decomposes at 180—190° in exactly the same manner as pinocampheol xanthate, forming the *terpene*, $C_{10}H_{16}$, b. p. 172—174°, $n_D^{20.5}$ 1·46972, $D_{20.5}^{20.5}$ 0·8382, $[\alpha]_D +131.93^\circ$.

The Sachgeisa oil or resin, which is used as a chewing gum by the natives of South Caucasia, when subjected to steam distillation, yields an oil consisting almost wholly of inactive pinene together with a small quantity of active terpene. The resin is analogous with that obtained from the bark of the tree *Pistacia lentiscus*, and known as mastic.

Z. K.

New Method for the Hydration of Pinene. PHILIPPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1907, 145, 1425—1427).—When pinene in acetic acid solution is treated with a solution of benzenesulphonic acid, it is converted to the extent of 52·3% into terpineol. For this purpose, freshly-distilled French pinene is dissolved in an equal weight of acetic acid, one-tenth of its weight of a 50% aqueous solution of benzenesulphonic acid added, and the mixture shaken until it becomes homogeneous. After twelve hours, water is added, and the insoluble layer washed, dried, and separated by distillation into two fractions, the first, boiling below 85°/15 mm., consists of unchanged pinene with a small quantity of a terpadiene, b. p. 175—178°, and the second fraction, boiling above 85°/15 mm., after saponification with alcoholic potassium hydroxide at 110—115°, is composed of terpineol, b. p. 100—105°/13 mm., m. p. 35°, together with a small quantity of borneol, fenchyl alcohol, and a viscous substance not identified.

When large quantities of purified pinene are submitted to the above reaction, a hydrocarbon having a lower boiling point than the original pinene can be isolated from the product.

M. A. W.

Santene. OSSIAN ASCHAN (*Ber.*, 1907, 40, 4918—4923).—In addition to *l*-pinene, *l*-camphene, phellandrene, Müller's santene has been isolated from Siberian turpentine and identified by conversion into the nitrosochloride, nitrosite, tribromide (m. p. 77—80°. Müller gives 62—63°), and hydrochloride, as well as by direct comparison with the santene obtained from sandal wood oil (*Abstr.*, 1900, i, 678). It has b. p. 140°, D^{15}_D 0·8698, $n^{19.2}_D$ 1·4690, and the formula C_9H_{14} is confirmed.

Santenol acetate, $C_9H_{15} \cdot OAc$, prepared by using acetic and sulphuric acids, is a clear liquid, resembling *isobornyl acetate* in odour, b. p. 215—219°/760 mm., and 88—89°/8 mm., D^{20}_4 0·9871, optically inactive, n^{19}_D 1·45929, thus showing the compound to be saturated.

The santenol, obtained on hydrolysis, is a solid mixture, two-thirds of which has b. p. 195—196°, and the remainder b. p. 196—198°, and the conjecture is made that it is similar to the *isborneol*-borneol mixture obtained from camphene. By recrystallisation from light petroleum, large, transparent plates, m. p. 97—98°, are obtained. The

phenylurethane forms long needles, m. p. 61—62°. Oxidation of santenol results in the formation in small quantity of a ketone (*semicarbazone*, m. p. 225—226°).

Santene is also a constituent of oils from *Pinus picea*, *Abies excelsa*, and a Swedish turpentine. W. R.

Russian Turpentine Oil and Russian Pine Tar Oil. IWAN SCHINDELMEISER (*Chem. Zeit.*, 1908, 32, 8).—Russian turpentine and pine tar oils contain sylvestrene, dipentene, and, in the pinene fraction, nopinene, identified by the formation of the sparingly soluble acid, m. p. 126°, and sparingly soluble sodium salt on oxidation with permanganate. The pine tar oil contains also toluene, cymene, and a quinone-like *substance*, which has a sharp odour, is resinified, becoming yellow, on treatment with sodium hydroxide and metallic sodium, and reacts with hydroxylamine and phenylhydrazine, together with saturated acyclic hydrocarbons, one of which, b. p. 98—99°, is probably a heptane. A sesquiterpene present in Russian pine tar oil is, perhaps, identical with the sesquiterpene occurring together with cadinene in cade oil.

G. Y.

Turmeric Oil. HANS RUPE (*Ber.*, 1907, 40, 4909—4910. Compare Jackson and Menke, *Abstr.*, 1883, 482).—When turmeric oil is boiled with dilute sodium hydroxide, the main product is a substance containing oxygen, b. p. 156°/12 mm., which is probably not identical with Jackson and Menke's turmerol, and does not exhibit the properties of an alcohol, aldehyde, acid, or ketone. When boiled with stronger alkali, it yields an optically active *ketone*, $C_{13}H_{18}O$, b. p. 119—120°/8 mm., which forms a *semicarbazone*, m. p. 119·5—120·5°, an *oxime*, b. p. 159°/11 mm., and well-crystallised condensation products with aromatic aldehydes. The ketone is oxidised by potassium permanganate to terephthalic acid and *p*-methylacetophenone, and yields, by treatment with alkali hypobromite, a *hydroxy-acid*, $C_{12}H_{16}O_3$, m. p. 150°, and an *acid*, $C_{12}H_{16}O_2$, m. p. 33—34°; the latter is oxidised by potassium permanganate to a dicarboxylic acid, $C_{12}H_{14}O_4$, m. p. 228°.

C. S.

Action of Nitrous Acid on Caoutchoucs. OTTO GOTTLÖB (*Zeitsch. angew. Chem.*, 1907, 20, 2213—2221. Compare Harries, *Abstr.*, 1905, i, 223; this vol., i, 39).—The products obtained by the action of nitrous fumes on crude or purified caoutchoucs vary in composition with the proportion of nitrogen peroxide present in the mixture of nitrogen oxides, but all are more or less impure forms of Harries' nitrosite, $C_{10}H_{15}O_7N_3$. The latter substance can only be obtained in a pure state by strictly following the directions given by Harries (*Abstr.*, 1903, i, 189). The existence of the nitrosate, $C_9H_{16}O_6N_2$, described by Alexander (*Abstr.*, 1905, i, 223; 1907, i, 433; *Zeitsch. angew. Chem.*, 1905, 18, 164) is doubtful. The same author's statement that carbon dioxide is liberated during the action of nitrous fumes on caoutchouc is correct, but the quantity evolved only corresponds with roughly 0·3% of the total carbon present in the caoutchouc treated.

W. H. G.

West African Copals, especially Angola and Cameroon Copals. ALEXANDER TSCHIRCH and H. RACKWITZ (*Arch. Pharm.*, 1907, 245, 415—426. Compare Abstr., 1897, i, 92).—The constants are given of samples of copal from Sierra Leone, Accra, Benin, Loango, Congo, and Benguela.

The Angola copal examined had m. p. 140—170°, acid number 135, saponification number 155, and iodine number 66. The copal was extracted with ether. From the ethereal solution, 1% aqueous ammonium carbonate did not extract anything, but 1% aqueous sodium carbonate extracted: (1) amorphous *angocopalolic acid*, $C_{23}H_{36}O_3$, m. p. 85°, acid number 157, corresponding with monobasicity (the *silver salt* was analysed), saponification number 155, and iodine number 71, corresponding with one double bond, precipitated in alcoholic solution by lead acetate, and (2) a resinous acid not so precipitated. By evaporating the ether and distilling with steam, an *essential oil*, b. p. 140—160°, D 0.853, passed over, whilst yellow, amorphous *α -angocopaloresen*, $C_{30}H_{54}O_6$, or $C_{30}H_{56}O_6$, m. p. 63—65°, remained behind. From the residue of the copal insoluble in ether, alcohol-ether extracted, in addition to traces of angocopalolic acid, yellow *β -angocopaloresen*, $C_{25}H_{38}O_4$, m. p. 220—224°. There remained insoluble in alcohol-ether a substance resembling bassorin, soluble in aqueous sodium hydroxide, and insoluble inorganic silicates. In 100 parts of the drug are contained: angocopalolic and other acids, soluble in ether, 64; essential oil, 2; *α -angocopaloresen*, 3; acid soluble in ether (?), 5; *β -angocopaloresen*, 20; substance resembling bassorin, 0.3; ash, 5.7.

The Cameroon copal examined had m. p. 105—125°, acid number 126, saponification number 157, and iodine number 68. After extraction with ether for three months, aqueous ammonium carbonate did not extract anything from the ethereal solution, but 1% aqueous sodium carbonate extracted: (1) amorphous *cameroocopalolic acid*, $C_{21}H_{36}O_3$, m. p. 98—100°, acid number 160, corresponding with monobasicity (the *silver salt* was analysed also), saponification number 188, and iodine number 76.5, corresponding with one double bond, precipitated in alcoholic solution by lead acetate; and (2) a resinous acid not so precipitated. By evaporating the ether and distilling with steam, a yellow *essential oil*, b. p. 145—155°, D 0.830, was driven over, whilst viscous *α -cameroocopaloresen* remained behind. From the residue of the copal insoluble in ether, alcohol-ether extracted *β -cameroocopaloresen*, $C_{25}H_{38}O_4$, m. p. 220—224°. There remained insoluble in alcohol-ether a *substance* resembling bassorin, soluble in aqueous sodium hydroxide, and an insoluble residue largely inorganic in character. In 100 parts of the drug are contained: cameroocopalolic and other acids, 70; essential oil, 2; *α -cameroocopaloresen*, 3; *β -cameroocopaloresen*, 20; substance resembling bassorin, 3; ash, 2.

C. F. B.

Heerabol Myrrh. OSCAR VON FRIEDRICHS (*Arch. Pharm.*, 1907, 245, 427—457. Compare Köhler, Abstr., 1890, 1317; Tucholka, Abstr., 1897, i, 584; and especially Tschirch and Bergmann, Abstr., 1906, i, 197; Lewinsohn, Abstr., 1906, i, 972).—Commercial samples of

Myrrha electa were examined, and consisted of yellowish-brown to reddish-brown pieces with a waxy, translucent fracture.

The following substances were isolated from it: (1) a volatile essential oil (8·8%), viscid, yellow to yellowish-green, D_4^{20} 1·011, n_D^{20} 1·5359, $[\alpha]_D^{20}$ -73·9°, acid number 6·15, and ester number 47·6. From this oil, there were separated formic and acetic acids and a crystalline acid, m. p. 159°, which was not volatile with steam, *m*-cresol, cuminaldehyde and cinnamaldehyde, and the crystalline, monobasic *myrrholic acid*, $C_{17}H_{22}O_5$, m. p. 236° (of which the amorphous *silver*, *lead*, and *copper* salts were analysed), and the sesquiterpene, *heerabolene*, $C_{15}H_{24}$, b. p. 130—136°/16 mm., D_4^{20} 0·943, n_D^{20} 1·5125, α_D^{20} 14°10' in 100 mm. tube, the molecular refraction indicating a tricyclic sesquiterpene; this yielded a crystalline *dihydrochloride*, $C_{15}H_{24} \cdot 2HCl$, m. p. 98—99°.

(2) That part of the resin which was soluble in light petroleum yielded some acetic acid when submitted to dry distillation.

From that part of the drug insoluble in light petroleum, but soluble in ether, the following constituents were separated: *α -commiphoric acid*, $C_{14}H_{18}O_4$, m. p. 201—203°, is monobasic; *β -commiphoric acid*, m. p. 205°, has the same formula and basicity; *γ -commiphoric acid*, $C_{17}H_{22}O_5$, m. p. 169—172°, is monobasic; all three acids are amorphous, yellow to brown, cannot be acetylated, and do not contain methoxy-groups. *α -Heerabo-myrrhol*, $C_{18}H_{26}O_5$, m. p. 248—250°, forms a *diacetyl* derivative of m. p. 228° (decomp.), and is precipitated from an alcoholic solution by lead acetate; *β -heerabo-myrrhol*, $C_{20}H_{26}O_6$, m. p. 168°, forms a *diacetyl* derivative. *Commiphorinic acid*, $C_{28}H_{36}O_8$, m. p. 135°, is brown, amorphous, and monobasic; the barium salt is insoluble in water and alcohol. A yellow *alcohol*, $C_{14}H_{22}O_2$, b. p. 264°, which forms a *monoacetyl* derivative of b. p. 243°, and is volatile with steam; and the non-volatile, yellow, amorphous *heeraboresen*, $C_{42}H_{56}O_8$, m. p. 100—102°, which contains one methoxyl group.

The part of the drug insoluble both in light petroleum and in ether was soluble in aqueous sodium carbonate. It was separated into (1) brown, amorphous, monobasic *α -heerabo-myrrholic acid*, $C_{15}H_{22}O_7$, m. p. 220—225°, of which the amorphous *silver* and *lead* salts were analysed, but no acetyl derivative could be prepared; it is precipitated in alcoholic solution by lead acetate, and (2) *β -myrrholic acid*, $C_{25}H_{32}O_6$, m. p. 187—190°, not so precipitated, brown, amorphous, and monobasic, of which the *silver* salt was analysed.

The *gum* had $[\alpha]_D + 23·8^\circ$ in 2% aqueous solution, and was mixed with an enzyme of the oxydase group; when oxidised with nitric acid, it yielded mucic acid, and when distilled with hydrochloric acid, furfuraldehyde; hence it probably contained galactose and arabinose.

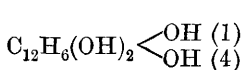
No bitter principle was detected, but the volatile oil has a biting, unpleasant taste.

C. F. B.

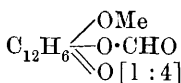
Baptisia Glucosides. IV. ψ -Baptisin. K. GORTER (*Arch. Pharm.*, 1907, 245, 561—572. Compare *Abstr.*, 1897, i, 627; 1898, i, 39; 1906, i, 973).—The presence of one hydroxyl group in ψ -baptigenin has been confirmed by the preparation of the *benzoate*, $C_{15}H_9O_5Bz$, crystallising in small, white needles, m. p. 216°.

The substance obtained by heating the sodium derivative of ψ -baptigenin with ethyl iodide and alcohol (compare Abstr., 1906, i, 973) is now shown to have the composition $C_{14}H_{10}O_4$, and is named ψ -baptigin; it crystallises in small, colourless plates, m. p. 172° (not 169° , as previously stated). It yields neither an acetyl nor a benzoyl derivative, and, consequently, cannot contain a hydroxyl group. Since the formation of ψ -baptigin is accompanied by the production of formic acid, it follows that ψ -baptigenin must have the partially structural formula $C_{14}H_8O_4:CH\cdot OH$. No ψ -baptigin results on heating sodium ψ -baptigenin with ethyl alcohol alone, and in the presence of ethyl iodide only one-half of the ψ -baptigenin is converted into ψ -baptigin. What probably happens in the latter case is as follows: part of the sodium ψ -baptigenin is converted into the ethyl ether, which is then hydrolysed, with the formation of ψ -baptigin and ethyl formate: $C_{14}H_8O_4:CH\cdot OEt + H_2O = C_{14}H_{10}O_4 + H\cdot CO_2Et$. The ethyl formate, together with ethyl alcohol, reacts with more sodium ψ -baptigenin, forming ethyl ether, sodium formate, and ψ -baptigenin: $C_{14}H_8O_4:CH\cdot ONa + H\cdot CO_2Et + EtOH = C_{14}H_8O_4:CH\cdot OH + H\cdot CO_2Na + OEt_2$.

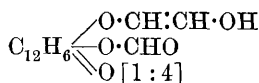
The substance, $C_{13}H_{12}O_4$, previously described (Abstr., 1898, i, 39), is now shown to be *methylbaptigenetin*, and is formed together with formic acid on hydrolysing ψ -baptigin with alcoholic potassium hydroxide. It yields on acetylation two acetyl derivatives, colourless, rhomboidal crystals, m. p. about 123° , and colourless, rectangular crystals, m. p. 148° . These could not be isolated in a pure state, but it is probable from an analysis of the mixture that the compounds formed are *triacetylmethylbaptigenetin* and *acetylanhydromethylbaptigenetin*. From the above facts, together with those previously published (*loc. cit.*), it follows that baptigenetin must have the partially structural formula (I), and ψ -baptigin the formula (II). Since ψ -baptigenin, when heated with potassium hydroxide solution, yields baptigenetin, formic acid, and methyl alcohol, it is probable that it has the formula (III):



(I.)



(II.)



(III.)

When heated under pressure with 5% hydrochloric acid at 200° for two hours, methylbaptigenetin yields a small quantity of a substance which has the properties of catechol. It is possible therefore that baptigenetin is a derivative of diphenylene oxide. W. H. G.

Chitin. THEODOR R. OFFER (*Biochem. Zeitsch.*, 1907, 7, 117—127).—Chitin, prepared from the carapace of the lobster by successive treatment with dilute hydrochloric acid, boiling 10% potassium hydroxide, potassium permanganate, and sodium hydrogen sulphite, was hydrolysed by 70% sulphuric acid at the ordinary temperature, and yielded two amorphous substances of the composition $C_{14}H_{26}O_{10}N_2$. One

of these is *acetyldiglucoamine*, m. p. 194° (decomp.), soluble in water, and optically inactive. The other is insoluble in water, gives a reddish-brown coloration with iodine, and is regarded as a polymeride of the former substance.

In *acetyldiglucoamine*, one amino-group is probably acetylated, whilst the amino-group of the second glucosamine molecule is condensed with the aldehyde group of the first.

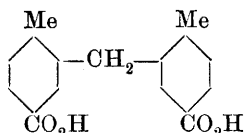
Chitin itself is regarded as a highly polymerised *acetyldiglucoamine*.
G. B.

Solanin from the Seeds and Flowers of *Solanum Tuberosum*.

AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 683—690; 755—762. Compare Oddo and Colombano, *Abstr.*, 1905, i, 455).—From a study of the physical and chemical characters of various samples of solanin, the author draws the conclusion that the latter exhibits properties varying with the source from which it is obtained. Thus solanin extracted from *Solanum tuberosum* differs essentially from that isolated from *S. sodomæum*, the two products yielding different solanidins when treated with boiling dilute hydrochloric acid.
T. H. P.

Phylloxanthin. LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, 7, 282—285. Compare *Abstr.*, 1907, i, 69, 71, 784, 787, 865, 866, 867, 948).—Polemical. The identity of certain chlorophyll derivatives described by Tsvett and Willstätter is discussed, and the former's spectroscopic results with phylloxanthin are described as incorrect.
W. D. H.

Rottlerin. FRANZ HERRMANN (*Arch. Pharm.*, 1907, 245, 572—585. Compare A. G. Perkin, *Trans.*, 1893, 63, 975; 1895, 67, 230; Telle, *Abstr.*, 1906, i, 973; 1907, i, 435; Thoms, *Abstr.*, 1907, i, 545).—Perkin's *isorottlerin* is considered to be impure *rottlerin*; his formula, $C_{33}H_{30}O_9$, for the latter compound is, however, confirmed. *Rottlerin* in alkaline solution yields, on oxidation with hydrogen peroxide at 75° , cinnamic and benzoic acids. 2:4:6-Trihydroxytoluene results on decomposing *rottlerin* with concentrated potassium hydroxide solution at 150° ; the same compound is also formed together with 2:4:6-trihydroxy-*m*-xylene, acetic acid, and a tarry substance by heating a solution of *rottlerin* in 15% aqueous sodium hydroxide a short time with zinc dust. The tarry substance is oxidised in alkaline solution by hydrogen peroxide, with the formation of a dibasic acid, $C_{17}H_{16}O_4$, crystallising in slender, colourless needles, m. p. 184° ; the *silver* salt, $C_{17}H_{14}O_4Ag_2$, and *ethyl* ester, crystallising in needles, m. p. 115° , were prepared. The acid is converted by cold fuming nitric acid into a *dinitro*-derivative,

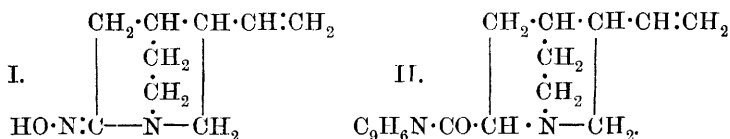


$C_{17}H_{14}O_4(NO_2)_2$,
crystallising in small, colourless, rhombic plates, m. p. 284° ; the corresponding *amine* forms hone-shaped crystals. The *dibromo*-derivative $C_{17}H_{14}O_4Br_2$, results on treating the acid with bromine in glacial

acetic acid; it forms stellate crystals, m. p. 172—173°. It is probable that the acid has the formula given on p. 99. W. H. G.

Cinchona Alkaloids. VIII. Constitution of Cinchonine. PAUL RABE [with OTTO BUCHHOLZ] (*Ber.*, 1908, 41, 62—70).—The base, $C_{19}H_{20}ON_2$ (Abstr., 1907, i, 954), obtained by oxidising cinchonine with chromic acid, is termed *cinchoninone* in order to indicate its relation to tropinone and codeinone. It is amphoteric in character, and exhibits keto-enolic tautomerism, since it yields both an oxime and an *O*-benzoyl derivative. It is readily reduced, and under special conditions can be converted back into cinchonine; under normal conditions, however, a rupture of the molecule occurs during the reduction.

Nitrous acid (amyl nitrite) decomposes the ketonic base, yielding cinchonic acid and an oxime, $C_9NH_{13} \cdot N \cdot OH$, a reaction which is analogous to the formation of diacetylmonoxime from ethyl methyl-acetoacetate. The presence of the grouping $-CO \cdot CH <$ is thus established. The oxime, when hydrolysed, yields meroquinine, and, assuming Koenig's formula for this compound, the following constitutional formulæ are deduced for the oxime, $C_9NH_{13} \cdot N \cdot OH$, and cinchoninone:



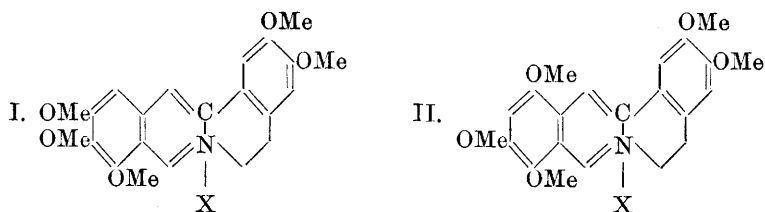
Cinchoninoneoxime, $C_{19}H_{21}ON_3$, obtained by the action of free hydroxylamine on the ketone in a strongly alkaline solution, forms a pale yellow, amorphous powder, m. p. 105—110°. It yields a *methiodide*, $C_{19}H_{21}ON_3 \cdot \text{MeI}$, which has no definite m. p.; it begins to soften at 135°, and decomposes at 145—150°. The *benzoyl* derivative, $C_{26}H_{24}O_2N_2$, of the base crystallises from light petroleum in colourless needles, m. p. 131°; it is readily hydrolysed by alkalis, and possesses very feeble basic properties. Cinchoninone methiodide also yields a *benzoyl* derivative, $C_{26}H_{24}O_2N_2 \cdot \text{MeI}$, which is hydrolysed when boiled with alcohol.

A 75% yield of α' -oximino- β -vinyl-quinuclidine (formula I above) is obtained by the action of amyl nitrite and sodic ethoxide on the ketone; it crystallises from ethyl acetate or a mixture of ether and light petroleum (b. p. 40°) in colourless prisms or needles, m. p. 146—147°, and yields a *methiodide*, $C_9H_{14}ON_2 \cdot \text{MeI}$, m. p. 224° (decomp.). J. J. S.

Alkaloids and Bitter Principles of Calumba Root. VIII. KARL FEIST (*Arch. Pharm.*, 1907, 245, 586—637. Compare Gadamer, Abstr., 1903, i, 50; 1906, i, 976).—Three alkaloids have been obtained from calumba root, namely, columbamine, jateorrhizine, and palmatine. Günzel's work on columbamine (Abstr., 1906, i, 976) has been confirmed; further investigation has shown that columb-

amine contains a hydroxyl group in addition to the four -OMe groups; columbamine iodide consequently has the partly structural formula: $C_{17}H_9NI(OMe)_4 \cdot OH$.

Jateorrhizine iodide, which has the empirical formula $C_{20}H_{20}O_5NI$, is found to contain three -OMe groups and two hydroxyl groups, so that the formula may be written $C_{17}H_9NI(OMe)_3(OH)_2$; in fact, columbamine is a monomethyl ether of jateorrhizine, since the monomethyl ether of columbamine is identical with the dimethyl ether of jateorrhizine. Both columbamine and jateorrhizine, also their methyl ethers, are very similar to berberine, yielding colourless tetrahydro-derivatives, &c. The methyl ether of columbamine yields, on oxidation with potassium permanganate, corydaldine (Dobbie and Lauder, *Trans.*, 1902, 81, 145) together with a trimethoxy-*o*-phthalic acid. The acid, which was not obtained in a pure state, melted at almost the same temperature as galloicarboxylic acid trimethyl ether (3:4:5-trimethoxy-*o*-phthalic acid), but crystallised in a different form. Should the two acids on further investigation be proved to be identical, then salts of columbamine methyl ether must be represented by formula I. If not, the only other trimethoxy-*o*-phthalic acid possible is 3:4:6-trimethoxy-*o*-phthalic acid, and salts of columbamine methyl ether would then have the formula II:



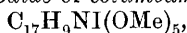
The third alkaloid, palmatine, only small quantities of which are present in calumba root, closely resembles berberine; it contains four OMe groups, but no hydroxyl group, and the iodide has the formula $C_{17}H_{10}O_2NI(OMe)_4$; the relationship existing between this alkaloid and columbamine is not yet known.

The discovery of a second bitter principle in calumba root, named provisionally "bitter principle II," led to an investigation of columbin. The value obtained for the mol. wt. of the latter compound by the boiling- and freezing-point methods varied considerably with the solvent employed; consequently, the mol. wt. of this substance is still unknown (compare Ulrich, *Abstr.*, 1907, i, 331). Owing to the similarity of the two substances, it is possible that the columbin hitherto investigated has been contaminated with "bitter principle II."

Columbamine nitrate, $C_{21}H_{22}O_8N_2 \cdot 2\frac{1}{2}H_2O$, crystallises in lemon-yellow needles, m. p. 232°; the *platinichloride*, $(C_{21}H_{21}O_5N)_2 \cdot H_2PtCl_6$, is a yellow powder, m. p. 238° (decomp.); the *aurichloride* forms slender needles, m. p. 220° (decomp.). Concentrated solutions of columbamine sulphate or nitrate yield on treatment with strong aqueous potassium hydroxide the inner *anhydride* of columbamine, which crystallises in violet-black prisms, commences to melt at 190°, and decomposes above this temperature. Tetrahydrocolumbamine is most readily prepared

by the reduction of columbamine nitrate; the *sulphate* crystallises in white, silky needles; the *chloride* forms a colourless, crystalline powder, commences to melt at 150° , and is completely molten at 215° . All attempts to separate tetrahydrocolumbamine into its optically active components were unsuccessful. Columbamine chloride reacts with benzoyl chloride, yielding a *substance*, obtained as a light yellow, crystalline powder, m. p. 152° . In pyridine solution, however, a *substance*, obtained as a light yellow powder, m. p. $212-213^{\circ}$, is formed. Acetyl chloride reacts with columbamine chloride in pyridine, forming a *substance* (acetyl derivative?) which crystallises in slender, yellow needles, m. p. 220° (decomp.).

None of these substances was obtained in a pure state. That columbamine contains a hydroxyl group is shown by the preparation of the methyl ether; the *iodide of columbamine methyl ether*,



results on heating columbamine iodide with potassium hydroxide, methyl alcohol, and methyl iodide in a sealed tube at 100° ; it crystallises in prisms, m. p. $238-240^{\circ}$; the *sulphate* results on treating columbamine iodide with methyl sulphate in the presence of alkali; the *nitrate* crystallises in slender, light yellow prisms, m. p. 236° (decomp.). A concentrated solution of the sulphate, when treated with 50% aqueous potassium hydroxide, yields the ψ -form of columbamine methyl ether; it crystallises in light yellow prisms, m. p. 136° . Columbamine methyl ether yields with chloroform an *additive* compound, $\text{C}_{22}\text{H}_{23}\text{O}_5\text{N}\cdot\text{CHCl}_3$, forming small, light grey crystals, m. p. 182° , and with acetone an *additive* compound, obtained as a dirty yellow, fine, crystalline powder.

Tetrahydrocolumbamine methyl ether is obtained by reducing the nitrate of columbamine methyl ether; it crystallises in colourless prisms, m. p. 148° .

Columbamine methyl ether yields, on oxidation with aqueous potassium permanganate, corydaldine, a *trimethoxyphthalic acid*, $\text{C}_6\text{H}(\text{OMe})_3(\text{CO}_2\text{H})_2$, crystallising in colourless, slender needles, m. p. 200° , and an *acid* containing nitrogen, crystallising in colourless prisms, m. p. $200-202^{\circ}$. The composition of the latter acid is not yet known; its *hydrochloride* forms colourless needles, m. p. 208° (decomp.), and *aureichloride* crystallises in slender, light yellow needles, m. p. 188° (decomp.). In order to compare the above trimethoxyphthalic acid with gallo-carboxylic acid methyl ether (3:4:5-*trimethoxyphthalic acid*), this compound was prepared by treating the acid with diazomethane in ethereal solution, and hydrolysing the dimethyl ester so formed with alcoholic potassium hydroxide; it crystallises in small, colourless, rhombic plates, m. p. 195° . Gallo-carboxylic acid yields on treatment with methyl sulphate, in the presence of alkali, a *substance*, probably a *monomethyl ether*, $\text{C}_8\text{H}_5\text{O}_6(\text{OMe})$, crystallising in colourless needles, m. p. 251° .

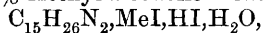
Jateorrhizine iodide, $\text{C}_{20}\text{H}_{20}\text{O}_5\text{NI}\cdot\text{H}_2\text{O}$, crystallises in reddish-yellow needles, m. p. $208-210^{\circ}$; the corresponding *chloride* crystallises from water with $\frac{1}{2}\text{H}_2\text{O}$ in light yellow needles, m. p. 206° , and from alcohol with $1\text{H}_2\text{O}$ in copper-coloured needles, m. p. 206° ; the *sulphate* forms brownish-yellow prisms; the *nitrate* crystallises in glistening,

golden-yellow needles, m. p. 225° (decomp.). The latter salt yields, on reduction, *tetrahydrojateorrhizine*, $C_{20}H_{23}O_5N$, crystallising in colourless needles, m. p. 206° . Jateorrhizine iodide yields on methylation a *dimethyl ether* identical with columbamine methyl ether iodide.

Palmatine iodide, $C_{17}H_{10}O_2NI(OMe)_4$, remains undissolved on treating the mixture of iodides of the alkaloids obtained from calumba root with aqueous sodium hydroxide; it crystallises in slender, yellow needles, m. p. $238-240^{\circ}$ (decomp.). The corresponding *nitrate*, $C_{21}H_{22}O_6N \cdot NO_3 \cdot 1\frac{1}{2}H_2O$, forms slender, lemon-yellow needles, m. p. $238-240^{\circ}$. Reduction of this salt leads to the formation of *tetrahydropalmatine*, $C_{21}H_{25}O_6N$, crystallising in colourless leaflets, m. p. 145° ; the *aurichloride*, $C_{21}H_{25}O_6N \cdot HAuCl_4$, forms small, cinnamon-brown crystals.

An alcoholic extract of calumba root yields on evaporation a mixture of orange-red prisms and nodular aggregates of yellow crystals. The orange-red substance was found on investigation to be jateorrhizine chloride with $2H_2O$. The yellow substance was found to be a mixture of columbamine nitrate with some "bitter principle II." The latter substance crystallises in prisms, m. p. 246° (decomp.), and is a lactone. In agreement with the statement of Ulrich (*loc. cit.*), columbic acid was not detected in the alcoholic extract. W. H. G.

isoSparteine, an Isomeride of Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1907, 145, 1343—1345. Compare this vol., i, 44).—*isoSparteine*, $C_{15}H_{26}N_2$, obtained by treating the hydriodide (*loc. cit.*) with sodium hydroxide, is a colourless, almost odourless oil, b. p. $177.5-177^{\circ}$ (corr.)/16.5 mm., $[\alpha]_D - 25.01^{\circ}$ in 10% alcohol solution, $D_4^{20} 1.02793$, $n_D^{20} 1.53319$; the *dihydrochloride* is a deliquescent, crystalline solid; the *platinichloride*, $C_{15}H_{26}N_2 \cdot H_2PtCl_6 \cdot 1.5H_2O$, forms silky tufts of crystals, blackens at 230° , and decomposes at $257-260^{\circ}$; the *sulphate* forms a thick syrup, soluble in water or the alcohols, and insoluble in acetone or ether; the hydriodide, m. p. 202° (corr.), has $\alpha_D - 33.2^{\circ}$ in 5.5% methyl-alcoholic solution; the *dihydriodide*, $C_{15}H_{26}N_2 \cdot 2HI \cdot H_2O$, is a crystalline salt, optically inactive, and yields the hydriodide on treatment with sodium carbonate; the *picrate*, $C_{15}H_{26}N_2 \cdot 2C_6H_3O_7N_3$, crystallises in needles, and has m. p. 178° (corr.). *isoSparteine methiodide* (*loc. cit.*) cannot be obtained by the action of methyl iodide on the base; it is a crystalline salt, m. p. 232° (corr.), $[\alpha]_D - 18.39^{\circ}$ in 1.25% aqueous solution, or -16.79° in 6.2% methyl-alcoholic solution; the hydriodide,



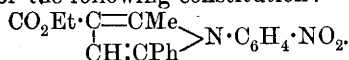
loses its water of crystallisation at 145° , decomposes with loss of MeI at $220-225^{\circ}$, and has $\alpha_D - 11.80^{\circ}$ in aqueous solution.

isoSparteine is a saturated ditertiary base; it does not reduce acid permanganate solution, and on treatment with hydrogen iodide does not yield methyl iodide; the compound therefore contains methyl groups associated with nitrogen (Herzig and Meyer, *Abstr.*, 1896, i, 68).

M. A. W.

Synthesis of Pyrrole and Piperazine Derivatives from the Three Nitroanilines. WALTHER BORSCHÉ and J. CAMPHER TITSINGH (*Ber.*, 1907, 40, 5008—5017).—The three nitroanilines, dis-

solved in acetic acid, react with ethyl phenacylacetate to give pyrrole derivatives of the following constitution:



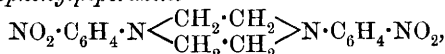
The yield in the case of the meta- and para-compounds is about 70%, but is much less from the ortho-derivative. Paal (*Habilitations-schrift*, Würzburg, 1890) found that *o*-nitroaniline did not react with ethyl phenacylacetate.

Ethyl-5-phenyl-1-m-nitrophenyl-2-methylpyrrole-3-carboxylate forms citron-yellow, rhombic plates, m. p. 146—147°; zinc chloride and hydrogen chloride reduce it to the corresponding base, *ethyl-5-phenyl-1-m-aminophenyl-2-methylpyrrole-3-carboxylate*, crystallising in colourless needles, m. p. 145°, which, when diazotised and combined with phenol, forms an orange *hydroxyazo*-compound.

The corresponding *p*-nitrophenylpyrrole derivative forms yellowish-red, thick plates, m. p. 116—117°, and the *p*-aminophenylpyrrole compound, colourless, matted needles, m. p. 161—162°. The *o*-nitrophenylpyrrole compound gives yellow needles, m. p. 96—97°, and the *o*-aminophenyl derivative, m. p. 109°, decomposes rapidly in the atmosphere, becoming red.

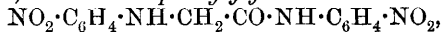
s-Bis-*m*-nitrophenylaminoethane, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ (compare Gattermann and Hager, *Abstr.*, 1884, 1142), prepared by the interaction of *m*-nitroaniline and ethylene dibromide in presence of sodium acetate at 150°, whereby, contrary to the experience with aniline, no cyclic compound is formed, has m. p. 206—208°. The corresponding *tetra-amine* crystallises in colourless, glistening plates or flat needles, m. p. 107°, and forms a *tetra-acetate* separating in colourless needles, m. p. 272°.

N-Di-m-nitrophenylpiperazine



prepared by further heating of nitrophenylaminoethane with ethylene dibromide, forms brownish-yellow needles, m. p. 220°. *s*-Bis-*p*-nitrophenylaminoethane (compare Jedlicka, *Abstr.*, 1893, i, 699) is obtained in small quantity only by this reaction. Still worse is the yield in the case of the *o*-compound (compare Jedlicka, *loc. cit.*), due to the decrease in basicity and less tendency to form quaternary ammonium compounds.

m-Nitroaniline reacts with chloroacetic acid to form a mixture of *m*-nitrophenylglycine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, a yellow compound, m. p. 158—159°, and *m*-nitrophenylglycine-*m*-nitroanilide,



a brown, crystalline powder, m. p. 201—202°. *p*-Nitroaniline reacts similarly to give *p*-nitrophenylglycine, m. p. 225°, and *p*-nitrophenylglycine-*p*-nitroanilide, m. p. 260°. *o*-Nitroaniline, on the other hand, gave only traces of *o*-nitrophenylglycine. E. F. A.

Catalytic Action of Finely-divided Metals on Nitrogen Compounds. MAURICE PADOA and C. CHIAVES (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 762—766. Compare *Abstr.*, 1907, i, 722).—When carbazole is heated at 200—220° for twelve to eighteen hours in

hydrogen under 8—10 atmospheres pressure, and in presence of reduced nickel, the following products are obtained: (1) a base, which yields a platinumchloride, m. p. 213° (decomp.); and (2) 2 : 3-diethylindole (?), $C_6H_4 \begin{smallmatrix} \text{CEt} \\ \text{NH} \end{smallmatrix} \text{CEt}$, which crystallises from light petroleum in scales, m. p. 95°, and forms a dark-red *picrate*, m. p. 172—173°, and a *picryl chloride* compound, $C_{12}H_{15}N, C_6H_2Cl(NO_2)_3$, m. p. 117°. T. H. P.

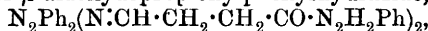
The Melting Point of Phenylhydrazine and of Certain Osazones. EMIL FISCHER (*Ber.*, 1908, 41, 73—77).—Phenylhydrazine was purified by fractional distillation at 15—20 mm., solidification and removal of the liquid portion (repeated four times), crystallisation from anhydrous ether at low temperatures, and finally by distillation under 0·5 mm. pressure. The melting point of the product, as determined by stirring with a normal thermometer, was found to be +19·6°.

For ordinary purposes, it is sufficient to crystallise the base once or twice from its own volume of pure ether and then to distil once under a pressure of 10—20 mm. The base should be coloured pale yellow, and should dissolve in ten times its vol. of a mixture of 50% acetic acid (1 part) and water (9 parts). In the preparation of osazones, it is an advantage to use the old method, namely, a mixture of 2 parts of phenylhydrazine hydrochloride and 3 of sodium acetate, as the sodium chloride thus formed facilitates the formation of the osazone. The phenylhydrazine hydrochloride must be colourless, and if coloured should be crystallised from alcohol.

The melting points of osazones depend to a certain extent on the manner in which the substances are heated. The previous melting points are confirmed, namely, 205° or 208° (corr.) for phenylglucosazone, when the osazone is heated fairly rapidly. Tutin's value of 217° (*Proc.*, 1907, 23, 250) could not be obtained.

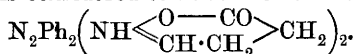
Certain phenylhydrazones, for example, pyruvic acid phenylhydrazone, which decompose when heated, melt differently, according to the rate at which they are heated. J. J. S.

Action of Phenylhydrazine on Dibromopyrotartaric Acid. FRITZ FICHTER and MARKUS GUGGENHEIM [and, in part, LUDWIG BRASCH] (*J. pr. Chem.*, 1907, [ii], 76, 545—551).—The action of phenylhydrazine on dibromopyrotartaric acid in hot aqueous solution leads to the formation of the phenylhydrazone of β -aldehydopropionylphenylhydrazide (Perkin and Sprankling, *Trans.*, 1899, 75, 11; Ellinger, *Abstr.*, 1904, i, 639). As Reitter and Bender have found this substance to be formed also by the action of phenylhydrazine on aconic acid (*Abstr.*, 1905, i, 669), the interaction of phenylhydrazine and dibromopyrotartaric acid takes place probably in two stages, the first consisting of the formation of phenylhydrazine hydrobromide and aconic acid. When boiled with mercuric oxide in alcoholic solution, the phenylhydrazone-hydrazide is oxidised, forming the *diphenyldihydrotetrazone* of β -aldehydopropionylphenylhydrazide,



which separates in yellowish- or reddish-brown crystals, m. p. 122°, gives with concentrated sulphuric acid a brown coloration becoming blue and finally violet, and when heated with phenylhydrazine on the

water-bath is reduced to the phenylhydrazone-hydrazide; the diphenyldihydrotetrazone is formed also, but in smaller yields, if a current of air is passed through a hot alcoholic solution of the phenylhydrazone-hydrazide. When treated with concentrated hydrochloric acid in the cold, the diphenyldihydrotetrazone is hydrolysed, forming the *diphenyldihydrotetrazone* of β -aldehydopropionic acid, which crystallises in colourless leaflets, m. p. 160°. As this substance has not an acid reaction and does not react with barium carbonate, but forms a readily soluble, yellowish-white *salt* when boiled with aqueous baryta, it is considered to have the constitution :



The *p*-bromophenylhydrazone of β -aldehydopropionyl-*p*-bromophenylhydrazide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_2\text{H}_2\cdot\text{C}_6\text{H}_4\text{Br}$, prepared by the action of *p*-bromophenylhydrazine on dibromopyrotartaric acid, crystallises in white needles, m. p. 206°.

The *p*-tolylhydrazone of β -aldehydopropionyl-*p*-tolylhydrazide, $\text{C}_{18}\text{H}_{22}\text{ON}_4$, crystallises in glistening leaflets, m. p. 217°, and, on oxidation by means of a current of air in alcoholic solution, yields the *di-p*-tolylidihydrotetrazone, $\text{C}_{36}\text{H}_{42}\text{O}_2\text{N}_8$, crystallising in yellow needles, m. p. 153°. G. Y.

Hofmann's Reaction with Amides and Hydrazine Derivatives of Carbonic Acid. AUGUST DARAPSKY (*J. pr. Chem.*, 1907, [ii], 76, 433—466. Compare Schestakoff, *Abstr.*, 1905, i, 332).—A detailed account of work previously published (*Abstr.*, 1907, i, 729). The following facts are new.

Benzoylsemicarbazide is best prepared by the action of potassium cyanate on benzoylhydrazide in glacial acetic acid solution; it is not oxidised to the azocarbonamide by chromic acid, and when treated with sodium hypochlorite yields nitrogen, carbon dioxide, and benzoic acid.

p-Bromophenylazocarbonamide sinters at 160°, m. p. 177° (m. p. 165°: Hantzsch and Glogauer, *Abstr.*, 1898, i, 78). The action of sodium hypochlorite on *p*-methyl-, *p*-bromo-, and *p*-nitro-phenylazocarbonamide leads to the formation of the corresponding azoimides together with small amounts of the *s*-azo-compounds.

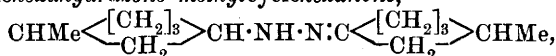
β -Naphthylazoimide (Culmann and Gasiorowski, *Abstr.*, 1889, 1156) crystallises in white prisms, m. p. 31—32°.

as-Dibenzyl- and *as*-diethyl-carbamides do not yield the *as*-disubstituted hydrazines when treated with sodium hypochlorite.

Benzoylhydrazide is converted by the hypochlorite into benzylidene-benzoylhydrazone, or dibenzoylhydrazide, and azodibenzoyl, depending on the conditions of the reaction. G. Y.

Conversion of the Azine of 1-Methylcyclohexone-3-one into 1-Methylcyclohexyl-3-hydrazine. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1240—1245. Compare *Abstr.*, 1900, i, 277, 333).—The azine is prepared by the action of hydrazine hydrate on methylcyclohexanone, b. p. 170—172°/770 mm., $\alpha_D +1.52^\circ$ (100 mm.), but when the azine is decomposed with hydrochloric acid it

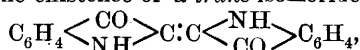
yields methylcyclohexanone, b. p. $169.5^{\circ}/750$ mm., and $\alpha_D + 12.20^{\circ}$. The alcoholic solution of the azine is reduced readily by sodium, forming methylcyclohexylamine, b. p. $154-155^{\circ}$, $\alpha_D - 1.70^{\circ}$ (100 mm.), and methylcyclohexahydrazone methylcyclohexanone,



b. p. $214^{\circ}/90$ mm., a thick, pale greenish-yellow liquid, $\alpha_D - 26.54^{\circ}$ (100 mm.). When treated with dilute acids, it decomposes, forming methylcyclohexanone and a salt of methylcyclohexylhydrazine, which with alkalis forms the free methylcyclohexylhydrazine, b. p. $209.5-210.5^{\circ}/760$ mm., $D_4^{20} 0.9274$, $n_D^{20} 1.4786$, $[\alpha]_D - 9.66^{\circ}$. It is a colourless liquid, becoming thick, but not crystallising, at -20° . It combines with hydrochloric and sulphuric acids, and also with benzaldehyde and menthone. The compound, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_7\text{H}_{13}$, crystallises in long needles, m. p. 135° , $[\alpha]_D - 17.66^{\circ}$. Methylcyclohexane has $n_D^{20} 1.4228$.
Z. K.

Stereochemistry of Indigotin. K. GEORGE FALK and JOHN M. NELSON (*J. Amer. Chem. Soc.*, 1907, 29, 1739—1744).—From the consideration of a number of compounds containing a double bond, and existing in two stereoisomeric modifications, it is inferred that, if one of the isomerides is coloured, the other will either be colourless or of a different colour from the first.

Indigotin has the constitution: $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \right\rangle \text{C} : \text{C} \left\langle \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \right\rangle \text{C}_6\text{H}_4$, the carbonyl groups being in the *cis*-position, since the compound yields only a mono-oxime (Thiele and Pickard, *Abstr.*, 1898, i, 493). There is a possibility of the existence of a *trans*-isomeride,



which would be expected to have a different colour from that of ordinary indigo.

Liebermann and Dickhuth (*Abstr.*, 1892, 480) have described a red diacetylindigotin. It is suggested that a stereoisomeric change takes place during the formation of this compound, and that it has the *trans*-configuration. Similarly, the *trans*-structure is proposed for other red indigotin derivatives. Liebermann and Dickhuth's work has been repeated, and their results confirmed. A general scheme is given of the relations between the acetyl derivatives of indigo and the best methods of passing from one compound to another. Liebermann and Dickhuth regarded α -diacetylindigo-white as containing the group $\cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot$, and the β -compound as containing the group, $\cdot \text{C}(\text{OH}) : \text{C} : \text{C} : \text{C}(\text{OH}) \cdot$. It is considered more likely, however, that the α -form is internally compensated, and that the β -form is a racemic mixture capable of resolution into its optically active components.

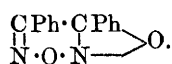
E. G.

Electrolytic Reduction of Indigotin. HENRI CHAUMAT (*Compt. rend.*, 1907, 145, 1419—1421).—Indigotin can be readily reduced by electrolytic hydrogen when it is intimately associated with the cathode of a cell in which sodium carbonate solution is undergoing electrolysis.

For this purpose, the indigotin, in a fine state of division, mixed with a slightly coarser powder of graphite is piled round a stick of carbon in a linen bag, and forms the cathode of an electrolytic cell charged with sodium carbonate solution and provided with a porous diaphragm to separate the two electrodes. The hydrogen liberated at the cathode during the electrolysis reduces the indigotin to indigo-white, which is dissolved by the equivalent of sodium hydroxide simultaneously formed. The introduction of the porous diaphragm to protect the reduced indigotin from the action of electrolytic oxygen liberated at the anode greatly increases the resistance of the cell, and can be dispensed with if a solution of alkali or alkaline earth sulphite, hydrogen sulphite, or sulphide is added to the bath, these salts being more readily oxidised than the indigo-white. M. A. W.

Constitution of the Glyoxime Peroxides. HEINRICH WIELAND and LEOPOLD SEMPER (*Annalen*, 1907, 358, 36—70. Compare Wieland, *Abstr.*, 1903, i, 764; 1904, i, 54).—The results of the investigation described in this paper have led the authors to suggest for the so-called glyoxime peroxide the structural formula: $\begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{N} \cdot \text{O} \cdot \text{N} \end{array} \text{---} \text{O}$,

which is an oxide of furazan and is termed furoxan. The nomenclature of the derivatives of glyoxime peroxide is altered accordingly; thus diphenylglyoxime peroxide, $\begin{array}{c} \text{CPh} \cdot \text{CPh} \\ | \quad | \\ \text{N} \cdot \text{O} \cdot \text{N} \end{array}$, becomes diphenylfuroxan,



The furoxans are readily converted into the corresponding furazans when heated with phosphorus pentachloride. In this manner, phenylfuroxan is prepared from phenylfuroxan. *Diphenylfuroxan*, $\text{C}_{14}\text{H}_{10}\text{ON}_2$, obtained from diphenylfuroxan, crystallises in colourless prisms, m. p. 94° , yields an odour of benzonitrile and phenylcarbimide when heated, and remains unchanged on treatment with Caro's acid.

Chloroanisylmethylfuroxan, $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \begin{array}{c} \text{C} \cdot \text{CMe} \\ | \quad | \\ \text{N} \cdot \text{O} \cdot \text{N} \end{array}$, is formed by

the action of phosphorus pentachloride on anisylmethylfuroxan; it crystallises in white plates, m. p. $79\text{--}81^\circ$.

Phenylfuroxan (Scholl, *Abstr.*, 1891, 317) crystallises in colourless plates, m. p. about 95° (slight decomp.), is stable in a desiccator, yields benzonitrile, but, contrary to Scholl's statement, not benzaldehyde on prolonged boiling with alcohol, dissolves unchanged in concentrated sulphuric acid or boiling concentrated hydrochloric acid, and does not give Liebermann's reaction or a coloration with ferric chloride. When treated with dilute sodium hydroxide, phenylfuroxan rapidly dissolves, evolving an odour of benzonitrile and phenylcarbylamine, and forming a yellow solution which must contain *oximinobenzoylformhydroxamic acid*, $\text{NOH} \cdot \text{CPh} \cdot \text{C}(\text{NOH}) \cdot \text{OH}$, as it gives with ferric chloride an intense brownish-red coloration stable towards mineral acids, and with copper acetate a dirty green, slimy precipitate, which after solution in an acid gives the coloration with ferric chloride. When treated with ice-cold alcoholic potassium hydroxide or aqueous sodium carbonate and

ether, phenylfuroxan undergoes isomerisation, which is explained with the aid of the hypothetical intermediate product, $\begin{smallmatrix} \text{CPh} \cdot \text{CH} \cdot \text{OH} \\ | \quad | \\ \text{N} \cdot \text{O} \cdot \text{N} \cdot \text{OH} \end{smallmatrix}$, and

leads to the formation of *hydroxyphenylfuroxan*, $\begin{smallmatrix} \text{CPh} \cdot \text{C} \cdot \text{OH} \\ | \quad | \\ \text{N} \cdot \text{O} \cdot \text{N} \end{smallmatrix}$; this

crystallises in colourless needles, m. p. 110—111° (decomp.), dissolves in aqueous alkalis, and can for the greater part be regained by immediate acidification, but is gradually decomposed by the alkali, forming the preceding hydroxamic acid and benzonitrile. The hydroxyfuroxan gives a brown coloration with alcoholic ferric chloride, forms a crystalline *acetate*, and reacts with phosphorus pentachloride with explosive violence, yielding a crystalline *product*.

Oximinobenzoylamidoxime, $\text{NOH} \cdot \text{CPh} \cdot \text{C}(\text{NOH}) \cdot \text{NH}_2$, prepared by treating phenylfuroxan in ethereal solution with ice-cold aqueous ammonia, or in small amount by prolonged boiling of oximinobenzoyl cyanide with hydroxylamine, crystallises in colourless leaflets, m. p. 154°, is soluble in alkalis or mineral acids, and gives an olive-brown coloration with ferric chloride. The *dibenzoyl* derivative, $\text{C}_{22}\text{H}_{17}\text{O}_4\text{N}_3$, forms leaflets, m. p. 175—176°.

Crystalline, substituted *amidoximes* are formed from phenylfuroxan by the action of phenylhydrazine, $\text{NOH} \cdot \text{CPh} \cdot \text{C}(\text{NOH}) \cdot \text{NH} \cdot \text{NHPh}$, m. p. 173° (decomp.), or aniline, $\text{NOH} \cdot \text{CPh} \cdot \text{C}(\text{NOH}) \cdot \text{NHPh}$, m. p. about 180° (decomp.).

When boiled with water, phenylfuroxan yields benzonitrile oxide, which polymerises forming diphenylfuroxan, formhydroxamic acid, and an odour of benzonitrile.

The transformation of furoxans into *isonitrosoisooxalines* has been described by Tönnies (Abstr., 1881, 167) and by Angeli (Abstr., 1892, 1198). *isoNitrosoanisylisooxazoline*,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \swarrow \text{C}(\text{NOH}) \cdot \text{CH}_2 \\ \searrow \text{N} \text{---} \text{O} \end{smallmatrix}$, formed by boiling anisylmethylfuroxan

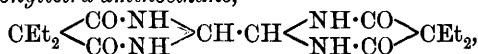
with methyl-alcoholic potassium hydroxide, crystallises in colourless needles, m. p. 172° (decomp.), is soluble in aqueous sodium carbonate, and is decomposed when treated with alkalis. The *benzoyl* derivative, $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2$, crystallises in white needles, m. p. 143°. The action of methyl sulphate on the solution obtained on heating anisylmethylfuroxan with methyl-alcoholic potassium hydroxide leads to the formation of a *methyl* derivative of *isonitrosoanisylisooxazoline*, $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_2$, crystallising in needles, m. p. 107—108°.

The disubstituted furoxans are less reactive than the mono-substituted, and are not attacked by ammonia, aniline, or phenylhydrazine even at high temperatures under pressure. Diphenylfuroxan remains almost unchanged on prolonged boiling with alcoholic potassium hydroxide. With magnesium organic compounds, the furoxans form labile *additive* products, from which they separate unchanged on treatment with water. The *additive* compound of magnesium ethyl iodide and anisylmethylfuroxan is an insoluble, yellow substance.

The *ψ-nitrosite*, $(\text{N}_2\text{O}_2)[\text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \cdot \text{CH}_2 \cdot \text{NO}_2]_2$, formed from *p*-methoxystyrene, is obtained as a white, crystalline powder, decomp.

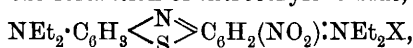
107°, gives the reactions for ψ -nitrosites, and on distillation in a current of steam yields nitroanisylethylene and the *nitro-oxime* of *p*-methoxystyrene, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NOH}) \cdot \text{CH}_2 \cdot \text{NO}_2$. This crystallises in colourless needles, m. p. 112°, decomp. 135°, dissolves in aqueous alkalis, and is precipitated by acids. This ψ -nitrosite and nitro-oxime differ from the homologous compounds derived from anethole in that they do not yield the corresponding furoxan. G. Y.

Reduction of Diethylthiobarbituric Acid. ALFRED EINHORN and HEINRICH VON DIESBACH (*Ber.*, 1907, 40, 4902—4903).—The reduction of diethylthiobarbituric acid by sodium amalgam leads to the formation mainly of diethylmalonamide; the by-products are 4:6-dihydroxy-5:5-diethyl-2:5-dihydropyrimidine (compare Tafel and Thompson, this vol., i, 58), which is isolated in the form of the double salt with mercuric chloride, $\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_3 \cdot \text{HgCl}_2$, m. p. 215—218°, and *bisdiethylmalonyltetra-aminoethane*,



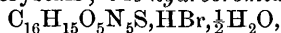
m. p. 340°, which separates from dilute alcohol in white prisms containing $2\text{H}_2\text{O}$. C. S.

Thiazines. II. Derivatives of Tetraethylthionine. ROBERT GNEHM and ALFRED SCHINDLER (*J. pr. Chem.*, 1907, [ii], 76, 471—488. Compare Gnehm and Walder, this vol., i, 63).—Tetraethylthionine (ethylene-blue) is more reactive than methylene-blue, as, whilst the action of the theoretical amount of nitric acid in glacial acetic acid solution leads to the formation of nitroethylene-blue,



the nitration readily proceeds further to the formation of the nitrate of a dinitronitroso-base, $\text{OH} \cdot \text{N} : \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \text{S} \end{array} \text{C}_6\text{H}(\text{NO}_2)_2 \cdot \text{NEt}_2, \text{HNO}_3$; the position of the nitro-groups in this base has not been determined. The paper contains an account of these substances and their reduction products.

Tetraethylthionine is prepared by the action of sodium thio-sulphate and hydrochloric acid on nitrosodiethylaniline hydrochloride and treatment of the product with diethylaniline hydrochloride, zinc chloride, and sodium dichromate in boiling aqueous solution. The *zincchloride* is salted out as a blackish-blue powder, and, when gently heated with nitric acid in acetic acid solution, yields *dinitroisonitroso-diethylaminothiazine nitrate*, $\text{C}_{16}\text{H}_{15}\text{O}_5\text{N}_5\text{S} \cdot \text{HNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, which separates from alcohol in green crystals; the *hydrobromide*,



prepared by the action of hydrobromic acid and methyl alcohol on the nitrate, is obtained in green crystals or as a brown powder, forms bluish-red dichroic solutions which, with the exception of the aqueous solution, are fluorescent, and with concentrated sulphuric acid gives a malachite-green coloration, becoming blue and finally rose-red on dilution. The free base, formed by the action of sodium hydroxide on the hydrobromide, is obtained as a brown, flocculent precipitate,

detonates when heated on platinum, is insoluble in alkalis, and again forms the dye on solution in hydrochloric acid. It gives with phenylhydrazine in acetic acid solution a brownish-yellow precipitate, with ferric chloride a blood-red coloration, with potassium ferricyanide a flesh-red solution, with phenol and concentrated sulphuric acid a green solution, becoming bluish-red when poured into dilute sodium hydroxide, and with aniline in methyl-alcoholic solution a violet coloration. The *hydrochloride* is crystalline. In Formanek's spectroscope, the aqueous solution of the dye shows a line at $\lambda = 573$, the alcoholic solution shows a line at $\lambda = 573.4$, and an absorption band in the blue; on addition of ammonia, the lines disappear, but the band persists.

Reduction of the dye with stannous chloride and hydrochloric acid leads to the formation of the *hydrochloride* of the leuco-base, $C_{16}H_{21}N_5S, 3HCl$, which separates from aqueous hydrogen chloride in crystals containing $5H_2O$, or from methyl-alcoholic hydrogen chloride in white crystals, $C_{16}H_{21}N_5S, 3HCl, 3CH_4O$. The light brown base, m. p. above 300° , is readily oxidised by air. The dye, prepared by oxidation of the leuco-base with ferric chloride, is isolated as the *zincchloride*, $C_{16}H_{19}N_5S, 2HCl, ZnCl_2, \frac{3}{4}CH_4O$. It forms green to brown solutions in water, alcohols, or acids; the spectrum of the alcoholic solution has strong absorption in the red, or, after addition of ammonia, a broad band in the green.

Ethylene-green (*nitroethylene-blue*, *nitrotetraethylthionine*) is isolated as the *zincbromide*, $C_{20}H_{24}O_2N_4SBr, \frac{1}{2}ZnBr_2, 2H_2O$; it dissolves in water, alcohols, or acetic acid, forming a bluish-green solution, gives with concentrated sulphuric acid a dirty blue coloration, becoming reddish-brown, violet, and, finally, bluish-green on addition of water, and with fuming nitric acid a reddish-violet, becoming deep blue on dilution. Addition of sodium hydroxide to the aqueous solution leads to the formation of a reddish-violet coloration, and a precipitate which yields the original dye on treatment with hydrochloric acid; potassium ferrocyanide in aqueous solution gives a light green coloration. The spectrum of the aqueous solution has a broad line at $\lambda = 639.7$, and that of the alcoholic solution a broad line at $\lambda = 672$. The *hydroiodide* crystallises in green needles.

Aminoethylene-blue, prepared by reduction of ethylene-green with stannous chloride and oxidation of the product with ferric chloride, is isolated as the *zincbromide*, $C_{20}H_{27}N_4SBr, \frac{1}{2}ZnBr_2, 1\frac{1}{2}H_2O$. It forms deep blue solutions, gives with concentrated sulphuric acid a reddish-brown, with concentrated hydrochloric acid a yellow, or with fuming nitric acid a reddish-violet, coloration, becoming violet to bluish-violet on dilution, and yields a brown precipitate with sodium hydroxide. The spectrum of the alcoholic solution has a line about $\lambda = 623.8$, and strong absorption in the red.

Bromoethylene-blue is formed by the action of bromine on ethylene-blue nitrate in glacial acetic acid solution; the *zincbromide*, $C_{20}H_{26}N_3SBr, HBr, \frac{1}{2}ZnBr_2, H_2O$, was analysed. The dye forms deep blue solutions, and gives with concentrated sulphuric acid an apple-green, with concentrated hydrochloric acid a bluish-green, and with fuming nitric acid a dark brown, coloration, becoming blue to violet-

blue on dilution. On addition of sodium hydroxide, the aqueous solution becomes violet, and when heated turbid; on addition of ammonia, the solution becomes reddish-violet and fluorescent, but blue when heated. With sodium hydroxide, the alcoholic solution gives a cherry-red precipitate. The spectrum of the aqueous solution has a broad line at $\lambda=670$, and a minor line at $\lambda=624$; after addition of potassium hydroxide, the broad line has $\lambda=676$, and the minor line $\lambda=614.8$.

The action of alcoholic ammonia on ethylene-blue nitrate at $145-150^\circ$ leads to the formation of *as-diethylthionine*, which on oxidation and treatment with zinc bromide yields the *zincobromide*, $\text{NH}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{N} \begin{smallmatrix} \diagup \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_5 \cdot \text{NEt}_2\text{Br} \cdot \text{ZnBr} \cdot \text{OH} \cdot \text{H}_2\text{O}$; this loses H_2O at $80-90^\circ/35$ mm. The dye is readily soluble, forming deep blue solutions, gives a reddish-brown *product* with fuming nitric acid, and a reddish-violet precipitate with sodium hydroxide, becoming blue on addition of hydrochloric acid, and is readily reduced to the leuco-base by stannous chloride. Ammonia deepens the shade of the dye, but on heating precipitates the base; potassium ferrocyanide in acetone solution gives a light green precipitate. The aqueous solution gives a spectrum with a line at $\lambda=676$, the alcoholic solution a line at $\lambda=662$, and strong absorption on the right. G. Y.

Thiazines. III. Derivatives of Alkylated Benzyanilines.

ROBERT GNEHM and ALBERT SCHÖNHOLZER (*J. pr. Chem.*, 1907, [ii], 76, 489—508. Compare preceding abstract; Scholtz, Rohde, and Bosch, *Abstr.*, 1904, i, 992).—Attempts to prepare simple thionines from benzylmethyl- and benzylethyl-aniline were unsuccessful, but, on the other hand, thiazines have been prepared from the sulphonic acids of these bases. The thiazines so obtained and a number of derivatives of benzylmethyl- and benzylethyl-aniline are described.

The *sulphate* of *as*-benzylethyl-*p*-phenylenediamine,



has m. p. $146-148^\circ$ (decomp.).

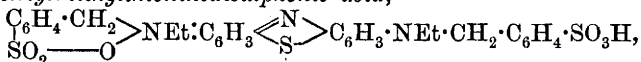
Benzylmethyl-p-nitrosoaniline, $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2\text{Ph}$, separates from benzene in steel-blue crystals, m. p. $52-53^\circ$; the *hydrochloride* forms a yellow, crystalline precipitate, m. p. 138° . The *diamine*, prepared by reduction of benzylmethyl-*p*-nitrosoaniline, is obtained as a black oil, and forms a *sulphate* crystallising in long, white needles.

Benzylethylanilinesulphonic acid, $\text{NEtPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, prepared by heating benzylethylaniline with sulphuric acid at $110-120^\circ$, crystallises in prisms, sinters at $160-170^\circ$, m. p. about 190° . The crystalline *barium*, $(\text{C}_{15}\text{H}_{16}\text{O}_3\text{NS})_2\text{Ba} \cdot 4\text{H}_2\text{O}$, and *potassium*, $\text{C}_{15}\text{H}_{16}\text{O}_3\text{NSK}$,

salts were analysed. The oxidation of the sulphonic acid with chromic acid leads to the formation of only small amounts of azobenzene and traces of benzoic acid. When heated with potassium hydroxide at $240-300^\circ$, the potassium sulphonate yields *p-hydroxybenzylethylaniline*, $\text{NEtPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, m. p. $62-63^\circ$, which does not form a rhodamine with phenol. The *nitroso*-derivative, prepared from the sulphonic acid or its potassium salt, is very soluble, forms a green, or in presence of

mineral acids an orange-red, solution, and yields a green, amorphous precipitate with lead acetate. On reduction with zinc dust and sulphuric acid, it forms an *amino-sulphonic acid*, which is formed also by reduction of the dark red, amorphous *azo-sulphonic acid*, prepared by coupling diazobenzene chloride and benzyloethylanilinesulphonic acid in alkaline solution; the amino-sulphonic acid cannot be isolated either in the free state or as a salt.

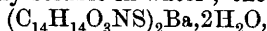
Dibenzyl-diethylthioninedisulphonic acid,



prepared from benzyloethylnitrosoanilinesulphonic acid by reduction with zinc dust and hydrochloric acid, and successive treatment of the product with sodium thiosulphate and dichromate, is identical with commercial thiocarmine. It is obtained as a bluish-black, amorphous powder, is readily soluble in water or alcohol, is precipitated by sulphuric acid, and gives with concentrated hydrochloric acid a green coloration, becoming blue on dilution. The *leuco*-compound, $\text{C}_{30}\text{H}_{31}\text{O}_6\text{N}_3\text{S}_3$, formed by reduction of the dye with zinc dust, separates as a yellow, flocculent precipitate on addition of sulphuric acid.

The derivatives of benzyloethylaniline are prepared in the same manner as those of benzyloethylaniline.

Benzylmethylanilinesulphonic acid, $\text{C}_{14}\text{H}_{15}\text{O}_3\text{NS}$, is obtained as a crystalline powder, readily soluble in water; the *barium*,



and *potassium*, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{NSK}$, salts are described.

p-Hydroxybenzylmethylaniline, $\text{C}_{14}\text{H}_{15}\text{ON}$, is obtained as a crystalline mass, m. p. 40—41°.

The *nitroso*-derivative of benzyloethylanilinesulphonic acid, prepared by the action of amyl nitrite on the sulphonic acid in glacial acetic acid solution, is obtained as a reddish-brown, crystalline powder; the *product* formed on reduction of this with zinc dust and sulphuric acid is not the *p*-amino-sulphonic acid.

Dibenzyl-dimethylthioninedisulphonic acid and its *salts* are readily soluble, and separate only as resins. The *leuco*-compound forms a yellow, flocculent precipitate, which decomposes, becoming black when dried in a vacuum.

m-Nitrobenzylmethylaniline, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2$, prepared by nitration of benzyloethylaniline by Groll's method (Abstr., 1886, 347), crystallises from alcohol in yellow leaflets, m. p. 51—52°; the *picrate*, m. p. 112—113°. Oxidation of the nitro-base leads to the formation of *m*-nitrobenzoic acid, whilst reduction with stannous chloride and hydrochloric acid leads to the formation of *m*-aminobenzylmethylaniline, which is isolated in the form of its *acetyl* derivative, $\text{NMePh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, crystallising in colourless leaflets, m. p. 88°.

Reduction of *m*-nitrobenzyloethylaniline and treatment of the product with acetic anhydride leads to the formation of the *acetyl* derivative, $\text{NEtPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, crystallising in leaflets, m. p. 96°. G. Y.

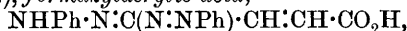
Reduction of Azo-compounds by Means of Sodium Hypo-sulphite. HARTWIG FRANZEN and P. STIELDORF (*J. pr. Chem.*, 1907, [ii], 76, 467—471. Compare Grandmougin, Abstr., 1907, i, 850).—

The reduction of an azo-compound, such as helianthin, to two primary amine molecules by means of sodium hyposulphite might take place according to the equation: (I) $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} + 2\text{Na}_2\text{S}_2\text{O}_4 + 4\text{H}_2\text{O} = \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 + \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} + 4\text{NaHSO}_3$, or (II) $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} + \text{Na}_2\text{S}_2\text{O}_4 + 3\text{H}_2\text{O} = \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 + \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} + \text{NaHSO}_3 + \text{NaHSO}_4$.

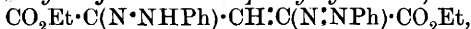
The authors have employed two methods to determine by which reaction the reduction takes place.

As 1 mol. of sodium hyposulphite requires 6 atoms, but 1 mol. of sodium sulphite only 2 atoms, of iodine when titrated, the product of reaction (I) must reduce two-thirds, but that of (II) only one-third, of the iodine required for the titration of the same amount of the original sodium hyposulphite solution. The results obtained with helianthin and *p*-sulphobenzeneazo- α -naphthol show that the reaction takes place according to equation (I). The same result is obtained by determining the amount of sulphuric acid in the hyposulphite solution before and after the reduction; only a very slight increase is found, whereas according to equation (II) each mol. of hyposulphite must yield 1 mol. of sulphuric acid. G. Y.

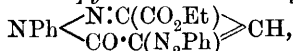
Action of Diazobenzene on Glutaconic Acid and Ethyl Glutaconate. FERDINAND HENRICH and W. THOMAS (*Ber.*, 1907, 40, 4924—4930).—When glutaconic acid is treated with diazobenzene chloride (2 mols.), *formazylacrylic acid*,



is obtained, accompanied by the evolution of carbon dioxide, crystallising from alcohol in reddish-brown, felted needles, m. p. 199° (decomp.). The *sodium* and *potassium* salts are sparingly soluble; the *silver* salt is dark coloured. The *ethyl* ester, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_4$, crystallises in long, slender, dark red needles, m. p. 123°, and is not identical with the formazyl compound previously obtained from ethyl glutaconate and diazobenzene chloride (*Abstr.*, 1902, i, 422). This is now shown to be *ethyl γ -phenylazoglutacononate-phenylhydrazone*,



as it readily loses alcohol on boiling its alcoholic solution, forming *ethyl 1-phenyl-5-benzeneazo-6-pyridazone-3-carboxylate*,



which crystallises in small, brownish-yellow crystals, m. p. 163—164°. The conclusion that the azohydrazone has the constitution ascribed to it, is supported by the fact that ethyl α -methylglutaconate does not give a corresponding derivative with diazobenzene chloride.

With ethyl glutaconate, the diazo-salts from *o*- and *p*-toluidine and chloro- and bromo-anilines give similar derivatives to diazobenzene; the tolyl compounds are deep dark red in colour, and the others are yellowish-red. W. R.

Action of Nitrous Acid on Proteins. ZACCARIA TREVES and GIOVANNI SALOMONE (*Biochem. Zeitsch.*, 1907, 7, 11—23).—Nitrous acid acting on proteins at 0° produces ill-defined substances, which the authors regard as diazo-compounds. The group of the protein

molecule concerned in diazotisation is not the same as that which is concerned in the fixation of labile sulphur, or in the combination with formaldehyde. The diazo-compounds show all the characteristic protein reactions, although somewhat slowly and less clearly. After precipitation of the diazo-compounds, no proteins remain in solution. On boiling with water and alkali, the diazo-compounds form proteins, which give a violet biuret reaction. The biuret reaction can scarcely depend on the presence of the complex $\text{CO}\cdot\text{NH}_2$, since this group would be destroyed by the action of nitrous acid. G. B.

Studies on Enzymes. I. Quantitative Measurement of Protein Hydrolysis by "Formaldehyde Titration." S. P. L. SÖRENSEN (*Biochem. Zeitsch.*, 1907, 7, 45—101).—The existing methods for estimating the extent of protein hydrolysis are arbitrary and unsatisfactory. A rational method must attempt the measurement of the quantity of carboxyl- and amino-groups formed during the hydrolysis. This is best done by titrating the carboxyl group with alkali after the aminic function has been abolished by formaldehyde according to Schiff's method (*Abstr.*, 1903, i, 232). The reversibility of this reaction and other circumstances render the employment of certain precautions necessary to ensure accuracy. The indicator must show an end point with as high a concentration of hydroxyl ions as possible; hence phenolphthalein or thymolphthalein (preferable in many cases) must be employed. The end point is not indicated by the appearance of a faint pink coloration, but the titration must be continued until the solution has the same strong red colour as a test solution which is prepared for comparison by adding a few drops of $N/5$ baryta to a dilute formaldehyde solution. The latter has been neutralised previously, so as to give only a faint pink colour with phenolphthalein, and by the addition of the baryta acquires the pronounced red colour which is desired.

Under these conditions, the amount of amino-acid found (in a pure $N/10$ solution) amounts on the average to 98% of the actual amount present. This applies to a large number of mono-, di-, and oxy-amino-acids; only in the case of phenylalanine and tyrosine is a considerably smaller amount found than that actually present.

The ratio between the extents of protein hydrolysis, as measured by this method and by precipitation with tannic acid, is generally greater than 1; at least in the early stages, formaldehyde titration indicates a greater degree of hydrolysis than tannic acid precipitation.

After the addition of formaldehyde, uric acid can be titrated sharply as a monobasic acid. G. B.

Hydrolysis of the Globulin from the Almond (Amandin). Hydrolysis of the Proteins of Maize. Hydrolysis of Gliadin from Rye. THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1908, 20, 470—476, 477—493, 493—499).—The following table gives the main results in percentages:

	Amandin.	Gliadin (rye).	Gliadin (wheat).	Hordein (barley).	Zein (maize).	Alkali-soluble protein of maize.
Glycine	0.51	0.13	0.02	absent	absent	0.25
Alanine	1.40	1.33	2.00	0.43	2.23	not isolated
Valine	0.16	not isolated	0.21	0.13	0.29	not isolated
Leucine	4.45	6.30	5.61	5.67	18.60	6.22
Proline.....	2.44	9.82	7.06	13.73	6.53	4.99
Phenylalanine ...	2.53	2.70	2.35	5.03	4.87	1.74
Aspartic acid	5.42	0.25	0.58	not isolated	1.41	0.65
Glutamic acid.....	23.14	33.81	37.33	36.33	18.28	12.72
Serine	(?)	0.06	0.13	not isolated	0.57	not isolated
Tyrosine	1.12	1.19	1.20	1.67	3.55	3.78
Arginine	11.85	2.22	3.16	2.16	1.16	7.06
Lysine	0.70	absent	absent	absent	absent	2.93
Histidine.....	1.58	0.39	0.61	1.28	0.43	3.00
Ammonia	3.70	5.11	5.11	4.87	3.61	2.12
Tryptophan	present	present	present	present	absent	present
Cystine	—	not deter- mined	0.45	not deter- mined	not deter- mined	—
Total	59.00	64.31	65.81	71.32	61.53	45.44

The amino-acids absent in zein are present in the alkali-soluble protein of maize, so that the mixture yields all the amino-acids usually obtained from proteins.

The gliadin of wheat and rye are probably identical, but the differences between it and hordein and zein are noteworthy. These three proteins are all soluble in alcohol, and form a group characterised by their high content of glutamic acid, protein, and ammonia, their low content of arginine and histidine, and absence of lysine. Zein also lacks tryptophan and glycine.

W. D. H.

Fatty Acids of Protein Putrefaction and Optically Active Valeric and Hexoic Acids. CARL NEUBERG and E. ROSENBERG (*Biochem. Zeitsch.*, 1907, 7, 178—190. Compare Abstr., 1906, i, 923).—One kilo. of casein yielded on putrefaction 117 grams of fatty acids. More than one-third of these consisted of butyric acid, which is considered to be derived from glutamic acid, since this acid occurs abundantly among the amino-acids formed in the hydrolysis of casein. Somewhat smaller quantities of formic, valeric, and hexoic acids were obtained, and still smaller yields of acetic, propionic, and a decoic acid. The valeric acid fraction had a rotation indicating the presence of 18% of *d*- α -methylbutyric acid, and the hexoic acid fraction probably contained 46% of β -methylvaleric acid (derived from *isoleucine*). Similar results were obtained with putrefied gelatin.

G. B.

Conversion of Optically Inactive Triolein into an Optically Active Glyceride and an Optically Active Acid. CARL NEUBERG and E. ROSENBERG (*Biochem. Zeitsch.*, 1907, 7, 191—198).—The authors have repeated and confirmed Neuberg's work on the diglyceride of dibromostearic acid (Abstr., 1906, i, 923).

JULIUS LEWKOWITSCH (*Chem. Zeit.*, 1908, 32, 54—55) ascribes the optical activity of Neuberg and Rosenberg's products to the introduction of optically active ricinus oil with the lipase employed in the hydrolysis of the glyceride.

G. Y.

Organic Chemistry.

Mechanism of Chemical Reactions. Intermediate Products and Intermediate Structures. MARC TIFFENEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 1221—1227).—A reply to Freundler (*ibid.*, 216) defending the use of (1) formulæ representing hypothetical intermediate products and (2) of "incomplete" formulæ, such as the second in the

$$\begin{array}{c} | \quad \downarrow \\ \text{OH} \cdot \text{CArR} \cdot \text{CHIR}' \rightarrow \text{OH} \cdot \text{CArR} \cdot \text{CR}' \rightarrow \text{OH} \cdot \text{CR} : \text{CArR}' \end{array}$$

on the ground of their convenience in illustrating the mechanism of complex reactions.

T. A. H.

Action of the Silent Electric Discharge on Moist Methane. WALTHER LÖB (*Ber.*, 1908, 41, 87—90).—By the action of the silent discharge on moist methane, a colourless solid is formed, insoluble in all solvents, along with small quantities of the methyl esters of higher aliphatic acids. The solid is a polymeride of $\text{C}_9\text{H}_{15}\text{O}$, and agrees with the solid obtained from acetylene by Losanitsch (this vol., ii, 32). Analysis of the gases formed during the experiment shows that in the first place hydrogen is eliminated and unsaturated hydrocarbons are formed, which condense with water to form the insoluble compound.

E. F. A.

Preparation of Ethylenic Hydrocarbons. Transformation of Primary Alcohols into Aldehydes and Hydrogen. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1908, [iv], 3, 117—119, 119—124).—The results recorded in both these papers were obtained in the course of an attempt to simplify and extend the range of applicability of Sabatier and Senderens' method (*Abstr.*, 1903, i, 393) of converting alcohols into aldehydes by the catalytic action of metals. In the first paper, it is pointed out that Ipatieff's results (*Abstr.*, 1903, i, 453, 593, 594, 595, 598) explain the fact observed by the author that, when metallic copper deposited on pumice-stone or on baked clay is employed as a catalyst in Sabatier and Senderens' process, more or less of the corresponding ethylenic hydrocarbon is always formed in addition to the aldehyde; this anomalous result being due to the catalytic action of the pumice and clay respectively. An apparatus suitable for use in applying Sabatier and Senderens' process to complex alcohols is described and figured in the second paper. It consists essentially of a glass or insulated copper tube, heated by a spiral of nickel ribbon conveying an electric current, and containing short rolls of fine copper gauze with finely-divided copper deposited on them by a special process, described in the original. The lower end of the tube is connected to a flask in which the alcohol vapours are generated, and the upper end communicates with a condenser leading to a receiver for the collection of the aldehyde (or ketone) formed. For the lower alcohols, the copper rolls are heated to 300° , but, for the more complex ones, better results are obtained by working under reduced pressure with the copper rolls

heated to 250°. Among the products which have been prepared in this way are decaldehyde, phenylacetaldehyde, ethyl *isovaleryl*acetate (from ethyl β -hydroxy- β -isobutylpropionate), and citral (from geraniol). In the case of unsaturated alcohols, the hydrogen simultaneously formed tends to saturate the ethylenic linking and give rise to the corresponding saturated aldehyde; thus undecylenyl alcohol is converted wholly by this process into undecaldehyde (which furnishes an *oxime*, m. p. 61°, crystallising in spangles). T. A. H.

Mysterious Lack of Carbon in the Condensation Products of Ethylene and Acetylene. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1908, 29, 1—4).—A supposed case of transformation of carbon or hydrogen into another element. The product obtained from ethylene in the author's "synthetisor" (following abstract) contains 13.13% to 13.82% of hydrogen and 79.84% to 80.44% of carbon, whilst the condensation product from acetylene contains 6.87% to 6.98% of hydrogen and 71.23% to 71.96% of carbon. The apparent loss of about 6% in the first, and of about 22% in the second, case is ascribed to the presence in the condensation products of a third element formed under the influence of the dark electric discharge. Both the products are strongly radioactive; especially is this the case with the product from acetylene.

The influence of the Tesla discharge on chemical reaction is of the same nature as that of the electric spark. G. Y.

Condensation Products Obtained from Ethylene and Acetylene by Means of the Dark Electric Discharge. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1908, 29, 5—14. Compare Losanitsch and Jovitschitsch, *Abstr.*, 1897, i, 179; Berthelot, *Abstr.*, 1898, i, 393).—The author has subjected ethylene and acetylene to the action of a current of 3 amperes and 100 volts in the apparatus previously described and now termed a "synthetisor."

The product obtained from ethylene is shown to have most probably the formula $C_{30}H_{54}$, and to be a cyclic condensation product. It is oxidised by bromine in ethereal solution, forming a brown, sticky product, which when heated with silver nitrate and nitric acid at 100° yields the *silver* salt of a nitro-derivative. When treated with nitric acid at 50—60°, the condensation product yields two *nitro*-derivatives, one of which, $C_7H_{11}O_2N$, is soluble, whilst the other, $C_6H_9O_2N$, is insoluble, in hot alcohol.

The condensation product from acetylene has probably the formula $C_{30}H_{26}$, and forms a *dibromide*, $C_{30}H_{26}Br_2$, with bromine at the ordinary temperature, or in ethereal solution at 100° a mixture of this with a *bromo-dibromide*, $C_{30}H_{25}Br_3$; with an excess of bromine at 100° in absence of a solvent, a *dibromo-dibromide*, $C_{30}H_{24}Br_4$, is formed. The condensation product reacts with fuming nitric acid, forming a product, $C_{30}H_{25}O_{30}N_3$. G. Y.

Colour of Ethylene Glycol and of Glycerol. WALTHER SPRING (*Arch. Sci. phys. nat.*, 1908, [iv], 25, 5—14; *Bull. Soc. chim. Belg.*, 1908, 22, 10—17).—In order to obtain evidence of the part played

by the hydroxyl group in the blue colour which water and ethyl alcohol exhibit when examined in long columns, the author has investigated the colour of pure ethylene glycol and glycerol. Ethylene glycol, purified by distillation at low pressures, has a yellow colour which is shown to be due to traces of impurities. Attempts were made to remove the yellow colour by treatment with freshly-calced animal charcoal, but it was found that the filtered liquid was almost opaque in consequence of the presence of ultra-microscopic particles of charcoal which could not be removed by filtration. When, however, the glycol was mixed with one-fifth of its volume of water, filtration after treatment with charcoal gave an optically clear liquid. A similar phenomenon was observed in the attempts to remove the green colour which glycerol shows after purification by distillation in steam under reduced pressure.

Ethylene glycol and glycerol, mixed with one-fifth volume of water and treated with animal charcoal as described, exhibit a blue colour, which is deeper than the blue colour of ethyl alcohol and water, when columns of the substances corresponding with equimolecular quantities are compared. The observations indicate that the hydroxyl group is the determining factor in the production of this colour.

H. M. D.

Alkylene Glycol-chlorohydrin Ethers and their Transformations. PAUL HOERING (*Ber.*, 1908, 41, 173—175).—Attention is drawn by the author to his investigations (*Abstr.*, 1905, i, 903; 1907, i, 624) and those of Hell and Hollenburg (*Abstr.*, 1896, i, 354) dealing with several of the points discussed in Houben and Fuhrer's paper (this vol., i, 73) of which these authors make no mention.

W. H. G.

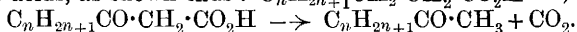
Preparation of Esters. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1907, 21, 428—434).—Krafft and Roos have shown (*Abstr.*, 1894, i, 91) that the sulphonic acids facilitate the formation of ethers and esters, and the Badische Anilin- und Soda-Fabrik has patented a process for the use of sulphonic acids in accelerating the action of acetic anhydride on cellulose (*Chem. Zentr.*, 1907, ii, 365). The author finds that camphorsulphonic acid greatly accelerates the action of acid anhydrides on phenols and alcohols, and has prepared in this way acetyl derivatives of geraniol, glycerol, phenol, quinol, gallic acid, salicylic acid, and methyl salicylate. Butyrates of the first and second, and benzoates of the first, third, and seventh, substances were also prepared. In most cases, simple addition of a small quantity of camphorsulphonic acid to the cold mixture of alcohol or phenol with the anhydride only is required, but in others the mixture must be heated.

T. A. H.

Oxidation of Ammonium Salts of Saturated Fatty Acids with Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 227—233).—The ammonium salts of the acids from formic to stearic are oxidisable by hydrogen peroxide even at room temperature.

In all cases, carbon dioxide is liberated. Formic acid is most

readily oxidised, then follow in order acetic, butyric, and *isobutyric*, and then valeric and *isovaleric* acids. The remaining acids show but slight variations among themselves, yielding about 1/10 gram-mol. of carbon dioxide for every gram-mol. of fatty acid. Propionic acid yields acetaldehyde, acetic acid, and a little formic acid. *isoButyric* and *isovaleric* acids both yield acetone. The higher acids from hexoic to stearic are oxidised, in part, with formation of ketones derived from β -ketonic acids, as shown thus : $C_nH_{2n+1}CH_2 \cdot CH_2 \cdot CO_2H \rightarrow$



Lower fatty acids and aldehydes are formed simultaneously. The reactions appear to have some biochemical relationships, which will be investigated further.

W. D. H.

Catalytic Ester Exchanges. II. ROBERT KREMANN (*Monatsh.*, 1908, 29, 23—44. Compare Abstr., 1905, ii, 630).—According to the view of the mechanism of the formation of ethyl acetate and glycerol from triacetin and ethyl alcohol put forward previously, the amount of triacetin in the equilibrium mixture must increase as the amount of alcohol is diminished ; moreover, triacetin, or a mixture of this with mono- and di-acetin, must be formed by the action of glycerol on ethyl acetate, the reaction being accelerated by addition of sodium hydroxide. These requirements are shown to be satisfied by the experimental results obtained. Stritar and Fanto's criticisms (Abstr., 1907, i, 464) are founded on a misapprehension of the present author's views. If hydrolysis does take place, both the triacetin and the ethyl acetate must undergo the reaction, but in absolute alcoholic solution the amount of hydrolysis is negligible. In aqueous alcohol, on the other hand, the velocity of the hydrolysis increases rapidly with the percentage of water.

The amounts of ethyl acetate formed by diacetyltartaric acid and its ethyl ester in varying concentrations of alcoholic sodium hydroxide have been determined. The yields of ethyl acetate from the diacetyl acid with the higher concentrations of the alkali are approximately the same as those obtained from tetra-acetylmucic acid, but diminish less rapidly with diminishing concentration of the alkali. Ethyl diacetyltartrate yields less ethyl acetate than does the acid with the higher, but more with the lower, concentrations of the alkali. It is remarkable that the ester exchange takes place with diacetyltartaric acid on addition of less alkali than is required for the neutralisation of the acid.

G. Y.

Constitution of Glucinum Salts of Fatty Acids. New Glucinum Ortho-Salts and Salts of Other Elements with Organic Ortho-Acids. BORIS GLASSMANN [and, in part, A. NOVICKY] (*Ber.*, 1908, 41, 33—38. Compare Abstr., 1907, i, 109).—Salts of the type Gl_2R_2O (R = acid radicle) are obtained by the action of glucinum carbonate on hydroxy-acids and halogen-substituted fatty acids ; it is assumed that these salts are derived from acids formed by the condensation of 2 mols. of an ortho-fatty acid. The author further shows that a large number of well-known salts of other metals may be regarded as salts of ortho-fatty acids, or acids formed by the

condensation of 2 or more mols. of these acids; for example, basic glucinum acetate, $\text{Gl}_4\text{O}(\text{OAc})_6$ (Steinmetz, Abstr., 1907, i, 673); zirconyl acetate, $\text{ZrO}(\text{OAc})_2$ (Rosenheim and Hertzmann, Abstr., 1907, ii, 271), and basic chromium propionate, $\text{Cr}_2\text{O}(\text{Et}\cdot\text{CO}_2)_4$ (Renard, Abstr., 1887, 654).

The following crystalline salts of glucinum were prepared and analysed: *lactate*, $\text{Gl}_2\text{O}(\text{C}_3\text{H}_5\text{O}_2)_2\cdot\text{H}_2\text{O}$; *glycollate*, $\text{Gl}_2\text{O}(\text{C}_2\text{H}_3\text{O}_3)_2\cdot\text{H}_2\text{O}$; *ethylglycollate*, $\text{Gl}_2\text{O}(\text{C}_4\text{H}_7\text{O}_3)_2\cdot\text{H}_2\text{O}$; *phenylglycollate*, $\text{Gl}_2\text{O}(\text{C}_8\text{H}_7\text{O}_3)_2$; *salicylate*, $\text{Gl}_2\text{O}(\text{C}_7\text{H}_5\text{O}_3)_2$, and *α -chloropropionate*, $\text{Gl}_2\text{O}(\text{C}_3\text{H}_4\text{O}_2\text{Cl})_2\cdot\text{H}_2\text{O}$; the *trichloroacetate*, $\text{Gl}_2\text{O}(\text{C}_2\text{O}_2\text{Cl}_3)_2$, is obtained as a glassy mass. The following crystalline glucinum salts of the type $\text{Gl}_4\text{R}_6\text{O}$, corresponding with the above-mentioned basic acetate, have also been obtained: *dichloroacetate*, $\text{Gl}_4\text{O}(\text{C}_2\text{HO}_2\text{Cl}_2)_6$; *bromoacetate*, $\text{Gl}_4\text{O}(\text{C}_2\text{H}_2\text{O}_2\text{Br})_6$; *chloroacetate*, $\text{Gl}_4\text{O}(\text{C}_2\text{H}_2\text{O}_2\text{Cl})_6$, and *α -bromopropionate*, $\text{Gl}_4\text{O}(\text{C}_3\text{H}_4\text{O}_2\text{Br})_6$; the *cianoacetate*, $\text{Gl}_4\text{O}(\text{C}_3\text{H}_2\text{O}_2\text{N})_6$, is obtained as a vitreous mass. The solution obtained by dissolving freshly precipitated stannous oxide in strong acetic acid yields on evaporation the crystalline *stannoacetate*, $\text{Sn}(\text{OAc})_2\cdot\text{O}$. W. H. G.

Some Cuprammonium Salts. V. DAVID W. HORN (*Amer. Chem. J.*, 1908, 39, 184—226. Compare Abstr., 1906, ii, 231; 1907, i, 595; ii, 871).—Experiments are described which have been carried out with the object of ascertaining whether the largest number of ammonia groups which can combine with copper salts is a function of the basicity of the acid residue.

The method adopted was that described previously (Abstr., 1907, ii, 532) for determining transition temperatures. The anhydrous copper salt is treated with liquid ammonia, a constant pressure of about one atmosphere is maintained, and by observing the thermometer it can be ascertained whether the same solid compound existing at the temperature at which the saturated solution boils persists until the whole system has attained the temperature of the room, or whether it decomposes to form a simpler compound at intermediate temperatures.

It has been found that at all pressures not greater than one atmosphere, and at all temperatures between -30° and $+20^\circ$, copper sulphate, oxalate, and succinate cannot combine with more than five ammonia groups, whilst the chloride, bromide, and iodide are capable of uniting with six ammonia groups. Copper acetate forms a salt containing 4NH_3 , and evidence was obtained of the existence of a salt containing still more ammonia, and having a tension of one atmosphere when it dissociates at about -22° ; its formula was not established.

Copper thiocyanate yields, in addition to the salts already described (Abstr., 1907, i, 596), a *compound*, $\text{Cu}(\text{SCN})_2\cdot 5\text{NH}_3$. When the salt, $\text{Cu}(\text{SCN})_2\cdot 2\text{NH}_3$, is treated with pyridine, a *compound*, probably $\text{Cu}(\text{SCN})_2\cdot 4\text{C}_5\text{H}_5\text{N}$, is produced.

When copper acetoiodide is treated with liquid ammonia, a mixture of the acetate, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 4\text{NH}_3$, and the iodide, $\text{CuI}_2\cdot 6\text{NH}_3$, appears to be formed. The acetobromide behaves in the same manner.

Copper dithionate does not form a compound containing more

ammonia than the salt, $2\text{CuS}_2\text{O}_6, 9\text{NH}_3$, at any temperature between -30° and $+20^\circ$. Copper *o*-phthalate yields a *salt*, $2\text{CuC}_8\text{H}_4\text{O}_4, 9\text{NH}_3$, and indications were obtained of the existence of a still higher salt with a tension of one atmosphere when dissociating at about -8° . In the case of copper carbonate, a salt containing more than 2NH_3 could not be obtained. Copper nitrate yields a *salt*,
 $4\text{Cu}(\text{NO}_3)_2, 23\text{NH}_3$.

A list of copper salts is given, arranged in the order of their solubility in liquid ammonia.

The colour of the cuprammonium compounds depends not only on the number of ammonia groups in the molecule, but also on the acid residues.

The order of the copper salts with regard to their affinity for ammonia is as follows: copper iodide, bromide, chloride, nitrate, sulphate, succinate, oxalate, thiocyanate, dithionate, acetate. The iodide, bromide, and chloride, containing 6NH_3 , dissociate under 2 cm. pressure at 67.4° , 54.9° , and 46.7° respectively. The sulphate, succinate, and oxalate, with 5NH_3 , when left over sulphuric acid at the ordinary temperature, lose 1NH_3 in one week, one day, and one and a-half hours respectively. The thiocyanate, $\text{Cu}(\text{SCN})_2, 5\text{NH}_3$, is less stable, as, under atmospheric pressure, it dissociates at about 10° , whilst all these other salts containing 5NH_3 dissociate at about 20° .

The nature of the affinity of copper salts for ammonia is discussed.

E. G.

Electrolytic Production of Saturated Acids and Esters from the corresponding Unsaturated Compounds. C. F. BOEHRINGER and SÖHNE (D.R.-P. 187788).—The unsaturated acids and their esters are readily reduced in the cathode cell to the corresponding saturated compounds, providing that a cathode of platinised platinum is employed. Cathodes of nickel or polished platinum are useless, owing to the small yield thereby obtained. The hydrogenation takes place in acid solutions, small current densities being employed. The unsaturated acid or its ester may be either in suspension or dissolved in a suitable solvent, such as alcohol.

Oleic acid is converted into stearic acid in alcoholic solution containing a small amount of sulphuric acid at 20 — 50° , the current density being 1 ampere per sq. metre with 4 to 6 volts.

Ethyl oleate and erucic acid are similarly reduced to ethyl stearate and behenic acid respectively.

G. T. M.

Magnesium, Calcium, and Strontium Salts of the Higher Brominated Fatty Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 187449).—An alcoholic solution of calcium chloride was saturated with ammonia, filtered from precipitated ammonium chloride, and treated with an alcoholic solution of bromobehenic acid. *Calcium bromobehenate*, $\text{Ca}(\text{C}_{22}\text{H}_{42}\text{BrO}_2)_2$, thus produced is a colourless, tasteless powder, insoluble in water or alcohol; it may also be prepared either by the direct treatment of the acid with saturated lime-water or by double decomposition from soluble calcium salts and the alkali bromobehenates in aqueous solution.

Strontium bromobehenate, $\text{Sr}(\text{C}_{22}\text{H}_{42}\text{BrO}_2)_2$, prepared by the interaction of strontium hydroxide and bromobehenic acid in methyl-alcoholic solution, resembles the preceding salt; the corresponding *magnesium* salt has similar properties, and is produced by comparable processes.

G. T. M.

The Addition of Hydrogen Iodide to the Unsaturated Fatty Acids. *FARBENFABRIKEN VORM. FRIEDR. BAYER & Co.* (D.R.-P. 187822).—It has been found that hydrogen iodide may be readily added to the unsaturated fatty acids by treating these with a metallic iodide and some stronger acid in the absence of water.

Erucic acid is converted into iodobehenic acid when shaken for two or three days at 40—50° with sodium iodide and glacial acetic acid saturated with hydrogen chloride.

Oleic acid is transformed into iodostearic acid by treatment at 70—80° with potassium iodide and oxalic acid suspended in benzene. Other metallic iodides may be employed instead of potassium iodide, and sulphuric, phosphoric, tartaric, or benzenesulphonic acid may be used as the condensing agent.

G. T. M.

Psylla Wax. IV. Psyllic Acid and its Salts. ERNST E. SUNDBYK (*Zeitsch. physiol. Chem.*, 1908, 54, 255—257. Compare Abstr., 1898, i, 617; 1901, i, 358; 1907, i, 887).—The alkali salts of psyllic acid (pysslostearic acid) are precipitated when alcoholic solutions of the acid and an alkali hydroxide are mixed. The *silver* and *barium* salts can be obtained by adding aqueous alcoholic solutions of silver nitrate and barium chloride to alcoholic solutions of the acid. The following salts have been analysed: $\text{C}_{33}\text{H}_{65}\text{O}_2\text{Na}$, $\text{C}_{66}\text{H}_{130}\text{O}_4\text{Ba}$, and $\text{C}_{33}\text{H}_{65}\text{O}_2\text{Ag}$. Psylla wax is hydrolysed by alcoholic potassium hydroxide as well as by hydrobromic acid.

J. J. S.

Alcoholysis of Linseed Oil. ALBIN HALLER (*Compt. rend.*, 1908, 146, 259—262. Compare Abstr., 1907, i, 9, 10, 379).—Four specimens of linseed oil having respectively the iodine numbers 176, 168, 171, and 172, and the saponification values 185, 190, 189, and 191, have been examined. The oil being insoluble in methyl and ethyl alcohols, addition of a second solvent was necessary; benzene, carbon tetrachloride, acetone, and ether were tried, of which the last was found most suitable. When linseed oil is boiled with a mixture of ethyl ether and methyl alcohol containing 2.5% of hydrogen chloride, methyl palmitate, arachate, stearate, oleate, linoleate, linolenate, and isolinolenate are formed. The glycerides of stearic acid, which occurs in appreciable proportions, and of arachic acid, which occurs only in very small quantities, have not previously been recognised in linseed oil.

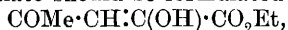
E. H.

Transformation of the α -Hydroxy-acids into Aldehydes by Boiling the Aqueous Solutions of their Mercuric Salts. Application to the Preparation of *l*-Arabinose by Means of Mercuric Gluconate. MARCEL GUERBET (*Compt. rend.*, 1908, 146, 132—135).—According to the equation $2\text{Hg}(\text{C}_3\text{H}_5\text{O}_3)_2 = \text{C}_3\text{H}_6\text{O}_3 + \text{Hg}_2(\text{C}_3\text{H}_5\text{O}_3)_2 + \text{C}_2\text{H}_4\text{O} + \text{CO}_2$, proposed by the author (Abstr., 1902,

i, 703) to explain the decomposition of an aqueous solution of mercuric lactate when boiled, 100 grams of this salt should give 57.8 grams of mercurous lactate, 9 grams of lactic acid, and 4.4 grams of acetaldehyde. In a quantitative experiment, the amounts obtained were 55.4 grams, 11.4 grams, and 3.9 grams respectively, and the conclusion is drawn that the chief reaction is represented by the above equation, the differences between the theoretical and experimental numbers probably being due to the gradual decomposition of the mercurous lactate into mercuric lactate and mercury. Mercuric glycollate and tartrate similarly decompose into the mercurous salts, the acids, carbon dioxide, and formaldehyde and glyoxal respectively, but here the reactions are slower than with the lactate. Mercuric gluconate undergoes the same reaction, and, as in this case the secondary change of the mercurous salt formed into mercuric gluconate and mercury is much more rapid than the corresponding change in the former reactions, two instead of one of the four molecules of gluconic acid present as mercuric salt are transformed into *L*-arabinose. The latter can be prepared advantageously by this reaction, a total yield of 22—24 grams being obtainable from 100 grams of calcium gluconate.

E. H.

Mechanism of the Acetoacetic Ester Synthesis. I. The Condensation of Acetone with Oxalic Ester. ROBERT H. CLARK (*J. Physical Chem.*, 1908, 12, 1—25).—The author has measured the velocity of formation of ethyl acetonoxalate in alcohol with various concentrations of acetone, ethyl oxalate, and sodium ethoxide (catalyst), and also the effect of water and of alcohol on the yield (compare Claisen and Stylos, *Abstr.*, 1887, 917). It was found that the degree of coloration produced by excess of ferric chloride in neutral solution is proportional to the amount of ethyl acetonoxalate present, and is not affected by water, alcohol, acetone, or ethyl oxalate; an equivalent of sodium ethoxide, however, doubles the intensity of the red colour produced. The author supposes that the sodium ethoxide gives rise to a new enol group (compare Schiff, *Abstr.*, 1898, i, 355), and argues that ethyl acetonoxalate should be formulated as



or $\text{OH}\cdot\text{CMe}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, neither of which formulæ agrees with the magnetic rotation and refractive index of the substance as determined by Perkin and Gladstone (*Trans.*, 1892, 61, 821).

Experiments made with a colorimeter showed that in strong, absolute alcoholic solutions the condensation is complete, but the yield is diminished somewhat by dilution with alcohol. Traces of water, however, have a very marked effect, the addition of only 1.065% of water lowering the yield from 96% to 10% of the theoretical. The condensation is shown to be a reversible reaction. In alcoholic solutions, the rate of condensation is proportional to the first power of the acetone condensation, and to a power of the concentration of ethyl oxalate and sodium ethoxide, which varies from 1.2 to 2 with increasing dilution. The author claims that his results lend support to Claisen's theory that the change is preceded by the association of sodium ethoxide with the ester, the degree of association depending on the concentration of the

solutions. The additive product must have twice the molecular weight assumed by Claisen and Lowman (Abstr., 1887, 583). R. J. C.

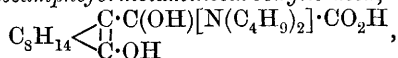
γ -Hydroxytetrollic Acid. ROBERT LESPIEAU and VIGUIER (*Compt. rend.*, 1908, 146, 294—296).—The authors have applied Jocitsch's reaction of organo-magnesium compounds on acetylenic hydrocarbons to propargyl alcohol. The latter (1 mol.) when treated with magnesium ethyl bromide (2 mols.) gives γ -hydroxytetrollic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{H}$, a white, crystalline substance, m. p. 115—116°, which decomposes carbonates, but, unlike Duisberg's hydroxytetrollic acid (Abstr., 1882, 1193), does not give a sky-blue coloration with ferric chloride. When treated in the dark in ethereal solution at -10° with bromine (1 mol.), it is converted into a mixture of much $\alpha\beta$ -dibromo- γ -hydroxy- Δ^a -butenoic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$, m. p. 137—138°, with a small quantity of Tönnies's lactone (Abstr., 1879, 918), which Hill (Abstr., 1894, i, 319) has shown to have the formula $\begin{array}{c} \text{CBr}-\text{CO} \\ | \\ \text{CBr}\cdot\text{CH}_2 \end{array} > \text{O}$; it has m. p. 91°.

When $\alpha\beta$ -dibromo- γ -hydroxy- Δ^a -butenoic acid is kept at 150° for two hours, its m. p. remains unchanged; when heated at 200° , it loses carbon dioxide and hydrogen bromide, but no lactone is formed. This seems to indicate that the acid belongs to the fumaric rather than to the maleic series. E. H.

Camphoroxalic Acid Derivatives. XI. Action of Certain Secondary Amines on Camphoroxalic Acid. J. BISHOP TINGLE and L. F. WILLIAMS (*Amer. Chem. J.*, 1908, 39, 105—124. Compare Abstr., 1899, i, 444; 1900, i, 302; 1901, i, 632; 1905, i, 799; 1906, i, 902).—In earlier papers, compounds of camphoroxalic acid with amines have been described. In the case of primary amines, derivatives are produced of the types: (I) $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{C}(\text{NHR})\cdot\text{CO}_2\text{NH}_3\text{R} \\ | \\ \text{CO} \end{array}$; (II) $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{C}(\text{NHR})\cdot\text{CO}_2\text{H} \\ | \\ \text{CO} \end{array}$, and (III) $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{CH}\cdot\text{NHR} \\ | \\ \text{CO} \end{array}$. In the formation of compounds of type I, it is probable that intermediate products, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}\cdot\text{C}(\text{OH})(\text{NHR})\cdot\text{CO}_2\cdot\text{NH}_3\text{R} \\ | \\ \text{CO} \end{array}$, are first formed, water being afterwards eliminated. Some of these intermediate compounds are stable, and have been described under the name of camphoformolamine derivatives.

The compounds derived from the secondary amines probably have the constitution $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}\cdot\text{C}(\text{OH})(\text{NR}_2)\cdot\text{CO}_2\text{H} \\ | \\ \text{C}\cdot\text{OH} \end{array}$, and are therefore termed *isocamphoformolamine* derivatives. They give an intense violet coloration with ferric chloride.

Diisobutylaminecamphoformolaminocarboxylic acid,



m. p. 179—180° (decomp.), forms white needles, and when heated above its m. p. is converted into *diisobutylcamphoformeneamine*,

$C_8H_{14} \begin{smallmatrix} \diagup C:CH \cdot N(C_4H_9)_2 \\ | \\ CO \end{smallmatrix}$, m. p. 73—74°. The following compounds are also described: *diamylisocamphoformolaminecarboxylic acid*, m. p. 160°; *diamylcamphoformeneamine*, m. p. 43°; *diisoamylisocamphoformolaminecarboxylic acid*, m. p. 156°; *diisoamylcamphoformeneamine*, m. p. 40°; *dibenzylcamphoformeneamine*, m. p. 152°; *phenylmethylcamphoformeneamine*, m. p. 126°; *phenylethylcamphoformeneamine*, b. p. 285°/110 mm.; *benzylethylisocamphoformolaminecarboxylic acid*, m. p. 158° (decomp.), and *benzylethylcamphoformeneamine*, m. p. 57°. By the action of acetylphenylhydrazine on camphoroxalic acid, *acetylphenylaminecamphoformeneamine*, $C_8H_{14} \begin{smallmatrix} \diagup C:CH(NAc) \cdot NPh \\ | \\ CO \end{smallmatrix}$, m. p. 174°, is obtained.

Benzoylphenylhydrazine, benzylphenylhydrazine, benzylmethylamine, phenylmethylhydrazine, benzylaniline, phenyl- β -naphthylamine, *p*-phenylhydrazinesulphonic acid, and various acyl derivatives of *o*- and *p*-aminophenols were heated with camphoroxalic acid, but condensation products were not formed.

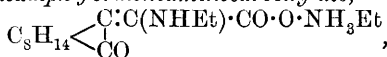
Dimroth's paper (Abstr., 1907, i, 662) on the interaction of *p*-nitrobenzenediazonium hydroxide and certain ketonic and enolic compounds is criticised. E. G.

Camphoroxalic Acid. XII. Action of Primary and Tertiary Amines on Camphoroxalic Acid. J. BISHOP TINGLE and L. F. WILLIAMS (*Amer. Chem. J.*, 1908, 39, 277—300. Compare preceding abstract).—In earlier papers, it has been shown that primary amines condense with camphoroxalic acid with formation of substances of three types: (I) $C_8H_{14} \begin{smallmatrix} \diagup C:C(NHR) \cdot CO \cdot O \cdot NH_3R \\ | \\ CO \end{smallmatrix}$,

(II) $C_8H_{14} \begin{smallmatrix} \diagup C:C(NHR) \cdot CO_2H \\ | \\ CO \end{smallmatrix}$, and (III) $C_8H_{14} \begin{smallmatrix} \diagup C:CH \cdot NHR \\ | \\ CO \end{smallmatrix}$

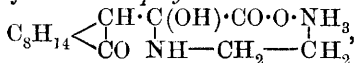
It is pointed out that, whilst certain amines yield compounds of all three types, others give only two, and some not more than one of them; in the last case, substances of type III being usually formed. Moreover, many amines do not react at all with camphoroxalic acid. In order to obtain evidence as to the causes underlying these differences in behaviour, the investigation has been extended to primary amines not previously examined. A study has also been made of the behaviour of certain tertiary bases towards camphoroxalic acid, particularly in the hope of obtaining well-crystallised salts which might possibly be of use in the resolution of the acid into structural isomerides.

Ethylamine ethylcamphoformeneaminecarboxylate,



m. p. 109°, forms white needles, and, when heated at 150°, is converted into *ethylcamphoformeneamine*, $C_8H_{14} \begin{smallmatrix} \diagup C:CH \cdot NHEt \\ | \\ CO \end{smallmatrix}$, m. p. 118°.

Ethylenediamine yields a *camphoformolamine* derivative,



m. p. 220°, which forms greyish-white, microscopic crystals.

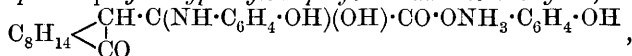
p-Nitrophenylcamphoformeneamine, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ \diagup \quad | \\ \text{CO} \end{array}$,

m. p. 156°, forms lustrous, brownish-yellow needles.

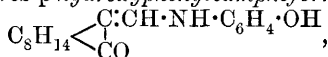
o-Aminophenol reacts with camphoroxalic acid with formation of the lactone of *o*-hydroxyphenylcamphoformeneaminecarboxylic acid,

$\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} = \text{C} \cdot \text{CO} \cdot \text{O} \\ \diagup \quad | \\ \text{CO} \quad \text{NH} - \text{C}_6\text{H}_4 \end{array}$, m. p. 159.5°, whilst *p*-aminophenol yields

p-aminophenol *p*-hydroxyphenylcamphoformolaminecarboxylate,



m. p. 190°, which is converted by dilute hydrochloric acid into the corresponding *acid*, m. p. 178° (decomp.). When this acid is heated above its m. p., it gives *p*-hydroxyphenylcamphoformeneamine,



m. p. 314°.

n-Propylamine and *m*- and *p*-phenylenediamines appear to react with camphoroxalic acid, but definite products could not be isolated.

The *camphoroxalates* of trimethylamine, m. p. 139—140° (decomp.), triethylamine, m. p. 102—103°, quinine, m. p. 160—161° (decomp.), strychnine, m. p. 214—215° (decomp.), and brucine, m. p. 235—236° (decomp.), are described. A crystalline camphoroxalate of tribenzylamine could not be obtained. Attempts to prepare two isomeric brucine camphoroxalates were unsuccessful.

Benzylideneaniline reacts with camphoroxalic acid with formation of phenylcamphoformeneaminecarboxylic acid, which was first obtained (Abstr., 1899, i, 444) by the action of aniline on camphoroxalic acid. The production of this compound is attributed to the hydrolysis of the benzylideneaniline into aniline and benzaldehyde.

Piperine does not react with camphoroxalic acid.

Tetraethylammonium camphoroxalate forms white needles, and is very unstable.

A list is appended of the various amines studied in this connexion, together with the formulæ and m. p.'s of the products obtained.

E. G.

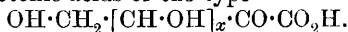
New Homologues of Diglycollic Acid. ÉMILE JUNGELEISCH and MARCEL GODCHOT (*Compt. rend.*, 1908, 146, 26—29. Compare Abstr., 1907, i, 748).—When ethyl α -bromobutyrate acts on the sodium compound of ethyl lactate, there is formed *ethyl α -methyl- α' -ethyl diglycolate*, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$, a liquid with an ethereal odour, having b. p. 130°/25 mm., $D_{16}^{20} 1.0774$. The free *acid*, which crystallises in small needles, m. p. 69°, loses water, partly on distillation in a vacuum and completely when boiled with acetyl chloride, giving the

anhydride, $O \left\langle \begin{array}{c} \text{CHEt} \cdots \text{CO} \\ \text{CHMe} \cdots \text{CO} \end{array} \right\rangle O$, a mobile liquid with a piquant odour, b. p. 125—130°/20 mm., D^{16} 1.1556.

By the action of alcoholic ammonia on the ethyl ester, the *diamide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CHEt} \cdot \text{CO} \cdot \text{NH}_2$, is formed in fine needles, m. p. 140—142°. A similar reaction with ethyl α -bromoisobutyrate gives *ethyl $\alpha\alpha$ -dimethyl- α' -methyl diglycollate*, $\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, a mobile liquid, b. p. 130—135°/25 mm., D^{16} 1.0507. The *acid*, which has not been obtained crystalline, is dehydrated by boiling acetyl chloride, giving the *anhydride*, $O \left\langle \begin{array}{c} \text{CMe}_2 \cdots \text{CO} \\ \text{CHMe} \cdots \text{CO} \end{array} \right\rangle O$, a liquid, b. p. 112—116°/20 mm., D^{16} 1.1531. The *diamide*, prepared from the ester, forms colourless lamellæ, m. p. 150° (after softening). *Ethyl α' -methyl- α -isopropyldiglycollate*, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CHPr}^i \cdot \text{CO}_2\text{Et}$, is similarly prepared. It is a colourless liquid, b. p. 137—140°/15 mm., D^{16} 1.0398. In the last reaction, the yield is very poor. By means of their brucine salts, the authors have separated $\alpha\alpha'$ -dimethyldiglycollic acid, $O(\text{CHMe} \cdot \text{CO}_2\text{H})_2$, into its two optically active modifications.

E. H.

Electrolysis of Sugars. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 7, 527—528).—*d*-Gluconic acid has been electrolysed in the hope of synthesising a polyhydric alcohol containing 10 carbon atoms. In reality, decomposition occurred, and *d*-arabinose was obtained. Other polyhydroxy-acids behave in a similar manner: *l*-arabonic acid yields *l*-erythrose; *i*-erythronic acid, *i*-glyceraldehyde; *i*-glyceric acid, glycolaldehyde, and glycollic acid, formaldehyde. In each case, the reaction consists in the elimination of a molecule of formic acid from one of the hydroxy-acid. In a few instances, indications were obtained of the formation of ketonic acids of the type



When melibiononic acid is subjected to electrolysis, a sugar containing 11 carbon atoms is formed. Saccharic acid, under similar conditions, yields the dialdehyde of tartaric acid, and tartaric acid itself yields glyoxal. Serine and *isoserine* when electrolysed yield products which react with *p*-nitrophenylhydrazine.

J. J. S.

Saccharinic Acids. HEINRICH KILIANI (*Ber.*, 1908, 41, 158—167).—Chiefly polemical against Nef (this vol., i, 5). The work of Kiliani and Loeffler (*Abstr.*, 1904, i, 373; 1905, i, 737) has been repeated on a large scale, and their results confirmed. No new compound was isolated from the product formed by the action of calcium hydroxide on lactose, but a new calcium saccharinate has been obtained by the action of calcium hydroxide on dextrose, the investigation of which is in progress.

W. H. G.

Decomposition of Calcium and Barium Tartrates by Alkali Chlorides. H. CANTONI and MADAME JOLKOWSKY (*Bull. Soc. chim.*, 1907, [iv], 1, 1181—1189. Compare *Abstr.*, 1905, i, 14, 633).—In previous papers, the solubilities of these tartrates in water at various temperatures were given, and attention was directed to the

fact that a difficulty was experienced in devising a method for the estimation of tartaric acid by the precipitation of an insoluble tartrate, since the precipitates formed proved to be more soluble in the solution of the second salt, simultaneously produced, than in water. In the present paper, it is shown that calcium tartrate is more soluble than barium tartrate in aqueous solutions of potassium, sodium, or ammonium chloride, and that the action of each of these three chlorides on each of the tartrates increases in the order given, although the differences are not great. In all cases, the solubility increases to about the same extent with rise of temperature. The attack of the tartrates by the chloride solutions is vigorous during the first hour, moderates considerably in the second hour, and equilibrium is reached at the end of about four hours. The solubility of each of the tartrates increases with increase of concentration of the chloride used, but the increase in the case of barium tartrate is more rapid than in the case of calcium tartrate.

Tables and curves illustrating in detail the results obtained are given in the original. T. A. H.

Sodium Antimonyl Tartrate. R. H. ADERS PLIMMER (*Proc. Roy. Soc.*, 1908, B, 80, 11—12).—Sodium antimonyl tartrate has the composition $C_4H_4O_7NaSb, 2\frac{1}{2}H_2O$. On drying at 105° , $2H_2O$ are lost, and the remaining $\frac{1}{2}$ mol. is removed by exposure in a vacuum over sulphuric acid. G. B.

Methyl α -Dibromo- and Dichloro-dicarboxyglutarate and the Formation of *cyclo*Trimethylene Derivatives from the Former. MAX GUTHZEIT and MARTIN LOBECK (*J. pr. Chem.*, 1908, [ii], 77, 43—60).—*Methyl α -dibromodicarboxyglutarate* [*methyl α -dibromopropanetetra-carboxylate*], $CH_2[CBBr(CO_2Me)_2]_2$, prepared by the action of bromine on methyl propanetetra-carboxylate in carbon disulphide solution at 35° , crystallises in prisms, m. p. 125 — 126° , and again forms methyl propanetetra-carboxylate when boiled with zinc dust in benzene solution. The *dichloro-ester*, prepared by the action of chlorine on methyl propanetetra-carboxylate at 50° , crystallises in prisms, m. p. 128 — 129° . The action of sodium on the dibromo-ester in boiling toluene solution leads to the formation of methyl *cyclotrimethylenetetra-carboxylate*, which is formed also when the dibromo-ester is heated with methyl disodiopropanetetra-carboxylate or sodium methoxide in methyl-alcoholic solution, or is treated with ammonia in hot methyl-alcoholic solution. *cyclo*Trimethylenetetra-carboxylic acid has m. p. 208° (decomp.) (200° , Guthzeit and Dressel, *Abstr.*, 1890, 879; 218 — 220° , Gregory and Perkin, *Trans.*, 1903, 83, 780). Ethyl dibromopropanetetra-carboxylate, under the same conditions, yields ethyl *cyclotrimethylenetetra-carboxylate* (Perkin, *Trans.*, 1905, 87, 358), m. p. 43° .

When saturated with ammonia in cooled methyl-alcoholic solution, methyl dibromopropanetetra-carboxylate yields a *product*, crystallising in needles, which on analysis gives figures agreeing approximately with those required by *cyclotrimethylenetetra-carboxylamide*; this readily loses ammonia, and on hydrolysis forms carbon dioxide and a

mixture of *cis*- and *trans*-cyclotrimethylenedicarboxylic acids, m. p. 165°. G. Y.

Antimony and Tin Compounds of Thioglycollic Acids. BROR HOLMBERG (*Zeitsch. anorg. Chem.*, 1908, **56**, 385—392).—In aqueous solution, sodium chloroacetate and sodium thiostannate react at the ordinary temperature, according to the equation :

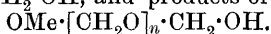
$2\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na} + \text{Na}_3\text{SbS}_4 = \text{S}_2(\text{CH}_2\cdot\text{CO}_2\text{Na})_2 + 2\text{NaCl} + \text{NaSbS}_3$, the sodium dithioglycollate remaining in solution. Sodium chloroacetate and thioarsenate react in an exactly corresponding way. Sodium chloroacetate and thiostannate give sodium chloride, sodium sulphide, and sodium thiodiglycollate, $\text{S}(\text{CH}_2\cdot\text{CO}_2\text{Na})_2$.

Attempts to prepare antimony trithioglycollate were unsuccessful ; by interaction of antimony trichloride and thioglycollic acid, only the compound $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{S}\cdot\text{Sb} \begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ | \\ \text{O}\cdot\text{CO} \end{smallmatrix}$, described by Klason and Carlson (Abstr., 1906, i, 232), was obtained. Sodium chloroacetate and thioantimonite interact in aqueous solution with formation of sodium metathioantimonite and sodium thiodiglycollate.

Stannic chloride, 1 mol., and thioglycollic acid, 2 mols., react readily in ethereal solution, forming the compound $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2, \text{SnCl}_2$.

This compound occurs in colourless crystals, which are unstable, decomposing with excess of water to form the corresponding dihydroxy-compound, $\text{S}_2(\text{CH}_2\cdot\text{CO}_2\text{H})_2, \text{Sn}(\text{OH})_2$. The latter occurs as a crystalline powder, practically insoluble in water, but soluble in hydrochloric acid with partial regeneration of the dichloride, and in sodium hydroxide with formation of the corresponding sodium salt. This salt, of the formula $\text{S}_2(\text{CH}_2\cdot\text{CO}_2\text{Na})_2, \text{Sn}(\text{OH})_2, 6\text{H}_2\text{O}$, occurs in large, transparent crystals, which slowly decompose in the air. The dichloride, dissolved in absolute alcohol, readily gives the ester, $\text{S}_2(\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5)_2, \text{SnCl}_2$, m. p. 157—158°. G. S.

Formaldehyde. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1189—1195; *Bull. Soc. chim. Belg.*, 1908, **22**, 17—20. Compare A. Lumière, L. Lumière, and Seyewetz, Abstr., 1905, i, 150).—By adding sodium (0.25 gram) to methyl alcohol (100 grams) and then adding trioxymethylene, sufficient of the latter can be dissolved to furnish a liquid containing the equivalent of 57% of formaldehyde. Such a product distils mainly between 89° and 92°, and can be separated into three fractions, whence it is concluded that it contains hydroxydimethyl ether, $\text{MeO}\cdot\text{CH}_2\cdot\text{OH}$, and products of the type



In this reaction, it is supposed that the polyoxymethylene complexes are first opened, yielding sodium alkyl oxides, which then react with methyl alcohol, forming sodium methoxide and products of the type indicated. A similar reaction takes place with ethyl or amyl alcohol, glycerol, or menthol, and, when, as in the case of menthol, sodium cannot be introduced directly, an equivalent quantity of sodium methoxide or ethoxide can be used.

Phenol containing a little sodium phenoxide reacts with trioxy-

methylene at 75—85°, forming an oily, yellow liquid, which is miscible with water and alcohol, partly soluble in ether, and slightly so in benzene. After a time, it becomes insoluble in alcohol. *p*-Cresol and trioxymethylene react at 80—85°, giving a slightly-coloured homogeneous mass, which, after about ten days, can be separated into 2 : 6-dimethylol-*p*-cresol and *p*-homosaligenin (compare Auwers, Abstr., 1907, i, 612). *o*- and *m*-Cresols also react with trioxymethylene, the former yielding crystalline products slowly. With β -naphthol, dihydroxydinaphthylmethane (compare Auwers, *loc. cit.*) is formed, but α -naphthol yields only a resinous product. T. A. H.

Formaldehyde. II. Solid Polymerides of Formaldehyde. FRIEDRICH AUERBACH and HERMANN BARSCHALL (*Chem. Zentr.*, 1907, ii, 1734—1735; from *Arb. Kais. Gesundh.-Amt.*, 1907, 27, 183—230. Compare Abstr., 1905, i, 859).—In view of the disagreements and obscurities existing in regard to the nature of the solid polymerides of formaldehyde, the authors have examined these with a view to determining in how far they are chemical individuals.

Paraformaldehyde, m. p. about 150—160°, which has a mol. wt. at least three times that of formaldehyde, is prepared by evaporation of pure formaldehyde solutions; it is amorphous and colloidal, contains varying amounts of adsorbed water, and reacts with sodium sulphite solution.

α -Polyoxymethylene, $(\text{CH}_2\text{O})_n$, formed by addition of 1 vol. of concentrated sulphuric acid to 10 vols. of aqueous formaldehyde, is indistinctly crystalline, m. p. 163—168° in a sealed tube, and at 189° yields a vapour consisting chiefly of formaldehyde molecules.

β -Polyoxymethylene, prepared by adding 4 vols. of concentrated sulphuric acid to 10 vols. of aqueous formaldehyde, is crystalline, m. p. 163—168° in a sealed tube, vapour density 32 at 184°, increasing slowly with the temperature, and reacts with sodium sulphite solution.

γ -Polyoxymethylene, formed together with the β -polymeride by the action of 4 vols. of sulphuric acid on 10 vols. of formalin, is crystalline, m. p. 163—165° in a sealed tube, does not react with sodium sulphite, and when boiled with water is converted into the δ -polymeride; at 184° and 198°, the vapour has D 40 and 60 respectively, the gas consisting of formaldehyde molecules mixed with polymeric molecules, the proportion of the latter increasing with the pressure, but diminishing as the temperature rises. When heated in the open, these three polyoxymethylenes volatilise without first melting.

δ -Polyoxymethylene is indistinctly crystalline, m. p. 169—170° in a sealed tube, melts when heated in the open, does not react with sodium sulphite, and at 190—240° yields a vapour consisting of polymeric molecules which dissociate only slowly.

α -Trioxymethylene, $\text{C}_3\text{H}_6\text{O}_3$, formed by sublimation of the polyoxymethylenes into water, crystallises in colourless needles, or strongly refracting prisms, m. p. 63—64° in a sealed tube, b. p. 114·5°/759 mm., volatilises to a marked extent at the ordinary temperature, differs from formaldehyde and the polyoxymethylenes in not giving the aldehyde or ketone reactions, and has therefore probably a cyclic constitution.

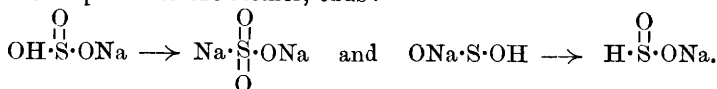
Paraformaldehyde differs from α -polyoxymethylene chiefly in being amorphous and in the adsorption of water. Paraformaldehyde and the four polyoxymethylenes yield formaldehyde as gas, or in aqueous solution, with an ease gradually diminishing from paraformaldehyde to δ -polyoxymethylene. The aqueous solutions are not to be distinguished from aqueous formaldehyde.

The conclusions to be drawn from the comparison of the vapour tensions of the four polyoxymethylenes are discussed; the vapour of the polyoxymethylenes at 25° can contain only very little formaldehyde, and must consist chiefly of polymeric molecules insoluble in water. α -Trioxymethylene, on the other hand, has a constant vapour tension and vapour density. G. Y.

So-called Formaldehyde-Sodium Hyposulphite. ERNST VON MEYER (*J. pr. Chem.*, 1908, [ii], 77, 61—64).—In spite of the work of various authors, it has not yet been determined whether sodium formaldehydesulphoxylate (Bazlen, *Abstr.*, 1905, ii, 240) and sodium hydrogen sulphiteformaldehyde, which are formed by the action of sodium hyposulphite on formaldehyde, exist as a double salt or are capable of separate existence in solution in presence of each other. It is now found that the two salts may be separated, at least partly, by fractional precipitation or fractional recrystallisation, and that 1000 mols. of water dissolve 120 mols. of the sulphoxylate and 146 mols. of the sulphite separately, but 93 mols. and 114 mols. respectively, of the two salts in presence of each other. Moreover, a transition point indicating a formation or decomposition of a double salt could not be observed between -14° and 55° either by the thermometric or the dilatometric method (van't Hoff, Goldschmidt, and Jorissen, *Abstr.*, 1895, ii, 380). Hence sodium hyposulphiteformaldehyde, still sometimes referred to as a chemical individual, consists of a mixture of sodium formaldehydesulphoxylate and sodium hydrogen sulphiteformaldehyde, which do not combine to form a double salt either in the solid state or in solution. G. Y.

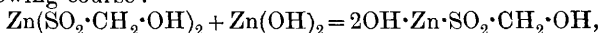
Constitution of Sodium Hyposulphite and Formaldehydesulphoxylate. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1588—1617. Compare Bucherer and Schwalbe, *Abstr.*, 1906, ii, 741).—A criticism of the existing theories as to the constitution of the hyposulphites and formaldehydesulphoxylates is given, and, chiefly on the ground of their reaction with neutral and alkaline solutions of potassium mercuric iodide, it is considered that the former consists of a mixture, $\text{ONa}\cdot\text{SO}\cdot\text{O}\cdot\text{SNa}\cdot\text{O}$ and $\text{ONa}\cdot\text{SO}\cdot\text{O}\cdot\text{SH}(\text{OH})\cdot\text{ONa}$, together with the free groups $\text{ONa}\cdot\text{SH}\cdot\text{O}$ and $\text{OH}\cdot\text{SNa}\cdot\text{O}$, the last two being formed when in the preparation of the hyposulphite an insufficient quantity of sodium hydrogen sulphite is employed, but, when sulphur dioxide reacts with metallic sodium, the hyposulphite consists wholly of $\text{SONa}\cdot\text{O}\cdot\text{SO}_2\text{Na}$. Sodium formaldehydesulphoxylate is a derivative of hyposulphurous acid, $\text{HS}\cdot\text{O}(\text{OH})$, and should therefore be termed sodium formaldehydehyposulphite. In aqueous solutions, it reacts with other substances in accordance with the constitutions $\text{O}\cdot\text{SNa}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{ONa}\cdot\text{S}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$. Sodium hydrogen form-

aldehydesulphite has the formula $\text{NaS} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{O} \cdot \text{CH}_2 \cdot \text{OH}$. Commercial sulphonylate contains considerable quantities of sodium hydrogen sulphite, sodium sulphite, and also the substance $\text{NaHSO}_3 \cdot \text{CH}_2\text{O}$. The compounds in which sulphur functions as a sexavalent element are more stable than those in which it is quadri- or bi-valent, consequently, where possible, there is always a tendency for the latter to pass into the former, thus:



Z. K.

Production of a Sparingly Soluble [Basic] Zinc Formaldehydesulphonylate. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 187494. Compare Abstr., 1906, i, 802).—One litre of 14% zinc hyposulphite solution at 70° is treated successively with 220 c.c. of 40% formaldehyde and 100 grams of zinc carbonate, the mixture being warmed and stirred until the reducing action of the solution has disappeared. The precipitated basic *zinc formaldehydesulphonylate*, $\text{OH} \cdot \text{Zn} \cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{OH}$, is then collected; it may be converted into the technically important sodium formaldehydesulphonylate by treatment with sodium carbonate. The foregoing reaction takes the following course:



and results in a separation of the sulphonylate from soluble zinc formaldehydesulphite, which under these conditions remains unchanged.

G. T. M.

Fission of Hydrogen Cyanide from Amides of α -Bromo-Fatty Acids Accompanied by the Formation of an Aldehyde or Ketone. GUSTAV MOSSLER (*Monatsh.*, 1908, 29, 69—82).—The formation of aldehydes or ketones by the splitting off of formic acid from α -hydroxy-acids is a well-known reaction. In an analogous manner, as now found, the amides of α -bromo-acids when heated with aqueous or alcoholic sodium hydroxide lose hydrogen bromide and hydrogen cyanide, and form an aldehyde or ketone according to their configurations. The amides are best prepared by the action of ammonia on the α -bromo-acid bromide in benzene solution. In this manner have been prepared acetaldehyde, propaldehyde, isobutaldehyde, and benzaldehyde, acetone, and diethyl ketone; with 20% alcoholic potassium hydroxide, the yields obtained range from 40.4% to 97.4%, in the order in which the substances are named.

G. Y.

Unimolecular Succindialdehyde. CARL D. HARRIES and PAUL HOHENEMSER (*Ber.*, 1908, 41, 255—260. Compare Abstr., 1901, i, 451; 1902, i, 345).—The glassy polymeric succindialdehyde does not yield the unimolecular variety on treatment with phosphoric oxide, but is completely destroyed (compare Abstr., 1907, i, 183). If, however, the polymerised form is distilled, the first fraction, below 169°, rejected as the dialdehyde in the distillate, contains water, and the

fraction, b. p. 169—171°, then repeatedly distilled under reduced pressure, the unimolecular form of succindialdehyde is obtained as a mobile liquid, b. p. 56—57°/8—10 mm.; D_{21}^{21} 1.0642; mol. wt. in glacial acetic acid, 104—111, calc. 86; n_D^{20} 1.42717. The molecular refraction is therefore normal for a dialdehyde, but not for an enolic modification. The liquid, b. p. 65—66°/11 mm., earlier observed is always obtained when water is present (1901, *loc. cit.*).

More careful determinations of the molecular refraction of the glassy and liquid forms at different temperatures show the conclusion previously drawn to be erroneous, that the transition temperature from M_5 to M_1 is 65° (1902, *loc. cit.*). Curves drawn connecting refractive index and temperature of both modifications intersect at 133°, and the dissociation temperature, although not determined, is therefore much higher than 65°.

The dielectric constant of the glassy form is 3.78, and that of the liquid form 28.5, temp. 20°, the aniline taken as the standard = 7.2.

In the preparation of succindialdehyde from the dialdoxime and nitrous fumes, it is important to use nitric acid of D 1.3; acid of D 1.4 leads to the formation almost exclusively of succinic acid. W. R.

A Synthesis of Certain Naturally-Occurring Aliphatic Ketones, and their Possible Mode of Formation in the Organism. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 221—225).—An examination was made of certain ketones which are constituents of certain vegetable essential oils in order to see whether they can be prepared by oxidation of the corresponding saturated fatty acid in a manner analogous to the formation of acetone by the oxidation of butyric acid. The oxidation, as in previous work, was accomplished by means of hydrogen peroxide, and this type of β -oxidation occurs in the animal body. Experiment showed this could be done; thus lauric acid, after conversion into its ammonium salt and warming with hydrogen peroxide, readily yields methyl *n*-nonyl ketone, an unstable β -ketonic acid being its precursor. In a similar fashion, decoic acid yields methyl *n*-heptyl ketone, and octoic acid, methyl *n*-amyl ketone. These ketones probably arise in a corresponding way in the plant organism.

W. D. H.

New Derivatives of Camphenilone; its Constitution. LOUIS BOUVEAULT and GUSTAV BLANC (*Compt. rend.*, 1908, 146, 233—235).—Dihydrocampholenamide (Semmler, Abstr., 1906, i, 681), obtained by the action of sodamide on camphenilone, yields on treatment with bromine and sodium methoxide (Jeffreys, Abstr., 1899, i, 730) the urethane, $C_8H_{15}\cdot NH\cdot CO_2Me$, b. p. 148°/17 mm., m. p. 26°. The amine, $C_8H_{15}\cdot NH_2$, obtained by heating the urethane at 120° with alcoholic potassium hydroxide, is a colourless liquid with a characteristic odour, b. p. 149°, and absorbs carbon dioxide from the air; when the hydrochloride is heated with potassium cyanate, it forms a crystalline carbamide, m. p. 163°, or when treated with sodium nitrite it is converted into the alcohol, $C_8H_{15}\cdot OH$, b. p. 81—82°/17 mm., and this on oxidation yields a ketone, b. p. 78—79°/17 mm, D_4^{20} 0.921, the semicarbazone, m. p. 198°, and dibenzylidene derivative, m. p. 143°, of

which are identical with the corresponding derivatives of *isopropylcyclopentane-3-one*, $\text{CHPr}^\beta \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix}$ (Blanc, private communication).

It follows, therefore, that the alcohol, amine, and amide described above are *isopropylcyclopentane-3-ol*, *3-amino-1-isopropylcyclopentane*, and *isopropylcyclopentane-3-carboxylamide* respectively. The formation of *isopropylcyclopentane-3-carboxylamide*, $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHPr}^\beta \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, from camphenilone is readily explained if camphenilone has the constitution assigned to it by Wagner and Majewski (Abstr., 1900, i, 629).
M. A. W.

Colorimetric Method of Determining the Molecular Size of Carbohydrates (Qualitative Demonstration of Aldehydes, Alcohols, and Carbohydrates). LEONHARD WACKER (*Ber.*, 1908, 41, 266—275).—The foundation of the method rests on the fact that phenylhydrazine-*p*-sulphonic acid in sodium hydroxide and in the presence of alcohols, acids, &c., develops a red colour in the air. It is found that (1) the intensity of the colour in equimolecular solutions is constant, and (2) that the velocity of the reaction is inversely proportional to the size of the molecule. The velocity is very different for differing classes of compounds; thus *N*/30,000 solution of formaldehyde or acetaldehyde develops the colour immediately, whilst *N*/2000 solutions of polyhydric alcohols and carbohydrates require fifteen minutes, primary alcohols require a strength of *N*/200, and concentrated solutions are required in the cases of acetone, lactic acid, citric acid, and proteins. The reaction in the cases of polyhydric alcohols and carbohydrates has been studied quantitatively, and from these determinations with compounds of known molecular weight it has been sought to determine the molecular weights of carbohydrates or pentosans. By comparing maltose with starch, amyloextrin, and erythroextrin, it is, for instance, inferred that the molecular weights of starch and amyloextrin are identical ($\text{?C}_{36}\text{H}_{60}\text{O}_{30}$) and are three times that of maltose; that of erythroextrin ($\text{?C}_{24}\text{H}_{40}\text{O}_{20}$) is twice that of maltose. Experiments carried out before and after inversion lead practically to the same conclusion.
W. R.

Rate of Oxidation of Sugars in an Acid Medium. H. H. BUNZEL (*Amer. J. Physiol.*, 1908, 21, 23—36).—Sugars may be oxidised in an acid medium (*N*/2 acetic acid); the relative initial velocities of the oxidation are as follows for the sugars used: lactose (the slowest), 1·0; maltose, 1·15; dextrose, 5·71; galactose, 8·72; mannose, 8·72; lævulose, 55·13. These figures are believed to represent the relative amount of dissociation that occurs. Hydrogen ions retard the oxidation, because they decrease the total number of free oxygen ions in solution, and diminish the dissociation of the sugar molecule.

W. D. H.

C₅ Sugars from Meta- and Para-saccharin. HEINRICH KILIANI (*Ber.*, 1908, 41, 120—124. Compare Abstr., 1907, i, 1011).—The oximes of the C₅ sugars, obtained on reduction of meta- and para-

saccharinic acid, were formerly shown to have identical properties. Crystallographic investigation proves them to be the same; a mixture of the two has m. p. 136° , and they both yield the same *tetrabenzoate*, m. p. 140° , crystallising in bunches of minute needles. The C_5 sugars from which the oximes were derived are also now shown to be the same; parasaccharopentose does not exist. They are crystallographically identical, whilst the difference in melting point formerly recorded is due to the deliquescence in moist air. The sugar from parasaccharinic acid is not a ketose, as, on oxidation with bromine, a butanetriolcarboxylic acid is formed, which yields the phenylhydrazide, m. p. 134° . It would appear that the β -ketose from parasaccharinic acid is extremely unstable, and is transformed into the aldose at the moment of its formation under the influence of the alkaline oxidising mixture.

E. F. A.

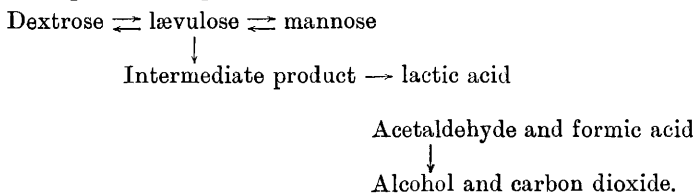
Transformation of *l*-Gulose and of *l*-Idose into *l*-Sorbose.

WILLIAM ALBERDA VAN EKENSTEIN and JAN. J. BLANKSMA (*Rec. trav. chim.*, 1908, 27, 1—4).—It has been shown that *d*-glucose and *d*-mannose are transformed by alkalis into *l*ævulose (Lobry de Bruyn and Alberda van Ekenstein, *Abstr.*, 1896, i, 116), that *d*-galactose and *d*-talose similarly are converted into *d*-tagatose (*Abstr.*, 1898, i, 225), and that the latter sugar by migration of a hydroxyl group gives *l*-sorbose (*Abstr.*, 1900, i, 332). Since *l*-sorbose is a ketose, yielding the same osazone as that obtained from *l*-gulose and *l*-idose, it is deduced theoretically that *l*-sorbose should be formed from *l*-gulose and *l*-idose by the action of alkali. The authors find this to be the case. According to Fischer's directions (*Abstr.*, 1890, 1398), the mixture of *l*-gulonic and *l*-idonic acids is prepared from xylose, from this the former acid is separated as its lactone, and the latter by conversion into the dibenzylidene derivative. From the two acids, the corresponding sugars are obtained by reduction with sodium amalgam. When either of the sugar syrups so obtained is warmed with baryta, it is partly converted into *l*-sorbose, which can be isolated in a crystalline condition, having m. p. 165° and $\alpha_D + 42.9^{\circ}$ (in 1% aqueous solution). The authors find that *d*-sorbose, prepared from the juice of mountain ash berries by Freund's *Bacterium xylinum*, has m. p. 165° and $\alpha_D - 42.9^{\circ}$ (in 1% aqueous solution).

E. H.

The Phenomena of Fermentation from the Catalytic Point of View. H. SCHADE (*Biochem. Zeitsch.*, 1908, 7, 299—326. Compare *Abstr.*, 1906, i, 932).—Attention is drawn to the fact that many processes of fermentation, induced by enzymes, can be artificially accomplished by the aid of common hydrolysing materials. Examples mentioned are starch \rightarrow dextrose, sucrose \rightarrow dextrose and *l*ævulose, lactose \rightarrow dextrose and galactose, glycogen \rightarrow dextrose, dextrose \rightarrow fatty acids, *l*ævulose \rightleftharpoons dextrose, mannose \rightleftharpoons dextrose, and dextrose \rightarrow lactic acid. It is now shown that the conversion of lactic acid into alcohol and carbon dioxide can be accomplished by means of simple inorganic catalysts. Mineral acids convert lactic acid into a mixture of acetaldehyde and formic acid, and this mixture yields alcohol and carbon dioxide when passed over finely-divided rhodium (rhodium-

black). Attention is drawn to the transformation of monoses under the influence of alkalis, and also to the probable formation of an intermediate product in the conversion of dextrose into lactic acid. The following scheme is given for the catalytic decomposition of monoses:



It is suggested that whichever of the three monoses is used, it is the labile laevulose which undergoes decomposition.

The suggestion is also put forward that the various fermentations which sugar can undergo, for example, alcoholic, lactic, formic, &c., are essentially of the same type. The process in each case consists of several distinct reactions, and the function of any specific ferment is merely to accelerate one of these, so that the chief products obtained are the products formed by the accelerated reaction, whereas the products formed in the other reactions are obtained in small amounts only.

J. J. S.

Some Mineral Salts which play the Part of Peroxydases.
 JULES WOLFF (*Compt. rend.*, 1908, 146, 142—144).—Tincture of guaiacum which has become partially peroxidised with age, or the fresh tincture after treatment with a trace of hydrogen peroxide, but not before, gives a very intense blue coloration when added to a 0.01% ferrous sulphate solution. The reaction is observed with a solution containing only one part of ferrous sulphate per million, a quantity which cannot be detected by potassium ferricyanide. The dilute ferrous sulphate solution loses its activity when boiled with a trace of hydrogen peroxide, being oxidised to ferric sulphate, which does not act on guaiacum after boiling. The reaction is very similar to those produced by different vegetable extracts, such as those of malt, barley, and wheat, containing a peroxydase, and, like them, is inhibited by very small quantities of mineral acids.

Small quantities of ferrous, ferric, and cupric sulphates in the presence of traces of hydrogen peroxide are capable of oxidising certain colouring matters and of liquefying starch. Thus dilute solutions of methyl-orange, methylene-blue, and magenta are decolorised by ferrous sulphate at the ordinary temperature, of ferric sulphate at 50°, and of cupric sulphate on boiling, in solutions containing 0.1—0.2 gram of anhydrous salt per litre and small quantities of hydrogen peroxide, whilst 50 c.c. of a 5% solution of starch are liquefied in 25 minutes at 70° by addition of 0.002 gram of ferrous sulphate and a quantity of hydrogen peroxide containing 0.0028 gram of active oxygen. In the latter reaction, cupric sulphate is twice as active as the ferrous salt.

These phenomena, which occur without the evolution of oxygen, cannot be of a catalytic nature, since hydrogen peroxide has not the

same power of decolorising dyes and liquefying starch when in conjunction with platinum-black.

As in the saccharification by amylase (Fernbach) and the diastatic liquefaction of starch, the solutions of iron salts have the highest liquefying power when their reaction is approximately neutral to methyl-orange. E. H.

Colloidal Properties of Starch and the Existence of a Perfect Solution of this Substance. EUGÈNE FOUARD (*Compt. rend.* 1908, 146, 285—287. Compare Abstr., 1907, i, 391, 677).—A 5% pseudo-solution of demineralised and partially hydrated starch, prepared at 80°, is filtered through a collodion membrane. The filtrate contains 2.74% of starch, and from its properties seems to be a true solution as distinguished from the colloidal solutions of the so-called "soluble starch." Thus the solution does not polarise light, is not acted on by an electric current, and has a viscosity only slightly greater than an equivalent solution of sucrose (an ordinary starch "solution" has a viscosity ten times as great). When treated with iodine, the solution gives an intense blue coloration, but no precipitate. The extreme dissemination of the starch molecules in this "true solution" is shown by its complete hydrolysis in five minutes when heated with 10% of hydrogen chloride on a boiling water-bath, an ordinary starch "solution" of the same strength being incompletely saccharified by six hours' similar treatment.

When kept, the "true solution" becomes very slightly opalescent, and this opalescence settles slowly, forming a slight pulverulent deposit consisting of very refringent spherical or ovoid granules, 2—3 μ in diameter, similar to the natural starch grains. The same granular transformation can be effected either by freezing or by evaporation in a vacuum.

The opalescence disappears on boiling. If a new "true solution" of starch containing 2.346% and having $[\alpha]_D^{186.6}$ is treated with one-quarter of its volume of water and boiled for fifteen minutes at a constant volume, it remains equally limpid, undergoes no saccharification, but $[\alpha]_D$ increases to 193°36'.

The conclusion is drawn that dissolved starch molecules occur in the ordinary colloidal solution, accompanied by starch in all degrees of molecular condensation. E. H.

The Chemistry of the Bleaching of Sulphite-Cellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1908, 21, 302—303).—In order to test Cross and Bevan's theory (*J. Soc. Chem. Ind.*, 1890, 450) that during the process of bleaching some cellulose is chlorinated, the author has made a number of chlorine determinations both in the bleaching agents and in the fibre, and finds that practically no chlorination takes place. P. H.

Action of *n*-Propyl Chloride on Ethylamine. EZIO COMANDUCCI and M. ARENA (*Chem. Zentr.*, 1907, ii, 1396; from *Giorn. Farm. Chim.*, 1907, 56, 385—388).—The product obtained by the action of *n* propyl chloride on ethylamine in molecular proportions in aqueous solution in

a sealed tube at 125—140° contains three parts of ethyl-*n*-propylamine and one part of ethyl-di-*n*-propylamine.

Ethyl-n-propylamine, NHEtPr , is a colourless, refracting liquid, b. p. 79·8°/747 mm., $D^{24} 0\cdot773$; the *hydrochloride*, m. p. 217—218°; the *aurichloride*, m. p. 86—87°; the *platinichloride*, orange-yellow needles, m. p. 198—199°. The *nitroso-derivative* is obtained as a greenish-yellow oil, b. p. 195°.

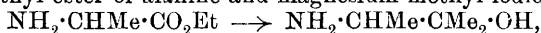
Ethyl-di-n-propylamine, NEtPr_2 , is a colourless liquid, b. p. 137·2°/749·9 mm., $D^{24} 0\cdot807$; the *hydrochloride*, m. p. 113—115°; the *aurichloride*, m. p. 93—94°; the yellow, crystalline *platinichloride*, m. p. 175°. G. Y.

White Precipitate. ERNST SCHMIDT [with L. KRAUSS] (*Chem. Zentr.*, 1907, ii, 1593; from *Zeitsch. Österr. Apoth.-Ver.*, 1907, 45, 541—543).—The constitution of fusible and infusible white precipitates, the composition of which appears to vary within certain limits with the method of preparation, has been the object of numerous investigations. A resume of the views of various authors and an account of a study of the action of methyl iodide are given.

When heated with methyl iodide, with or without addition of methyl alcohol, in a sealed tube at 100°, infusible white precipitate forms tetramethylammonium mercuric iodide, $\text{NMe}_4\text{I}, \text{HgI}_2$ (Risse, *Annalen*, 1858, 107, 223), which, after precipitation of the mercury by means of hydrogen sulphide, yields the *aurichloride*, $\text{NMe}_4\text{AuCl}_4$, crystallising in long, yellow needles. At the ordinary temperature, the action of methyl iodide on infusible white precipitate leads to the formation of the iodide, $2\text{NMe}_4\text{I}, 3\text{HgI}_2$ (Risse, *loc. cit.*), m. p. 187°, which is formed also by heating the preceding iodide with mercuric iodide. A third, yellow, crystalline *iodide*, m. p. 110°, obtained from the mother liquors, gives a red coloration with lime, becoming yellow on exposure to air, and yields mercuric iodide when treated with water.

Under the same conditions, fusible white precipitate yields tetramethylammonium mercuric iodide, $\text{NMe}_4\text{I}, \text{HgI}_2$, only. G. Y.

The Order of the Addition of Ammonia to Organic α -*a*-Oxides. K. KRASSUSKY (*Compt. rend.*, 1908, 146, 236—239. Compare Wurtz, *Ann. Chim. Phys.*, 1857, [iii], 49, 381; Knorr, *Abstr.*, 1897, i, 313; 1899, i, 461).— β -Methyl- Δ^{β} -butylene oxide does not combine with anhydrous ammonia, but when heated in sealed tubes at 100° with a 33% solution of ammonia it yields *dimethyl α -aminoethylcarbinol*, $\text{NH}_2\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{OH}$, b. p. 157—158°/743 mm., m. p. 26°, $D^{15} 0\cdot9291$ or $D^{20} 0\cdot9251$, which forms hygroscopic, crystalline salts, and a *platinichloride* in large, orange-red prisms. The constitution of this amino-alcohol has been determined by its synthesis from the ethyl ester of alanine and magnesium methyl iodide,



and the same compound is also obtained by the action of ammonia on β -methyl- Δ^{β} -butylene chlorohydrin, but in this reaction β -methyl- Δ^{β} -butylene oxide is formed as an intermediate compound.

*iso*Butylene oxide combines with aqueous ammonia to form *amino-trimethylcarbinol*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$, b. p. 150·5—151·5°/762 mm.,

D⁰ 0.9500 or D¹⁴ 0.9389; the *platinichloride* forms red, prismatic needles; this alcohol is identical with the synthetic compound obtained by the action of magnesium methyl iodide on the ethyl ester of glycine. It follows, therefore, that *as*- α -oxides combine with ammonia to form amino-alcohols in which the hydroxyl is attached to the carbon atom, which in the original compound was associated with the least number of hydrogen atoms.

In addition to the amino-alcohols just described, β -methyl- Δ^2 -butylene and *isobutylene* oxides yield with ammonia the secondary hydroxyamines, $(C_5H_{11}O)_2NH$ and $(C_4H_9O)_2NH$, respectively.

M. A. W.

New Compounds of Amino-acids and Ammonia. II. PETER BERGELL and JOHANNES FEIGL (*Zeitsch. physiol. Chem.*, 1908, 54, 258—287).—Diglycinimide (Abstr., 1907, i, 394) has been further investigated; it is extremely stable towards mineral acids even at 120°, but is decomposed very readily by cold alkalis, although definite products could not be isolated. It has been found possible to obtain acyl derivatives of the imide by the reaction of certain acyl chlorides in the presence of magnesium oxide or sodium hydrogen carbonate, and the products of hydrolysis of these acyl derivatives confirm the constitution of the imide arrived at previously, for example, benzoyldiglycinimide yields hippuric acid, glycine, and ammonia.

Chloroacetyldiglycinimide reacts with ammonia, yielding a compound, $C_6H_9O_3N_3$, m. p. 228°, which in all probability has the cyclic constitution $NH \begin{smallmatrix} \diagup CO \cdot CH_2 \cdot NH \cdot CH_2 \\ \diagdown CO \cdot CH_2 \cdot NH \cdot CO \end{smallmatrix}$ (compare Zelinsky, Abstr., 1907, i, 780).

Homologues of diglycinimide have been prepared, for example, alaninyglycinimide, by the action of ammonia on the product obtained by the condensation of chloroacetic acid and α -chloropropionitrile.

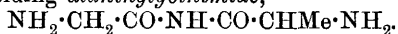
Diglycinimide platinichloride, $(C_4H_9O_2N_3)_2PtCl_6$, crystallises from water in well-developed, prismatic plates. Double salts with cadmium chloride and mercuric chloride have been obtained, and also a crystalline phosphomolybdate and an amorphous phosphotungstate. The *picrate*, $C_4H_9O_2N_3 \cdot C_6H_4O_7N_3$, crystallises from dilute alcohol in long, plastic needles, m. p. 231°. The *picrolonate*, $C_4H_9O_2N_3 \cdot C_{10}H_8O_5N_4$, crystallises in pointed plates, which decompose at 212°. *Benzoyldiglycinimide*, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot NH \cdot COPh$, crystallises from alcohol in microcrystalline aggregates, m. p. 231°, and is not basic in nature.

Carbethoxydiglycinimide, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot NH \cdot CO_2Et$, obtained by the action of ethyl chlorocarbonate on diglycinimide hydrochloride in the presence of sodium hydrogen carbonate, crystallises from alcohol in colourless plates, m. p. 172°, and is decomposed when boiled with water. *Chloroacetyldiglycinimide*,

$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl$, crystallises from alcohol in colourless prisms, m. p. 174°.

Full details for the preparation of chloropropionitrile by the action of phosphorus pentachloride on lactonitrile are given. The nitrile condenses with dry chloroacetic acid at 103° in a shaking-oven, yielding

methyldichlorodiacetimide, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CHMeCl}$, which crystallises from a mixture of benzene and light petroleum in felted needles, m. p. 108° . The chloro-derivative reacts with ammonia at low temperatures, yielding *alanineglycinimide*,



The *hydrochloride* is precipitated by the addition of alcohol to its aqueous solution in the form of slender needles, m. p. 236° .

J. J. S.

Ethyl Dioximosuccinate. Action of Nitric Acid on Ethyl Dioximosuccinate. ANDRÉ WAHL (*Bull. Soc. chim.*, 1908, [iv], 3, 22—27, 27—31).—Most of the facts recorded in these two papers have been published already (Abstr., 1906, i, 624; 1907, i, 493). Ethyl dioxysuccinate, b. p. $120\text{—}125^\circ/13\text{ mm.}$, in contact with water forms a *hydrate*, m. p. 133° , which separates from ether in small prisms. In preparing ethyl dioximosuccinate from ethyl dioxysuccinate there is formed, in addition to the by-products already recorded, some ethyl tartronate.

Ethyl glyoxime-peroxide-dicarboxylate, $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_6$, produced by the action of nitric acid on ethyl dioximosuccinate (Beckh, Abstr., 1897, i, 213) on treatment with ammonia, yields an amide, m. p. 250° , concerning the properties of which many discrepant statements have been made (Pröpper, Abstr., 1883, 573; Cramer, Abstr., 1892, i, 699; Beckh, *ibid.*, 1897, i, 213; Bouveault and Bongert, *Bull. Soc. chim.*, 1902, 27, 1170; Ulpiani and Bernardini, Abstr., 1904, i, 971; 1905, i, 750; Wieland, *ibid.*, 1907, i, 527). Determination of its molecular weight by ebullioscopic methods indicates that it has the empirical formula $(\text{CONH})_3$, and may, therefore, be the amide of the acid, $\begin{array}{c} \text{C}(\text{CO}_2\text{H})\cdot\text{N}\cdot\text{O} \\ | \\ \text{CH}=\text{N}\cdot\text{O} \end{array}$, described by Jovitschitsch (Abstr., 1906, i, 733).

T. A. H.

Platinum-Blue. KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1908, 41, 312—314. Compare Abstr., 1907, i, 489).—The blue solution obtained by the action of silver nitrate on platinous chloride bisacetoneitrile contains *platinous acetamide*, and the crystalline compound, $\text{Pt}(\text{NHAc})_2\cdot\text{H}_2\text{O}$, may be isolated by shaking a mixture of equal weights of silver sulphate and platinous chloride bisacetoneitrile with five times its weight of water, adding methyl alcohol, filtering, and precipitating the filtrate with ether. The same compound can be prepared directly from acetamide and potassium platinochloride by the addition of silver nitrate. Other salts which yield acids in the presence of platinous chloride can be used in place of silver nitrate, and it is not necessary actually to isolate the acetoneitrile platinochloride. The compound can be prepared from a mixture of the nitrile and potassium platinochloride by the action of a solution of sodium acetate.

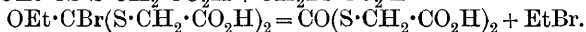
J. J. S.

Dimethylol Compounds of Carbamide. ALFRED EINHORN and ALEXANDER HAMBURGER (*Ber.*, 1908, 41, 24—28).—The fact that the *N*-methylol compounds, prepared by Einhorn (Abstr., 1906, i, 245) from acid amides, are all extremely well-characterised, crystalline

substances, suggested that Goldschmidt's dimethylolcarbamide (Abstr., 1898, i, 178) required re-investigation. Repetition of his work has shown that the white, amorphous precipitate, obtained by the action of carbamide on formaldehyde in the presence of potassium hydroxide, and assumed to be dimethylolcarbamide, varies in composition with the concentration of the alkali. *Dimethylolcarbamide*, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{OH})_2$, can, however, be obtained if barium hydroxide is employed, and the reaction stopped when Tollens' silver solution is no longer instantly reduced by saturating the solution with carbon dioxide. It crystallises in small, well-defined prisms, sinters at 121° , m. p. 126° , becomes solid again at $137\text{--}138^\circ$, and then decomp. at 260° . When heated, it evolves formaldehyde, and forms basic decomposition products; it gradually reduces Tollens' silver solution. Amorphous condensation products of varying composition are formed when a solution in water is treated with 1% potassium carbonate, but one of the constituents may result from the removal of the elements of water from two molecules of dimethylolcarbamide.

Monomethylolcarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, prepared when only half the quantity of formaldehyde is employed, has not yet been obtained quite pure, and crystallises in rosettes of prisms, m. p. 116° . Dilute mineral acids instantly, and alkalis slowly, cause separation of amorphous precipitates of variable composition. W. R.

Constitution of Thioamides. EINAR BIILMANN (*Chem. Zentr.*, 1907, ii, 1778—1780; from *Oversigt Danske Vidensk. Selskabs Forhandl.*, 1907, 83—104. Compare Abstr., 1905, i, 625).—Tautomerism has been ascribed to the thioamides chiefly because of the formation of iminothiol ethers, $\cdot\text{C}(\text{SR})\text{:NH}$, and thiolurethanes, $\text{NH}_2\cdot\text{CO}\cdot\text{SR}$, by the action of alkyl iodides on thioamides, $\cdot\text{CS}\cdot\text{NH}_2$, and thionurethanes, $\text{NH}_2\cdot\text{CS}\cdot\text{OR}'$, which are considered to react in the tautomeric forms, $\cdot\text{C}(\text{SH})\text{:NH}$ and $\text{NH}\cdot\text{C}(\text{SH})\cdot\text{OR}'$, respectively. This explanation, however, assumes the direct interaction of the free thiol group, SH, and the alkyl iodide, whereas no case is known of the direct alkylation of an undoubted thiol group. On the other hand, it is now shown that alkylation of a thiocarbonyl group may take place in the absence of a mobile hydrogen atom. Xanthylacetic acid and bromoacetic acid interact at 120° , yielding ethyl bromide and dithiolcarbonateacetic acid. This reaction must take place in the two stages: $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{CH}_3\text{Br}\cdot\text{CO}_2\text{H} =$



In the same manner, β -xanthylpropionic acid and β -iodopropionic acid form β -dithiolcarbonatepropionic acid, $\text{CO}(\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, and ethyl iodide. The yields are not quantitative, partly, at least, because the ethyl haloid, formed during the reaction, reacts with the xanthate; thus the action of ethyl iodide on xanthylacetic acid leads to the formation of ethyldithiolcarbonateacetic acid, $\text{SEt}\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Similar reactions take place with xanthylacetic acid and diphenylmethyl bromide, forming diphenylmethyldithiolcarbonateacetic acid, and with diphenylmethyl bromide and potassium xanthate, forming ethyl diphenylmethylxanthate and, by action of a further mol. of the bromide, diphenylmethyl dithiolcarbonate.

It is argued that, in analogy with these reactions, the action of alkyl haloids on thioamides and thionurethanes must take place in two stages, the first being an addition of the alkyl haloid to the thiocarbonyl group (compare Wheeler and Barnes, *Abstr.*, 1900, i, 564).

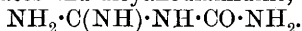
Dithiolcarbonateacetic acid, $C_5H_6O_5S_2$, forms white crystals, m. p. 156.6° (corr.); the *ethyl ester*, $C_9H_{14}O_5S_2$, white needles, m. p. 49.2° . *β -Dithiolcarbonatepropionic acid*, $C_7H_{10}O_5S_2$, white needles, m. p. $115-116^\circ$, when heated with alcoholic sodium hydroxide, yields thiohydracrylic acid and sodium carbonate.

Diphenylmethyl dithiolcarbonateacetic acid, $CHPh_2 \cdot S \cdot CO \cdot S \cdot CH_2 \cdot CO_2H$, forms crystals, m. p. 130.6° , and on treatment with alcoholic sodium hydroxide, yields thiobenzhydrol, sodium thioglycollate, and sodium carbonate.

Diphenylmethyl dithiolcarbonate, $CO(S \cdot CHPh_2)_2$, crystallises in white needles, m. p. 135.8° , forms an intensely blue substance (thiobenzophenone?) when heated, and yields thiobenzhydrol and sodium carbonate on treatment with alcoholic sodium hydroxide. Oxidation of the alkaline solution with iodine leads to the formation of *diphenylmethyl disulphide*, $S_2(CHPh_2)_2$, m. p. 152° . G. Y.

Influence of Addition of Chloride on the Reaction between Barium Carbonate, Carbon, and Nitrogen. OTTO KÜHLING and O. BERKHOLD (*Ber.*, 1908, 41, 28—32. Compare *Abstr.*, 1907, ii, 166).—Pure barium carbonate (1 mol.) and sugar charcoal were well mixed with 2, 5, 10, 15, 20, and 30% of barium chloride and placed in unglazed porcelain boats heated in porcelain tubes in an electric furnace at $920-1180^\circ$. Nitrogen, free from carbon dioxide, moisture, and oxygen, was passed over the heated mixture for one hour, and the product analysed. As a result, it was ascertained that (1) more than 2% barium chloride lowers the temperature at which the nitrogen begins to be absorbed; (2) there is no quantitative relationship between temperature of combination and quantity of chloride; (3) the yield of cyanide falls as the barium chloride is increased, with small quantities the yield is either the same or very little smaller, and (4) the yield of cyanamide is, however, smaller throughout. W. R.

Action of Sulphuric Acid on Calcium Cyanamide. TEMISTOCLE JONA (*Gazzetta*, 1907, 37, ii, 558—562).—The action of sulphuric acid on calcium cyanamide (compare E. Pollacci and G. Pollacci, *Staz. sper. agrar. ital.*, 1907, 40, 580—592) yields calcium and ammonium sulphates and dicyanodiamidine,



T. H. P.

Reactivity of Mercuric Cyanide. KARL A. HOFMANN and H. WAGNER (*Ber.*, 1908, 41, 317—321).—Although an aqueous solution of mercuric cyanide is practically a non-electrolyte, it reacts with aqueous solutions of silver acetate or nitrite, yielding precipitates of silver cyanide. The precipitation is not complete, as the reaction is reversible, and the amount precipitated depends largely on the concentration of the solutions. Silver nitrate does not yield a pre-

precipitate in dilute solutions, and with concentrated solutions the sparingly soluble compound, $\text{HgC}_2\text{N}_2 \cdot \text{AgNO}_3 \cdot 2\text{H}_2\text{O}$, is deposited. Silver sulphate produces a precipitate, but not to the same extent as the nitrite and acetate.

The double cyanide-acetate, $\text{HgC}_2\text{N}_2 \cdot \text{Hg}(\text{OAc})_2$, may be prepared from the two components; it crystallises in long, pointed, doubly-refracting prisms, and its clear aqueous solution gives a cloudiness with a large excess of silver acetate.

Mercuric cyanide is much more soluble in potassium hydroxide solution than in water, and the solution obtained reacts as an oxidising agent towards alcohol, glycerol, dextrose, quinol, and gallic acid. It reacts with benzaldehyde and benzoin, yielding precipitates of mercury, and with picric acid yields potassium isopurpurate. Crystals having the composition $\text{HgC}_2\text{N}_2 \cdot \text{KOH} \cdot \text{H}_2\text{O}$ have been isolated from the solution. They dissolve readily in water, yielding a strongly alkaline solution, and the addition of silver nitrate produces a precipitate of silver cyanide.

A compound, $\text{HgC}_2\text{N}_2 \cdot \text{KOH}$, has also been isolated; it crystallises in colourless, rhombic plates. Finely-divided mercuric cyanide reacts with a saturated solution of potassium hydroxide, yielding yellow mercuric oxide, but, when diluted with water, a clear solution is obtained.

J. J. S.

Action of Hydrazine on Diazoacetamide and on Ethyl Diazoacetate. THEODOR CURTIUS, AUGUST DARAPSKY, and AUGUST BOCKMÜHL (*Ber.*, 1908, 41, 344—356).—Diazoacetamide reacts readily with hydrazine hydrate, yielding ammonia and *azoimideacetylhydrazide*, $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, which may be isolated in the form of its *benzylidene* derivative, $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CHPh}$. The same compound can be obtained by the action of excess of free hydrazine on ethyl diazoacetate, and its constitution follows from its synthetical formation from ethyl azoimideacetate, which can be prepared from silver azoimide and ethyl iodoacetate. When warmed with moderately concentrated sulphuric acid, the condensation product yields nitrogen and hydrazine sulphate. The reaction between ethyl diazoacetate and hydrazine is represented by the following equations: $\text{NH}_2 \cdot \text{NH}_2 + \text{N}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Et} \rightarrow \text{NH}_2 \cdot \text{NH} \cdot \text{N} : \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \rightarrow \text{NH}_3 + \text{N}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ and $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{NH}_2 \cdot \text{NH}_2 \rightarrow \text{N}_3 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2 + \text{EtOH}$.

Diazoacetamide (27% yield) (Abstr., 1884, 988) is obtained by shaking methyl diazoacetate with 10% ammonium hydroxide until a clear solution is obtained, and keeping this at the ordinary temperature for three months.

Benzylideneazoimideacetylhydrazide crystallises from alcohol in long, felted needles, m. p. 149° (decomp.). In the preparation of this compound, a small amount of benzaldazine is obtained, but may be removed by washing the benzylidene derivative with ether.

Ethyl azoimideacetate is most readily freed from excess of ethyl iodoacetate by means of diethylamine; it is a colourless oil, b. p. 75°/21 mm.

Azoimideacetylhydrazide hydrochloride may be obtained by hydro-

lysing the benzylidene compound with cold concentrated hydrochloric acid, and forms an extremely deliquescent, crystalline mass. *Azoimide-acetylazoimide*, $N_3 \cdot CH_2 \cdot CO \cdot N_3$, is a colourless oil with a penetrating odour, is insoluble in water, and is hydrolysed by potassium hydroxide solution to potassium azoimideacetate and potassium azoimide.

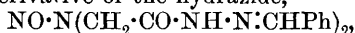
The *sodium*, *barium*, and *silver* salts of azoimideacetic acid have been prepared. The free acid forms a colourless oil with a penetrating odour, and dissolves in water, yielding a strongly acidic solution.

Sulphuric acid hydrolyses ethyl azoimideacetate, forming nitrogen, ammonia, and formaldehyde; potassium hydroxide yields nitrogen, ammonia, and oxalic acid.

J. J. S.

Methyl Ester and Hydrazone of Nitrosoiminoacetic Acid.

THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1908, 41, 356—358).—Commercial glycine methyl ester contains *methyl iminoacetate*, $NH(CH_2 \cdot CO_2Me)_2$, and this with nitrous acid yields the *nitroso-derivative*, $NO \cdot N(CH_2 \cdot CO_2Me)_2$, which is therefore contained in commercial ethyl diazoacetate prepared from glycine methyl ester. The nitroso-derivative is a thick, yellow oil, b. p. $162^\circ/17$ mm., and reacts with hydrazine hydrate, yielding the corresponding *hydrazone*, $NO \cdot N(CH_2 \cdot CO \cdot NH \cdot NH_2)_2$, which crystallises from warm water in large, glistening plates, m. p. 175° (decomp.). It gives Liebermann's reaction, and, when boiled with dilute sulphuric acids, yields azoimide. The *dibenzylidene* derivative of the hydrazone,



has m. p. 215° (decomp.), and is practically insoluble in the ordinary solvents. The *azoimide*, $NO \cdot N(CH_2 \cdot CO \cdot N_3)_2$, is a yellow oil with a penetrating odour.

J. J. S.

Action of Alkaline Mercuric Cyanide on Halogen Derivatives of Ethylene and Acetylene. KARL A. HOFMANN and H. KIRMREUTHER (*Ber.*, 1908, 41, 314—317).—Mercury acetylide is formed when pure acetylene is passed into an aqueous solution of mercuric cyanide to which a small amount of potassium hydroxide has been added. In the absence of the alkali, a precipitate is not formed. A solution of 50 grams of the cyanide and 23 grams of potassium hydroxide in 200 grams of water is an energetic reagent for the removal of hydrogen halides, and in certain cases for replacing hydrogen by mercury.

Mercuric tribromoethylene, $Hg(CBr \cdot CBr)_2$, is obtained when acetylene tetrabromide is shaken with the above solution for some ten hours. Crystals of $HgC_2N_2 \cdot KBr \cdot H_2O$ are deposited, and a certain amount of dibromoacetylidene is also formed. The tribromo-derivative crystallises from ether in colourless, doubly-refractive prisms, m. p. 141° . When shaken with yellow ammonium sulphide, it yields tribromoethylene, but is not decomposed when boiled with water or 10% hydrochloric acid.

Mercuric trichloroethylene, $Hg(CCl \cdot CCl)_2$, is most readily obtained by shaking trichloroethylene with the cyanide solution, and has m. p. 83° .

Mercuric chloroacetylene, $Hg(C \cdot CCl)_2$, is formed when the gas obtained by heating trichloroethylene with alcoholic potassium hydr-

oxide is washed with water and concentrated sulphuric acid, and then led into the cyanide solution. It is deposited as a white precipitate, and crystallises from ether in glistening plates, m. p. 185°. It decomposes at 195°, but is not attacked by concentrated hydrochloric acid. J. J. S.

Influences Governing Orientation in the Benzene Nucleus. JULIUS OBERMILLER (*J. pr. Chem.*, 1908, [ii], 77, 65—84. Compare Abstr., 1907, i, 200).—A reply to the criticisms of Flürscheim (Abstr., 1907, i, 834). G. Y.

Chemical Dynamics of the Bromination of Toluene. LUDWIK BRUNER and MILE. J. DLUSKA (*Bull. Acad. Sci. Cracow*, 1907, 691—730. Compare Bruner, 1902, ii, 447).—A study of the action of small amounts of bromine on toluene alone and in presence of a solvent.

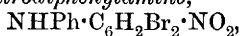
It is found that in absence of a solvent and with the concentration of the bromine not greater than 1 mol. per 30 mols. of toluene, the bromination of toluene is a unimolecular reaction, the substitution in the nucleus and that in the side-chain being independent reactions. At temperatures between 0° and 74°, the distribution of the bromine between the two side reactions does not vary with the concentration. For the temperature interval, 25—35°, the nucleus substitution has a temperature-coefficient, 1.3—1.5; the side-chain substitution, a coefficient usually greater than 4.0. The nucleus substitution is accelerated by iodine bromide in proportion to the square of the concentration of this halogen carrier; the lower the temperature at which the bromination takes place, the wider the concentration limits within which this rule holds good, whilst it ceases to apply to reactions above about 35°. The temperature-coefficient, 1.0—1.2, of the catalysis is notably small.

The distribution of the bromine between the nucleus and the side-chain and the unimolecular nature of the reaction are maintained in carbon tetrachloride solution, but the velocity of the reaction is diminished very nearly in proportion to the diminution of the toluene concentration. In nitrobenzene solution, on the other hand, the reaction is hindered probably by the hydrogen bromide formed, and the yield of benzyl bromide is markedly diminished; hence the nitrobenzene favours the nucleus substitution as does the halogen carrier. The velocity of the bromination of the side-chain under the influence of light also varies with the solvent, being accelerated by associating mediums, but diminished by solvents, such as nitrobenzene, amyl acetate, and acetic acid, which favour dissociation of the halogen. The retardation of the reaction in nitrobenzene cannot be caused by protection of the reacting substances from the light by the solvent, since toluene decolorises bromine instantaneously on exposure to sunlight even when the reaction mixture is jacketed with nitrobenzene.

It is argued that the course of the bromination depends on the extent to which the bromine is electrolytically dissociated, the side-chain substitution being a reaction of bromine molecules, and the nucleus substitution one of bromine or iodine bromide ions. G. Y.

Nitration of *s*-m-Dichloro- and *s*-m-Dibromo-nitrobenzene.

JAN J. BLANKSMA (*Rec. trav. chim.*, 1908, 27, 42—48. Compare Abstr., 1906, i, 11).—Unlike *s*-nitro-*m*-xylene, *s*-dibromonitrobenzene is only slowly nitrated by nitric acid, D 1.52, but, when heated on a water-bath with a mixture of the latter and sulphuric acid, it forms 1:3-dibromo-4:5-dinitrobenzene, $C_6H_2Br_2(NO_2)_2$, as colourless crystals, m. p. 86°, of which the constitution is fixed by the formation of 4:6-dibromo-2-nitroaniline when heated with alcoholic ammonia in a sealed tube. 1:3-Dibromo-4:5-dinitrobenzene gives 4:6-dibromo-2-nitrophenol when heated with alkali hydroxide solution, 4:6-dibromo-2-nitrophenyl methyl ether (Körner, Abstr., 1876, 204) by the action of sodium methoxide, 4:6-dibromo-2-nitromethylaniline (Blanksma, Abstr., 1902, i, 600) when heated with alcoholic methylamine, 4:6-dibromo-2-nitrodiphenylamine,



orange-red crystals, m. p. 80°, by heating with aniline, 4:6:4':6'-tetrabromo-2:2'-dinitrodiphenyl sulphide, $S(C_6H_2Br_2 \cdot NO_2)_2$, a yellow powder, m. p. 90° (approx.), by the action of sodium sulphide, and 4:6:4':6'-tetrabromo-2:2'-dinitrodiphenyl disulphide, $S_2(C_6H_2Br_2 \cdot NO_2)_2$, brilliant yellow crystals, m. p. 207°, with sodium disulphide. By oxidation with nitric acid, the latter derivative gives 4:6-dibromo-2-nitrobenzenesulphonic acid.

Similarly, *s*-dichloronitrobenzene gives 1:3-dichloro-4:5-dinitrobenzene, which forms crystals, m. p. 98°. The constitution of this chloro-derivative is also determined by the production of 4:6-dichloro-2-nitroaniline. By treatment with the reagents mentioned above, 1:3-dichloro-4:5-dinitrobenzene gives 4:6-dichloro-2-nitrophenol, 4:6-dichloro-2-nitrophenyl methyl ether, 4:6-dichloro-2-nitromethylaniline, $NHMe \cdot C_6H_2Cl_2 \cdot NO_2$, orange-red crystals, m. p. 80°, 4:6-dichloro-2-nitrodiphenylamine, $NHPh \cdot C_6H_2Cl_2 \cdot NO_2$, yellow crystals, m. p. 72°, 4:6:4':6'-tetrachloro-2:2'-dinitrodiphenyl sulphide, m. p. 70—80°, and 4:6:4':6'-tetrachloro-2:2'-dinitrodiphenyl disulphide, $S_2(C_6H_2Cl_2 \cdot NO_2)_2$, yellow crystals, m. p. 190°. The latter compound is oxidised by nitric acid to 4:6-dichloro-2-nitrobenzenesulphonic acid.

E. H.

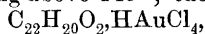
The Question of the Miscibility and Form-Analogy in Aromatic Nitro- and Nitroso-compounds. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1907 (1908), 10, 436—440).—Crystallographic determinations are given of *o*-nitroacetanilide and of *o*-nitrosoacetanilide; both are monoclinic, with $a:b:c = 0.8935:1:1.9198$ and $a:b:c = 0.8940:1:0.7295$ respectively. There is thus a similarity in the ratio of $a:b$. The two substances appear to be capable of mixing in solid solution to only a limited extent.

L. J. S.

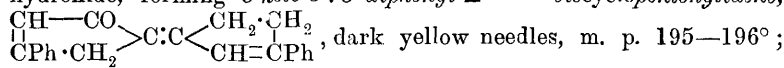
The Phenylcyclopentane Group. WALTHER BORSCHKE and W. MENZ [in part, ALBERT FELS] (*Ber.*, 1908, 41, 190—210).—Members of the phenylcyclopentane group have not hitherto been subjected to a thorough investigation. The hydrocarbon itself is obtained from 1-phenyl- Δ^1 cyclopentene-3-one by way of 1-phenylcyclopentane-3-ol, 1-phenyl-3-bromocyclopentane, and 1-phenylcyclopentane-3-carboxylic

acid. The compound described by Paal (Abstr., 1884, 1177) as dehydrophenacylacetone is undoubtedly 1-phenyl- Δ^1 -cyclopentene-3-one as stated by Borsche and Fels (Abstr., 1906, i, 509), for on reduction it is converted into a saturated alcohol, which yields on oxidation a ketone containing the group $-\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2-$, since it condenses with benzaldehyde yielding a dibenzylidene derivative.

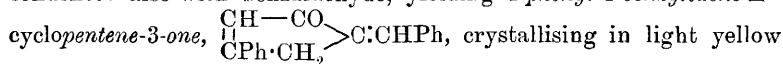
1-Phenyl- Δ^1 -cyclopentene-3-one is formed together with β -benzoyl-propionic acid on warming ethyl phenacylacetate with 2% aqueous sodium hydroxide solution; it may also be prepared by treating phenacylacetone with 2% aqueous sodium hydroxide or by boiling phenuvic acid with strong hydrochloric acid. The *hydrochloride*, $\text{C}_{11}\text{H}_{10}\text{O}\cdot\text{HCl}$, forms bright red crystals, sinters at 62° , m. p. $68-69^\circ$; the *platinichloride*, $(\text{C}_{11}\text{H}_{10}\text{O})_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, forms slender, orange-yellow needles, decomposing above 145° ; the *aurichloride*,



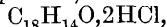
crystallises in golden-yellow leaflets, m. p. $130-131^\circ$ (decomp.). 1-Phenyl- Δ^1 -cyclopentene-3-one in ethereal solution combines with mercuric chloride, forming the additive *product*, $\text{C}_{11}\text{H}_{10}\text{O}\cdot\text{HgCl}_2$, obtained as large, colourless, transparent crystals, and with ferric chloride, yielding the additive *product*, $\text{C}_{11}\text{H}_{10}\text{O}\cdot\text{FeCl}_3\cdot\text{OEt}_2$, crystallising in ruby-red needles with a metallic lustre; both compounds are decomposed by water into their components. The *oxime*, $\text{C}_{11}\text{H}_{10}\cdot\text{NOH}$, crystallises in white needles, m. p. $146-147^\circ$; the *semicarbazone*, $\text{C}_{11}\text{H}_{10}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in small, white needles, m. p. 234° (decomp.); it may be obtained directly from phenacylacetone by acting on this compound with semicarbazide hydrochloride in the presence of sodium acetate. 1-Phenyl- Δ^1 -cyclopentene-3-one condenses with itself in alcoholic solution in the presence of a small quantity of sodium hydroxide, forming 5-keto-3:3'-diphenyl- $\Delta^{(1):3:3'}$ -biscyclopentenylidene,



the *hydrochloride*, $\text{C}_{22}\text{H}_{18}\text{O}_2\cdot 2\text{HCl}$, is a dark red substance. The ketone condenses also with benzaldehyde, yielding 1-phenyl-4-benzylidene- Δ^1 -

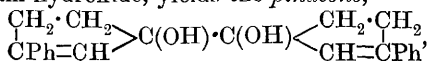


scales, m. p. $186-187^\circ$, b. p. $260^\circ/10 \text{ mm.}$; the *hydrochloride*,

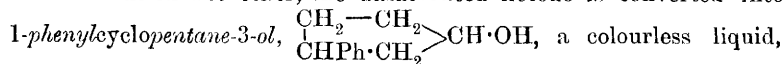


is an orange-red, crystalline powder, m. p. 178° ; the corresponding *o*-hydroxybenzylidene derivative, $\text{C}_{18}\text{H}_{14}\text{O}_2$, crystallises in brilliant, small, greenish-yellow prisms, m. p. $183-184^\circ$, and the *p*-dimethyl-aminobenzylidene derivative, $\text{C}_{20}\text{H}_{19}\text{ON}$ forms short, cinnamon-red prisms, m. p. $153-154^\circ$.

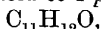
1-Phenyl- Δ^1 -cyclopentene-3-one, on reduction with zinc dust and aqueous potassium hydroxide, yields the *pinacone*,



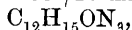
a yellowish-white, crystalline powder, m. p. about 235° ; when reduced with sodium in wet ether, the unsaturated ketone is converted into



b. p. 155—156°/10 mm., which sets to a jelly when cooled in a freezing mixture; the *acetate*, $C_{11}H_{13}OAc$, is a colourless, viscid oil, b. p. 154°/12 mm.; the *phenylurethane*, $C_{11}H_{13}O \cdot CO \cdot NHPh$, crystallises in glistening leaflets, m. p. 99—100°. The alcohol is oxidised by chromic acid in glacial acetic acid to 1-phenylcyclopentane-3-one,



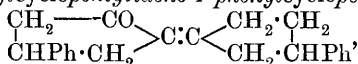
a colourless liquid, b. p. 154—155°/10 mm.; the *semicarbazone*,



crystallises in white leaflets, m. p. 181° (decomp.). The ketone condenses with benzaldehyde in the presence of a small quantity of sodium hydroxide, forming 1-phenyl-2 : 4-dibenzylidenecyclopentane-3-one,



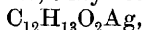
light yellow leaflets, m. p. 181°, and is converted by sodium ethoxide in alcohol into 4-phenylcyclopentylidene-1-phenylcyclopentane-3-one,



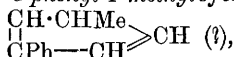
a yellow, viscid oil, b. p. 235°/10 mm.

When heated with fuming hydrobromic acid in a sealed tube at 100°, 1-phenylcyclopentane-3-ol is converted into 3-bromo-1-phenylcyclopentane, $C_{11}H_{13}Br$, a colourless liquid, b. p. 139—140°/10 mm.; the latter compound reacts with magnesium, forming an additive product, which is decomposed by dilute sulphuric acid, yielding *phenylcyclopentane*, $C_{11}H_{14}$, a colourless, limpid oil, b. p. 213—215°/760 mm., D_{17}^{20} 0.958, n_D^{20} 1.5320. 3-Bromo-1-phenylcyclopentane, when treated with alcoholic potassium hydroxide solution, yields *phenylcyclopentene*, $C_{11}H_{12}$, a colourless, limpid liquid, b. p. 223—225°, D_{20}^{20} 0.965, n_D^{20} 1.5356; the product so obtained is probably a mixture of 1-phenyl- Δ^2 -cyclopentene and 1-phenyl- Δ^3 -cyclopentene. The same compound is formed on heating 1-phenylcyclopentane-3-ol with zinc chloride.

1-Phenylcyclopentane-3-carboxylic acid, $\begin{array}{c} CH_2 - CH_2 \\ | \quad \quad | \\ CHPh \cdot CH_2 \end{array} > CH \cdot CO_2H$, is prepared by treating magnesium 3-bromo-1-phenylcyclopentane with carbon dioxide; it is a viscid, colourless oil, which solidifies to a vitreous mass in a freezing mixture; the *ammonium* salt, long, white needles, *calcium* salt, $C_{24}H_{26}O_4Ca$, white, silky needles, and *silver* salt,

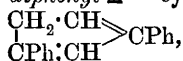


were prepared. The product formed by the action of magnesium methyl iodide on 1-phenylcyclopentane-3-one is decomposed by dilute sulphuric acid, yielding 3-phenyl-1-methylcyclopentadiene,



large, colourless crystals, b. p. 151°/12 mm., m. p. 62°; it decomposes when exposed to the air, but is stable in an atmosphere of hydrogen; it is reduced by sodium in wet ether to 3-phenyl-1-methylcyclopentane, $C_{12}H_{16}$, a colourless liquid, b. p. 230—235°, D_{17}^{20} 0.950, n_D^{20} 1.5276. The following compounds are prepared in a similar manner: 3-phenyl-1-ethylcyclopentadiene, $C_{13}H_{14}$, b. p. 170—175°/12 mm., is obtained as a semi-solid mass at the ordinary temperature, which solidifies to white, silky needles at low temperatures; 3-phenyl-1-ethylcyclopentane, $C_{13}H_{18}$, is a colourless, limpid liquid, b. p. 270°,

$D_{17}^{17} 0.948$, $n_D^{17} 1.5276$; 1:3-diphenyl- $\Delta^{1:3}$ -cyclopentadiene,



crystallises in yellowish-white needles, m. p. 156° ; its solutions exhibit a strong, blue fluorescence. W. H. G.

Preparation of Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, 41, 423—425).—The paper gives a detailed account of the apparatus and of the operations whereby triphenylmethyl can be obtained rapidly and conveniently in accordance with the equation $\text{CPh}_3 \cdot \text{MgCl} + \text{CPh}_3\text{Cl} = 2\text{CPh}_3 + \text{MgCl}_2$. The apparatus can be used for the preparation of β -magnesium triphenylmethyl chloride, which crystallises in colourless prisms, carbonises on heating, forms a yellow solution in benzene, and reacts with oxygen even more rapidly than triphenylmethyl, yielding the peroxide and magnesium oxychloride.

C. S.

Structural Formula of Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, 41, 426—430).—Triphenylmethyl and α -magnesium triphenylmethyl chloride result when magnesium in moderate excess reacts gently with an ethereal solution of triphenylmethyl chloride in the presence of a moderate amount of iodine (*Abstr.*, 1907, i, 26). With a large excess of iodine, the amount of triphenylmethyl is greatly diminished, and, if the reaction proceeds vigorously, a partial conversion of α -magnesium triphenylmethyl chloride into the β -isomeride occurs (*Abstr.*, 1906, i, 392). Tschitschibabin employed the latter conditions in the experiments (*Abstr.*, 1907, i, 1022), the results of which led him to doubt the existence of two isomeric magnesium triphenylmethyl chlorides. The author points out that Tschitschibabin's solution can have contained little or none of the α -isomeride, that his explanation of the formation of *p*-benzoyltriphenylmethane is impossible, and that its production from triphenylmethyl is negatived by the three following experiments. An ethereal solution of triphenylmethyl, free from the magnesium compound, does not react with benzaldehyde. Solid triphenylmethyl in benzene solution is equally non-reactive. The reaction between magnesium and triphenylmethyl chloride was so performed that the ethereal solution contained the triphenylmethyl, whilst the α -magnesium triphenylmethyl chloride was present exclusively in the precipitate; the solution did not react with benzaldehyde, whereas the precipitate yielded *p*-benzoyltriphenylmethane.

Tschitschibabin's argument that the so-called α - and β -magnesium triphenylmethyl chlorides react in the same way with benzoyl chloride and ethyl benzoate is countered by the statement that, under these conditions, the labile α -form changes into the stable β -isomeride.

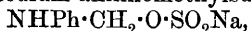
C. S.

Various Cases of the Simultaneous Production of 1:6- and 2:7-Dimethylantracenes. JAMES LAVAUX (*Compt. rend.*, 1908, 146, 135—137. Compare *Abstr.*, 1905, i, 43, 125, 640, 698; 1907, i, 25).—The author considers that 4-dimethylantracene, which gives

a quinone, m. p. 169° , is the 1:6-isomeride. It is different from Louise's dimethylantracene (*Ann. Chim. Phys.*, 1885, [vi], 6, 187), which forms a quinone, m. p. 170° , since a mixture of the quinones has a m. p. 15° lower. 1:6- and 2:7-Dimethylantracenes, which have respectively m. p. 240° and m. p. 244.5° , form a curious mixture, apparently of a eutectic nature, which has the sharp m. p. 225° . This mixture is contained in the "dimethylantracenes" obtained by Friedel and Crafts by the action of aluminium chloride on (1) xylyl chloride, (2) a mixture of methylene dichloride and toluene, and (3) benzyl chloride mixed with toluene, by Elbs and Wittich, and by Anschütz, using respectively chloroform and ethylene tetrabromide in place of methylene dichloride, and by Anschütz and Immendorff by the action of aluminium chloride on toluene, and also in the product isolated by Zincke and Waschendorff from coal tar. It cannot be separated into its components either by continued sublimation or fractional crystallisation; but repeated recrystallisation, carried out so that only a small portion of the dissolved solid separates, results in a gradual rise of the m. p. of the latter, and a small quantity of the 1:6-isomeride is thus obtained. The solid remaining in solution has m. p. 225° .

The mixture of quinones obtained on oxidation is, however, separable by alcohol, in which 1:6-dimethylantraquinone is much more soluble than the 2:7-derivative. Reduction of the quinones thus separated gives the corresponding hydrocarbons. The author considers that the phenomenon of the formation of an eutectic mixture explains largely the confusion which exists in the literature on the subject. E. H.

Interaction of Aniline, Formaldehyde, and Sodium Hypo-sulphite. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 188837).—A mixture of methylenedianiline and sodium hypsulphite in water was shaken until the greater portion of the methylene compound had dissolved, and then treated rapidly with 30% formaldehyde and again shaken. The filtered solution was evaporated to dryness under reduced pressure, when a stable product was obtained, consisting of sodium anilinomethylsulphite,



and sodium formaldehydesulphoxylate, $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}$. When the above conditions are employed, the unstable sodium anilinomethylsulphoxylate, $\text{NHPh}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}$, is not produced. G. T. M.

Action of Magnesium Organic Compounds on Hydramides. MAX BUSCH and LUDWIG LEEFHLM (*J. pr. Chem.*, 1908, [ii], 77, 1—20).—Busch and Rinck (*Abstr.*, 1905, i, 519) showed that the action of magnesium alkyl haloids on Schiff's bases leads to the formation of *C*-alkylated primary bases. It was to be expected that the hydramides, $\text{CHR}\cdot\text{N}\cdot\text{CHR}\cdot\text{N}\cdot\text{CHR}$, which contain the typical grouping of Schiff's bases twice in the molecule, would yield in the same manner either monoalkylated, $\text{CHR}\cdot\text{N}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CHR}\cdot\text{Alk}$, or dialkylated, $\text{CHR}(\text{NH}\cdot\text{CHR}\cdot\text{Alk})_2$, derivatives. It is found, however, that the magnesium alkyl haloid not only forms an additive

compound with the unsaturated groupings, but also resolves a single carbon-nitrogen linking, this second action resembling the reduction of hydrobenzamide by sodium amalgam and alcohol to benzylamine and dibenzylamine. The reaction takes place according to two schemes: (I) $\text{CHPh}(\text{N}:\text{CHPh})_2 + 3\text{MgMeI} \rightarrow \text{CHMePh}\cdot\text{N}(\text{MgI})_2 + \text{CHMePh}\cdot\text{N}(\text{MgI})\cdot\text{CHMePh} \rightarrow (+3\text{H}_2\text{O}) \rightarrow \text{CHMePh}\cdot\text{NH}_2 + \text{NH}(\text{CHMePh})_2 + 3\text{Mg}(\text{OH})\text{I}$; (II) $\text{CHPh}(\text{N}:\text{CHPh})_2 + 2\text{MgMeI} \rightarrow \text{CHPh}[\text{N}(\text{MgI})\cdot\text{CHMePh}]_2 \rightarrow (+3\text{H}_2\text{O}) \rightarrow \text{CHO}\cdot\text{Ph} + 2\text{NH}_2\cdot\text{CHMePh} + 2\text{Mg}(\text{OH})\text{I}$. Hydrobenzamide enters into reaction with magnesium aliphyl haloids according to both schemes, the proportions of primary and secondary bases formed varying with the aliphyl haloid and the conditions, but with magnesium aryl haloids only according to scheme II. Anishydramide yields only primary amines, either with magnesium aryl or aliphyl haloids. The behaviour of magnesium naphthyl bromide with hydrobenzamide is abnormal, in that considerable amounts of isoamarine are formed; this intramolecular change, which occurs with hydrobenzamide hydrochloride only at 240° , takes place here below 100° .

Di- α -phenylethylamine, $\text{NH}(\text{CHMePh})_2$, is a viscid, yellow oil, which does not form a carbonate on exposure to air; the *hydrochloride*, $\text{C}_{16}\text{H}_{19}\text{N}\cdot\text{HCl}$, sublimes unchanged above 240° ; the *benzoyl* derivative, $\text{C}_{23}\text{H}_{23}\text{ON}$, white needles, m. p. 92° ; the *phenylcarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{CHMePh})_2$, colourless prisms, m. p. 140° .

α -Phenylpropylamine hydrochloride, $\text{CHEtPh}\cdot\text{NH}_2\cdot\text{HCl}$, crystallises in needles, m. p. 194° ; the *benzoyl* derivative, $\text{C}_{16}\text{H}_{17}\text{ON}$, needles, m. p. 115 — 116° ; the *phenylthiocarbamide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CHEtPh}$, needles or leaflets, m. p. 126 — 127° ; the *benzenesulphonamide*, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CHEtPh}$, needles, m. p. 81° , is sparingly soluble in dilute sodium hydroxide.

Di- α -phenylpropylamine, $\text{NH}(\text{CHEtPh})_2$, is a yellow oil, b. p. 293 — $294^\circ/733$ mm., and has an aromatic odour; the *hydrochloride*, $\text{C}_{18}\text{H}_{23}\text{N}\cdot\text{HCl}$, long needles, m. p. 258° ; the *benzoyl* derivative, $\text{C}_{25}\text{H}_{27}\text{ON}$, needles, m. p. 152° ; the *benzenesulphonamide*, $\text{C}_{24}\text{H}_{27}\text{O}_2\text{NS}$, needles, m. p. 206° ; the *nitrosoamine*, $\text{C}_{18}\text{H}_{23}\text{N}\cdot\text{NO}$, almost colourless needles, m. p. 74° , and gives Liebermann's reaction.

Benzoylphenylbutylamine, $\text{C}_{10}\text{H}_{14}\text{NBz}$, crystallises in white needles, m. p. 128° . *Di- α -phenylbutylamine*, $\text{NH}(\text{CHPh}\cdot\text{C}_3\text{H}_7)_2$, forms a viscid oil; the *hydrochloride*, $\text{C}_{20}\text{H}_{27}\text{N}\cdot\text{HCl}$, crystallises in needles, m. p. 276° .

Tetraphenyldiethylamine, $\text{NH}(\text{CHPh}\cdot\text{CH}_2\text{Ph})_2$, crystallises in soft needles, m. p. 99 — 100° , b. p. 266 — $268^\circ/16$ mm.; the *nitrosoamine*, $\text{C}_{28}\text{H}_{26}\text{N}\cdot\text{NO}$, white needles, m. p. 153 — 154° .

Benzhydrylamine nitrate crystallises in needles, m. p. 197° ; the *sulphate*, m. p. 210° ; the *benzoyl* derivative, $\text{CHPh}_2\cdot\text{NHBz}$, needles, m. p. 172° ; the *benzenesulphonamide*, glistening needles, m. p. 182° .

α -Naphthylbenzylamine, $\text{NH}\cdot\text{CHPh}\cdot\text{C}_{10}\text{H}_7$, crystallises in needles, m. p. 121° , b. p. $255^\circ/15$ mm.; the *hydrochloride*, $\text{C}_{17}\text{H}_{15}\text{N}\cdot\text{HCl}$, white needles, m. p. 275° , and, when treated with nitrite solution, yields phenyl-naphthylcarbinol.

Benzoylisoamarine, $C_{21}H_{17}N_2Bz$, crystallises from alcohol in short needles, m. p. 288° .

The following substances are obtained from anishydramide.

α -*Anisylethylamine*, $NH_2 \cdot CHMe \cdot C_6H_4 \cdot OMe$, is a transparent oil, b. p. $127-131^\circ/12$ mm., has a characteristic odour, and forms a *carbonate* on exposure to air; the *hydrochloride*, $C_9H_{13}ON \cdot HCl$, needles, m. p. 157° ; the *nitrate*, $C_9H_{13}ON \cdot HNO_3$, needles, m. p. 114° . α -*Phenyl-b-anisylethylthiocarbamide*, $NHPh \cdot CS \cdot NH \cdot CHMe \cdot C_6H_4 \cdot OMe$, leaflets, m. p. 125.5° .

α -*Anisylpropylamine*, $NH_2 \cdot CHEt \cdot C_6H_4 \cdot OMe$, is a transparent oil, b. p. $136-140^\circ/12$ mm.; the *hydrochloride*, $C_{10}H_{15}ON \cdot HCl$, needles, m. p. $217-218^\circ$; the *nitrate*, leaflets, m. p. 176° ; the *hydrogen sulphate*, $C_{10}H_{15}ON \cdot H_2SO_4$, needles, m. p. 214° . The *benzoyl* derivative, $C_{10}H_{14}ONBz$, needles, m. p. 118° .

p -*Methoxybenzhydramine*, $NH_2 \cdot CHPh \cdot C_6H_4 \cdot OMe$ (Hantzsch and Kraft, Abstr., 1892, 338), b. p. $202-206^\circ/12$ mm.; the *nitrate*, leaflets, m. p. 164° ; the *benzoyl* derivative, $C_{21}H_{19}O_2N$, needles, m. p. 174° . The *hydrochloride*, m. p. 194° (191° : Hantzsch and Kraft, *loc. cit.*), when treated with sodium nitrite, yields *p-methoxybenzhydrol*, $OH \cdot CHPh \cdot C_6H_4 \cdot OMe$, which crystallises in white needles, m. p. 58° .

G. Y.

Action of Magnesium Organic Compounds on Benzyldene-alphylamines. MAX BUSCH and LUDWIG LEEFHELM (*J. pr. Chem.*, 1908, [ii], 77, 20-24).—Busch and Rinck's method of preparing secondary bases by the action of magnesium organic compounds on Schiff's bases (Abstr., 1905, i, 519) is found to give good yields with benzyldene-methylamine and -ethylamine. The new secondary bases are colourless oils, which have an aromatic odour, distil unchanged, and form salts stable in aqueous solution.

α -*Phenylethylmethylamine*, $NHMe \cdot CHMePh$, from benzyldene-methylamine and magnesium methyl iodide, b. p. $87^\circ/18$ mm. or $184^\circ/730$ mm.; the *hydrochloride*, $C_9H_{14}NCl$, colourless needles, m. p. 173° . α -*Phenylpropylmethylamine*, $NHMe \cdot CHEtPh$, from benzyldene-methylamine and magnesium ethyl iodide, b. p. $96^\circ/20$ mm.; the *hydrochloride*, $C_{10}H_{15}N \cdot HCl$, needles or prisms, m. p. 153° . *Methylbenzhydramine* (as-*diphenyldimethylamine*), $NHMe \cdot CHPh_2$, from benzyldene-methylamine and magnesium phenyl bromide, forms crystals, m. p. 40° , b. p. $168^\circ/20$ mm.; the *hydrochloride*, m. p. 238° ; the *nitrate*, $C_{14}H_{15}N \cdot HNO_3$, m. p. 146° .

α -*Phenylethylethylamine*, $NHEt \cdot CHMePh$, b. p. $90^\circ/16$ mm. or $194^\circ/728$ mm.; the *hydrochloride*, $C_{10}H_{15}N \cdot HCl$, m. p. 201° . α -*Phenylpropylethylamine*, $NHEt \cdot CHEtPh$, b. p. $99^\circ/20$ mm. or $207-208^\circ/729$ mm.; the *hydrochloride*, m. p. 180° . *Ethylbenzhydramine*, $NHEt \cdot CHPh_2$, b. p. $175^\circ/20$ mm.; the *hydrochloride* becomes brown at 240° , m. p. 248° ; the *nitrate*, m. p. 142° .

Di- α -phenylpropylamine (Busch and Leefhelm, preceding abstract) is prepared from benzyldene-phenylpropylamine and magnesium ethyl iodide.

G. Y.

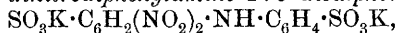
Benzylaminoacetal and Analogues. LEOPOLD RÜGHEIMER and P. SCHÖN (*Ber.*, 1908, 41, 17-18).—A good yield of benzylamino-

acetal is obtained by heating together benzylamine and chloroacetal at 130—140° (compare E. Fischer, Abstr., 1893, i, 300). Veratrylamine also reacts with chloroacetal at 100°.

Veratrylamine (2:4-dimethoxybenzylamine) is best prepared by reducing methylvanillin oxime with zinc dust and acetic acid. The yield is 70%; there is also produced at the same time the secondary amine, $\text{NH}[\text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2]_2$, b. p. above 250°/14 mm. (compare Juliusberg, Abstr., 1907, i, 219). W. R.

Dinitrodiphenylaminesulphonic Acids and their Transformation into Triphenylmethane Colouring Matters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 186989).—1-Chloro-2:6-dinitrobenzene-4-sulphonic and 1-chloro-2:4-dinitrobenzene-6-sulphonic acids readily condense with metanilic acid in the presence of boiling aqueous sodium acetate to yield dinitrodiphenylaminesulphonic acids.

Potassium 2:6-dinitrodiphenylamine-4:3'-disulphonate,



produced in this way, crystallises from water in readily soluble, yellow, filamentous needles. When condensed in sulphuric acid with tetramethyldiaminobenzhydrol, this salt furnishes a leuco-derivative, which may be oxidised with manganic hydroxide to a triphenylmethane colouring matter. G. T. M.

The Hydroxycarbamides and Carbamidoximes. II.

A. CONDUCHÉ (*Ann. Chim. Phys.*, 1908, [viii], 13, 5—90. Compare this vol., i, 12).—The author has prepared a large series of carbamidoximes of the type $\text{O} < \begin{smallmatrix} \text{CHR} \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$ by the condensation of isohydroxycarbamide with aromatic aldehydes. Anisylidenecarbamidoxime,

m. p. 133°. *Cinnamylidenecarbamidoxime*, $\text{O} < \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CHPh} \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 154—155°. *Salicylidenecarbamidoxime*, m. p. 102—105°, is very unstable, and decomposes in the light. Like the corresponding benzylidenecarbamidoxime (Abstr., 1905, i, 289; 1906, i, 593), all these compounds decompose on melting, yield the corresponding nitrile when treated with aqueous hydrochloric acid, or the hydrochloride of the corresponding acid amide when treated with alcoholic hydrogen chloride, the corresponding substituted carbamide when treated with reducing agents, and the corresponding oxime when treated with aqueous or alcoholic potassium hydroxide. In the case of salicylidenecarbamidoxime, the *indoxazen*, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH} \\ \text{O} \end{smallmatrix} > \text{N}$, b. p.

86—87°/11 mm. or 90—92°/15 mm., is also formed in addition to the oxime by the action of aqueous potassium hydroxide, whilst with alcoholic potassium hydroxide it yields the nitrile.

Anisylcarbamide has m. p. 160° (Goldschmidt and Polonowska give 167°).

Furfurylidenecarbamidoxime, m. p. 144—145° (Abstr., 1905, i, 289); *piperonylidenecarbamidoxime*, $\text{O} < \begin{smallmatrix} \text{CH} \cdot \text{C}_7\text{H}_5\text{O}_2 \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 156—157°;

vanillylidencarbamidoxime, $O \leq \begin{smallmatrix} \text{CH} \cdot \text{C}_7\text{H}_7\text{O}_2 \\ | \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 134—135°;

cuminylidencarbamidoxime, $O \leq \begin{smallmatrix} \text{CH} \cdot \text{C}_9\text{H}_{11} \\ | \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 121—122°; *p-tolyl-*

idenecarbamidoxime, $O \leq \begin{smallmatrix} \text{CH} \cdot \text{C}_7\text{H}_7 \\ | \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 142—143°, are all well-defined, crystalline compounds.

When nitrated with fuming nitric acid in the presence of concentrated sulphuric acid at -15° , benzylidenecarbamidoxime yields a mixture of the three isomeric nitro-derivatives, in which the ortho- and meta-compounds preponderate; the same compounds can also be prepared directly from the corresponding nitrobenzaldehyde, *o-nitrobenzylidenecarbamidoxime*, $O \leq \begin{smallmatrix} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ | \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 146—147°, forms yellow

needles; *m-nitrobenzylidenecarbamidoxime*, m. p. 180°, forms yellow crystals, and *p-nitrobenzylidenecarbamidoxime*, m. p. 160°, forms plates.

With the exception of heptaldehyde, the aliphatic aldehydes do not yield carbamidoximes with isohydroxycarbamide. *Heptylidencarbamidoxime*, $O \leq \begin{smallmatrix} \text{CH} \cdot \text{C}_6\text{H}_{13} \\ | \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, has m. p. 85—86°.

Acetone condenses with isohydroxycarbamide to form *acetcarbamidoxime* (*dimethylcarbamidketoxime*), $O \leq \begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, which crystallises in massive prisms, m. p. 118—119°; is hydrolysed by hydrochloric acid forming the hydrochloride of hydroxycarbamide, mesityl oxide, and phorone; yields *isopropylcarbamide*, $\text{CHMe}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, m. p. 154°, on reduction; acetoxime and potassium cyanate on treatment with potassium hydroxide, and benzylidenecarbamidoxime on boiling with benzaldehyde. Attempts to form corresponding carbamidoximes from methyl ethyl ketone or acetophenone were unsuccessful.

as-Diphenylhydroxycarbamide, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$, decomp. 135°, prepared by the action of hydroxylamine hydrochloride on diphenylcarbamylic chloride, forms colourless needles; the hydrated compound,

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2 \cdot 2\text{H}_2\text{O}$, forms massive, pale red crystals, which, when heated, decompose at 100°, solidify, and decompose again at 130°. It forms a *sodium salt*, $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_2\text{Na} \cdot \text{H}_2\text{O}$, and does not yield condensation products with aromatic aldehydes or with ketones. With acetaldehyde, it forms the molecular compound, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{CH}_3 \cdot \text{CHO}$, which is unstable in solution and decomposes at 129—130°; in view of all these facts, it is suggested that *as-diphenylhydroxycarbamide* has the constitution represented by the formula $\text{OH} \cdot \text{C}(\text{NPh}_2) \cdot \text{N} \cdot \text{OH}$, analogous to the hydroxycarbamide, m. p. 140° (this vol., i, 12).

Hydroxyurethane does not condense with aromatic aldehydes, and probably has the constitution $\text{OH} \cdot \text{C}(\text{OEt}) \cdot \text{N} \cdot \text{OH}$.

Formamidoxime (*isouretine*) reacts with benzaldehyde to form hydroxyphenylethenylamidoxime, $\text{OH} \cdot \text{CHPh} \cdot \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{OH}$, m. p. 163—164° (Tiemann, Abstr., 1884, 734, gives m. p. 140°).

M. A. W.

Molecular Refractions of some Carbamidoximes. A. CONDUCHÉ (*Ann. Chim. Phys.*, 1908, [viii], 13, 91—95).—A determination of the molecular refractions of acetone, benzaldehyde, anisaldehyde, vanillin, piperonal and furfuraldehyde, and of the corresponding carbamidoximes (preceding abstract), show that the mean difference between the molecular refraction of the aldehyde and carbamidoxime is 13.06 for aliphatic, and 13.75 for aromatic, derivatives; the corresponding values calculated from Brühl and Conrady's values for the atomic refractions are 12.68 and 13.55 respectively.

M. A. W.

Some Transformations of *cyclo*Butanol. NIKOLAUS J. DEMJANOFF and M. DOJARENKO (*Ber.*, 1908, 41, 43—46. Compare Abstr., 1907, i, 605).—*cyclo*Butanol yields on oxidation with chromic acid, *cyclo*propanealdehyde and *cyclo*butanone; the semicarbazone of the former has m. p. 127—128°; the semicarbazone of the latter has m. p. 201° (compare Demjanoff, Abstr., 1907, i, 1023; Demjanoff and Fortunatoff, *ibid.*, 1032). *cyclo*Butanol yields on treatment with concentrated hydrobromic acid at 70° a monobromide; this compound has been described by W. H. Perkin (*Trans.*, 1894, 65, 950) as bromo-*cyclo*butane; it is a liquid, b. p. 105—106°, n_D^{20} 1.476, D_4^{25} 1.4155, D_4^{23} 1.406, and is consequently very similar in its physical properties to the bromide obtained from *cyclo*propylcarbinol (Demjanoff and Fortunatoff, *loc. cit.*). In order to ascertain whether the *cyclo*butane compound had changed into a derivative of *cyclo*propane, the above bromide was converted into the magnesium compound, and treated with carbon dioxide. The calcium salt of the acid thus formed, $(C_5H_7O_2)_2Ca \cdot 2H_2O$, crystallises in glistening leaflets; the silver salt, $C_5H_7O_2Ag$, is likewise crystalline. It follows, therefore, that the acid is not *cyclo*butanecarboxylic acid, and since it does not correspond in properties with any known acid of the same composition it is probably *cyclopropylacetic acid*, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CH \cdot CH_2 \cdot CO_2H$.

W. H. G.

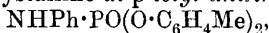
Reaction between Phenols and Phosphorus Pentachloride. WILHELM AUTENRIETH and ALFRED GEYER (*Ber.*, 1908, 41, 146—158).—An investigation on the course of the reaction between phosphorus pentachloride and phenols. When phenol, a cresol or β -naphthol (3 mols.) is treated with phosphorus pentachloride (1 mol.), the first product formed which can be isolated is a triarylphosphoryl dichloride, having the general formula $PCl_2(OR)_3$, where $R = Ph$, C_6H_4Me or $C_{10}H_7$. These compounds are identical with those prepared by Anschütz and Emery (Abstr., 1890, 34) by acting on esters of phosphorous acid, $P(OR)_3$, with chlorine, and are obtained as relatively stable, yellow or brown viscid oils, decomposing into hydrogen chloride and a chlorinated benzene derivative when heated at 200—300°. They react with aniline with the formation of a diaryl anilino-phosphate and a substituted aniline, thus: $PCl_2(OR)_3 + 4NH_2Ph = NHPPh \cdot PO(OR)_2 + NHRPh + 2NH_2Ph \cdot HCl$.

These facts are not opposed to the views of Anschütz and Emery (*loc. cit.*), for it is quite probable that in the action of phosphorus

pentachloride on phenol, the first compound formed is phenylphosphoryl tetrachloride, which then reacts with more phenol, thus: $\text{PCl}_4 \cdot \text{OPh} + \text{Ph} \cdot \text{OH} \rightarrow \text{HCl} + \text{PCl}_3(\text{OPh})_2$; $\text{PCl}_3(\text{OPh})_2 + \text{Ph} \cdot \text{OH} \rightarrow \text{PCl}_2(\text{OPh})_3$; at present, however, the only compound to be isolated has been the triarylphosphoryl dichloride.

Triphenylphosphoryl dichloride, prepared by the action of phosphorus pentachloride (1 mol.) on phenol (3 mols.), or by the method of Anschütz and Emery (*loc. cit.*), is stable below 180° , but decomposes fairly readily at 200 – 210° with the liberation of chlorobenzene. It reacts with aniline, yielding diphenyl anilinophosphate (compare Michaelis and Schulze, *Abstr.*, 1894, i, 128, 588), diphenylamine, and aniline hydrochloride.

Tri-p-tolylphosphoryl dichloride, $\text{PCl}_2(\text{O} \cdot \text{C}_6\text{H}_4\text{Me})_3$, prepared by heating *p*-cresol with phosphorus pentachloride at 140° , or by the action of chlorine on *p*-tolyl phosphite, is a yellow oil which decomposes at 200 – 210° , liberating *p*-chlorotoluene. It reacts with aniline, yielding the crystalline *di-p-tolyl anilinophosphate*,



m. p. 125° . The following compounds were prepared by the same methods: *Tri-m-tolylphosphoryl dichloride* is a yellow oil decomposing at about 210° . *Di-m-tolyl anilinophosphate* crystallises in prisms, m. p. 87° . *Tri-o-tolylphosphoryl dichloride* is a yellowish-brown oil, decomposing at about 180° . *Di-o-tolyl anilinophosphate* crystallises in brilliant prisms, m. p. 126 – 127° . *Tri-β-naphthylphosphoryl dichloride* is a viscid, brown oil, decomposing above 310° . *Di-β-naphthyl anilinophosphate*, $\text{C}_{26}\text{H}_{20}\text{O}_3\text{NP}$, crystallises in glistening prisms and long needles, m. p. 193 – 195° .

W. H. G.

Preparation of 5-Nitro-2-aminophenol-4-sulphonic Acid.

FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 188378).—Carbonyl-2-aminophenol-4-sulphonic acid, obtained by passing carbonyl chloride into a cold solution of the basic sodium salt of 2-aminophenol-4-sulphonic acid, is nitrated to 5-nitrocarbonyl-2-aminophenol-4-sulphonic acid in a cold mixture of concentrated sulphuric and nitric acids, the product separating as the potassium salt on adding potassium chloride to an ice-cold aqueous solution of the sulphonation mixture. This salt is hydrolysed by warming at 90° with aqueous sodium hydroxide, and the solution, when acidified and cooled, deposits yellow crystals of 5-nitro-2-aminophenol-4-sulphonic acid; the diazo-derivative of the new acid is readily soluble.

G. T. M.

2:3:4-Trinitrophenetole and some of its Derivatives. JAN J. BLANKSMA (*Rec. trav. chim.*, 1908, 27, 49–57).—Wender's dinitro-aceto-*p*-phenetidine (*Abstr.*, 1890, 751), contrary to that author's statement, is hydrolysed by boiling hydrochloric acid. Elimination of the amino-group from dinitro-*p*-phenetidine by diazotisation gives bright yellow leaflets, m. p. 101° , of 2:3-dinitrophenetole, $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, of which the constitution is established by the formation of Bantlin's 2:3-dinitrophenol (*Abstr.*, 1879, 237) when it is heated with hydrochloric acid in a sealed tube. On nitration, 2:3-dinitrophenetole gives a trinitro-

phenetole, $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, in the form of colourless crystals, m. p. 117° . This cannot be 2:3:5-trinitrophenetole, which has m. p. 80° (Abstr., 1905, i, 431), and, since, by the action of alcoholic ammonia and subsequent removal of the amino-group by diazotisation it gives 2:4-dinitrophenetole, it must be 2:3:4-trinitrophenetole. The latter, when heated with alcoholic ammonia (1 mol.), is converted into 2:6-dinitro-3-ethoxyaniline, $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NH}_2$, which forms yellow crystals, m. p. 130° ; with excess of alcoholic ammonia, the product consists of a mixture of Barr's 2:4-dinitro-*m*-phenylenediamine (Abstr., 1888, 822) and dinitrophenetidine. Elimination of the amino-group from 2:6-dinitro-3-ethoxyaniline gives 2:4-dinitrophenetole, which, by the action of alcoholic ammonia, is transformed into 2:4-dinitroaniline. By the action of methylamine (2 mols.) on 2:3:4-trinitrophenetole, yellow leaflets of 2:6-dinitro-3-ethoxymethylaniline, $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NHMe}$, m. p. 147° , are formed, which on nitration give colourless crystals of 2:4:6-trinitro-3-ethoxynitromethylaminobenzene, $\text{OEt}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{NMe}\cdot\text{NO}_2$ (van Romburgh, Abstr., 1889, 1154). When heated in a sealed tube at 165° with alcoholic methylamine solution, 2:6-dinitro-3-ethoxymethylaniline gives 2:4-dinitro-*m*-phenylenedimethyldiamine, $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{NHMe})_2$, in the form of yellow crystals, m. p. 170° , which are transformed by the action of nitric acid into van Romburgh's trinitro-*m*-phenylenedinitrodimethyldiamine (Abstr., 1888, 1185). 2:3:4-Trinitrophenetole reacts with an alcoholic solution of aniline, giving 2:6-dinitro-3-ethoxydiphenylamine, $\text{NHPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OEt}$, in the form of brilliant yellow crystals, m. p. 125° . By alcoholic sodium ethoxide solution, it is converted into 2:4-dinitro-1:3-diethoxybenzene, $\text{C}_6\text{H}_2(\text{NO}_2)_2(\text{OEt})_2$, colourless crystals, m. p. 57° , which become ruby-red on exposure to sunlight, possibly owing to isomeric change (compare Hantzsch, Abstr., 1906, i, 352). The constitution of the dinitrodiethoxybenzene is established by its conversion into 2:4-dinitroresorcinol when hydrolysed with hydrochloric acid. 2:4-Dinitro-1:3-diethoxybenzene, on nitration, gives Stenhouse's 2:4:6-trinitro-1:3-diethoxybenzene (*Annalen*, 1867, 141, 226). Sodium methoxide in methyl-alcoholic solution converts 2:3:4-trinitrophenetole into 2:6-dinitro-1-methoxy-3-ethoxybenzene, $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\text{OEt}$, which forms colourless crystals, m. p. 69° , becoming reddish-brown on exposure to sunlight. The latter substance, when dissolved in a mixture of nitric (D 1.52) and sulphuric acids, gives 2:4:6-trinitro-1-methoxy-3-ethoxybenzene, $\text{OMe}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{OEt}$, in the form of colourless crystals, m. p. 92° , becoming red in the light. The constitution of this substance is fixed by its conversion by ammonia or methylamine into 2:4:6-trinitro-*m*-phenylenediamine or 2:4:6-trinitro-*m*-phenylenedimethylamine (van Romburgh, *loc. cit.*). By boiling with aqueous sodium carbonate solution for three hours, 2:3:4-trinitrophenetole is transformed into 2:4-dinitro-3-hydroxyphenetole, $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\text{OH}$, which forms bright yellow crystals, m. p. 118° , becoming red on exposure to light. E. H.

Action of Chlorodimethyl Ether on the Phenoxides of the Alkali Metals. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1195—1198).—On diluting an alcoholic solution of hydroxydimethyl

ether (prepared as described, this vol., i, 130) with benzene and passing in a current of hydrogen chloride, a solution of chlorodimethyl ether in benzene is obtained. With sodium phenoxide, this furnishes methylene phenylmethyl ether, $\text{OPh}\cdot\text{CH}_2\cdot\text{OMe}$ (compare Breslau and Pictet, Abstr., 1907, i, 915), b. p. 189—190°, D_{15}^{25} 1.048, having an odour similar to that of phenetole. Methylene α -naphthyl methyl ether, prepared in an analogous manner, is an oily liquid, b. p. 296° (corr.), D_{15}^{25} 1.071, and is only volatilised by a current of steam. Methylene β -naphthyl methyl ether is a slightly yellow oily liquid, b. p. 301° (corr.), D_{15}^{25} 1.068. These three substances are insoluble in water, soluble in the usual organic solvents, are not attacked by alkaline liquids, but are decomposed by mineral acids, yielding variously coloured solids, similar to those produced by the action of formaldehyde on phenols (compare Baeyer, Abstr., 1873, 501, and Blumer, D.R.-P. 172877). When methyl salicylate reacts with chlorodimethyl ether in presence of alcohol containing a little sodium ethoxide, the *mixed ether*, $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, b. p. 156°/20 mm. and 284°(corr.)/atmospheric pressure, D_4^{17} 1.162, is formed. It is a colourless liquid, which resinifies when sulphuric acid is added to its solution in acetic acid or alcohol, and on hydrolysis by potassium hydroxide solution in alcohol furnishes the *potassium* salt of the methoxymethyl ether of salicylic acid, $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{K}$, which is soluble in water, and is decomposed by dilute hydrochloric acid, yielding salicylic acid.

T. A. H.

Action of Chlorodimethyl Ether on Magnesium Phenyl Bromide. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1198—1200).—Chlorodimethyl ether, prepared as already described (this vol., i, 130), does not react with magnesium in ether even in presence of a trace of iodine, and, like chloroform (Abstr., 1906, ii, 836), inhibits the reaction of magnesium with methyl iodide and ethyl bromide. It reacts vigorously with magnesium phenyl bromide in ether, furnishing, as a principal product, benzyl methyl ether.

Chlorodimethyl ether also reacts with magnesium bornyl chloride, prepared by Hesse's method (Abstr., 1906, i, 375), yielding, in addition to camphene, camphane, and other products, bornyl dimethyl ether, $\text{C}_{10}\text{H}_{17}\cdot\text{CH}_2\cdot\text{OMe}$, which was not isolated in a pure state. T. A. H.

Action of Potassium Persulphate on *p*-Cresol. T. KUMAGAI and RICHARD WOLFFENSTEIN (*Ber.*, 1908, 41, 297—300).—In the cases of toluene and *p*-toluonitrile, the interaction of persulphate leads to the formation of dibenzyl derivatives (Abstr., 1899, i, 424; 1901, i, 594). An extension of the research to *p*-cresol shows that the product obtained is dependent on the conditions of the experiment. In neutral solution, dihydroxydibenzyl is formed, but in acid solution, 2:5-dihydroxytoluene is the product obtained, the methyl group migrating during the change to an ortho-position (compare Bamberger, Abstr., 1895, i, 217). In alkaline persulphate solution, on the other hand, 3:4-dihydroxytoluene is formed [Chemische Fabrik auf Actien (vorm. Schering), D.R.-P. 81068, 81298].

W. R.

***o*-Vinylphenols.** KARL FRIES and G. FICKEWIRTH (*Ber.*, 1907, **41**, 367—373).—Contrary to Kunz-Krause's statement (*Abstr.*, 1899, **i**, 200), the product obtained on distilling *o*-coumaric acid under the ordinary pressure is not *o*-vinylphenol, but a polymeride of this substance. It is found that the unimolecular *o*-vinylphenol may be prepared by heating *o*-coumaric acid under 15 mm. pressure. In the preparation of the homologues of vinylphenol, on the other hand, the corresponding coumaric acids may be distilled under the ordinary pressure. The vinylphenols are obtained as oils which gradually solidify, forming bimolecular, or more complicated, polymerides; the constitution of these is discussed. The unimolecular substances are again formed when the polymerides are heated at high temperatures.

o-Vinylphenol (*o*-hydroxystyrene), $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}_2$, crystallises in needles, m. p. 29° , b. p. $108^\circ/15$ mm., decomp. on distillation under the ordinary pressure, forming a red and violet resin, yields *o*-vinylphenoxyacetic acid, $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 139° , when treated with bromoacetic acid in alkaline solution, and reacts with bromine in glacial acetic acid solution, forming 3:5-dibromo-2-hydroxystyrene dibromide, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, which separates from light petroleum in small crystals, m. p. 105° , and behaves as a ψ -bromide, reacting with alkalis and alkali carbonates at the ordinary temperature. The dimolecular *o*-vinylphenol is insoluble in alkalis, does not form crystalline derivatives, and, on distillation under the ordinary pressure, decomposes in the same manner as the unimolecular substance.

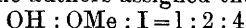
2-Hydroxy- α :4-dimethylstyrene, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CMe}\cdot\text{CH}_2$, b. p. 217° , is prepared from β :4-dimethylcoumaric acid, and when heated, or more rapidly when boiled with hydrochloric acid, forms the polymeride, $(\text{C}_{10}\text{H}_{12}\text{O})_2$; this is obtained as a white powder, m. p. 72 — 74° , b. p. $232^\circ/15$ mm., forms a crystalline, additive compound with ether, and is converted into the unimolecular phenol when distilled under the ordinary pressure. With bromine in glacial acetic acid solution, 2-hydro- α :4-dimethylstyrene forms hexabromothymol, m. p. 152° (148 — 149° : Baeyer and Seuffert, *Abstr.*, 1901, **i**, 216), and on reduction with zinc dust in alkaline solution yields thymol.

6-Hydroxy- α :3-dimethylstyrene, $\text{C}_{10}\text{H}_{12}\text{O}$, b. p. 217° . The benzoyl derivative, $\text{C}_{17}\text{H}_{16}\text{O}_2$, crystallises in plates, m. p. 49° . The polymeride, $(\text{C}_{10}\text{H}_{12}\text{O})_2$, does not form a crystalline additive compound with ether, and therefore could not be obtained free from the unimolecular phenol, into which it is transformed on distillation. These vinylphenols and their polymerides give red to reddish-brown colorations with concentrated sulphuric acid. G. Y.

Preparation of 5-Amino- α -naphthol-3-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 188505).— α -Naphthylamine-5-sulphonic acid, when sulphonated with about 7 parts of fuming sulphuric acid (30% SO_3) first at 80° for eight and then at 120° for thirty hours, furnishes α -naphthylamine-2:5:7-trisulphonic acid, obtained by salting out in the form of its disodium salt; this compound on fusion with potassium hydroxide at 165 — 175° gives rise to 5-amino- α -naphthol-3:6-disulphonic acid, which, after acidifying the fused product, separates as the

alkali hydrogen salt. 5-Amino-*o*-naphthol-3-sulphonic acid is obtained by heating the preceding disulphonate with 10% sulphuric acid at 130—135°. G. T. M.

Constitution of Iodoguaiacol. EUGÈNE TASSILLY and J. LEROIDE (*Bull. Soc. chim.*, 1908, [iv], 3, 124—126).—In a previous paper (Abstr., 1907, i, 515), the authors assigned the constitution



to an iodoguaiacol they prepared, and they now call attention to the fact that this constitution is incorrect in view of the work of Paul (Abstr., 1906, i, 843) and of Mameli (Abstr., 1908, i, 18).

T. A. H.

Separation of *o*- and *p*-Guaiacolsulphonic Acids. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 188506).—The sulphonation of guaiacol is preferably carried out at 30—60°, and the product, when converted into normal calcium salt, is treated with calcium oxide ($\frac{1}{2}$ mol. CaO : 1 mol. guaiacol) or the corresponding amount of calcium chloride in ammoniacal solution. The solution of the basic salts rapidly deposits colourless, prismatic crystals of the basic calcium guaiacol-*p*-sulphonate; the basic salt of the ortho-sulphonate remains in solution. This separation may also be effected by means of the lead salts. A hot solution of the normal lead salts, when treated with lead acetate corresponding with $\frac{1}{2}$ mol. of PbO, gives a white precipitate, which at the boiling temperature contains only the basic para-sulphonate, the ortho-compound separating only on cooling. The patent gives a comparison of the properties of the potassium salts of *o*- and *p*-guaiacolsulphonic acid. The most striking differences are obtained with ammoniacal calcium or barium chloride, or with concentrated nitric acid. The former reagent gives a white precipitate with the para-salt, but no appreciable change with the ortho-isomeride. The latter reagent precipitates yellow dinitroguaiacol (m. p. 122°) from a 10% solution of the para-salt, but merely develops a dark red coloration with the ortho-salt. It is important that the guaiacol-*o*-sulphonic acid, employed therapeutically, should be quite free from the para-compound, as the latter has an unpleasant secondary reaction. G. T. M.

Successive Preparation of Mono- and Di-nitrosoresorcinols and of Resorubrin. MICHELE BARBERIO (*Gazzetta*, 1907, 37, ii, 577—585).—The author has determined the conditions of the reaction of nitrous acid with resorcinol which lead to the simultaneous formation of mono- and di-nitrosoresorcinols and of a colouring matter to which the name resorubrin is given.

The dinitrosoresorcinol obtained has the characters of the one prepared by Fitz (*Ber.*, 1875, 8, 631. Compare also Fèvre, Abstr., 1883, 733; Walker, Abstr., 1884, 1003; Henrich, Abstr., 1903, i, 88).

The mononitrosoresorcinol, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{NO} \cdot 2\text{H}_2\text{O}$, begins to turn brown at 130°, and deflagrates slightly at 134°; it seems to be isomeric with the compound prepared by Fèvre (*loc. cit.*).

Resorubrin is obtained as a dark green, amorphous substance,

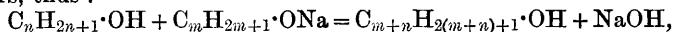
which, when rubbed, acquires a red colour with green fluorescence. It is a sensitive indicator, the violet colour imparted by it to a neutral aqueous solution being turned to blue by a trace of alkali, and to yellow by a trace of acid. In presence of ammonium salts, its sensitiveness is less marked, but is always greater than that exhibited by the other indicators. It dissolves in acetone or methyl, ethyl, or amyl alcohol, and, to a slight extent, in water or ether. Resorubrin behaves very similarly to diazoresorcinol in many ways, and also resembles lacmoid and resorcinol-blue in certain of its characters.

T. H. P.

Preparation of Dithymol: Action of Bromine on Dithymol. HENRI COUSIN and HENRI HERISSEY (*Compt. rend.*, 1908, 146, 292—294. Compare this vol., i, 84; Dianine, Abstr., 1882, 623; Messinger and Vortmann, Abstr., 1889, 1150).—Dithymol is best prepared as follows. A solution of thymol (5 grams) in alcohol (50 c.c.) is poured into water (10 litres) at 50—60°, the liquid shaken, cooled, filtered, and the filtrate treated with (60 c.c.) ferric chloride solution (D 1.26). After three to four days, the precipitate is collected, dissolved in alkali, reprecipitated by acetic acid, and the crude dithymol so obtained purified by recrystallisation from 60% alcohol. The product is identical with Dianine's compound, except that it does not give an orange-yellow coloration with alkalis. Dithymol when brominated in chloroform solution gives *dibromodithymol*, $C_{20}H_{24}Br_2O_2$, which forms yellowish-white, prismatic crystals, m. p. 156—157° (corr.). Dibromodithymol is converted by bromine in chloroform solution into *dibromodithymoquinone* in the form of small, dark, garnet-red needles, m. p. 134° (corr. decomp.), which give an intense blue coloration with guaiacol.

E. H.

Action of Alcohols on Sodium Benzyloxide. MARCEL GUERBET (*Compt. rend.*, 1908, 146, 298—301).—It has been shown previously (Abstr., 1901, i, 182, 207; 1903, i, 3) that, when the primary aliphatic alcohols are heated at 220°—230° with their sodium derivatives, or the sodium compounds of other alcohols, condensation occurs, thus:



the alcohol formed being partially converted by the sodium hydroxide into the corresponding acid with liberation of hydrogen. This reaction is now extended to the aromatic series. When benzyl alcohol is heated at 220—230° with sodium benzyloxide, not phenylbenzylcarbinol, $CH_2Ph\cdot CHPh\cdot OH$, but stilbene, dibenzyl, toluene, and benzoic acid are formed. Probably the stilbene and dibenzyl arise from the decomposition of phenylbenzylcarbinol formed at first, since Limpricht and Schwanert have shown (*Annalen*, 1870, 155, 62) that this alcohol, when heated at 170° with alcoholic potash, loses water, forming stilbene. This change would probably be also effected by sodium benzyloxide, and part of the stilbene formed reduced by nascent hydrogen to dibenzyl. The toluene is probably formed by a reaction similar to the action of heat on benzyl alcohol and alcoholic potash (Cannizzaro *Annalen*, 1854, 92, 114), and also by the reduction of dibenzyl. When sodium benzyloxide is heated with ethyl alcohol, benzyl alcohol and

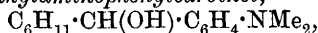
phenylpropyl alcohol, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, are formed. With *n*-propyl alcohol, an *alcohol*, $\text{C}_{10}\text{H}_{14}\text{O}$, b. p. 244—246°, probably having the constitution $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, is produced. E. H.

Action of Organo-magnesium Derivatives on Ethylene Oxides. ERNEST FOURNEAU and MARC TIFFENEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 1227—1233).—It had been shown previously by Jositsch (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 96; 1904, 36, 6) that by the action of epichlorohydrin on ethyl magnesium bromide, a chloro-alcohol having the formula $\text{CH}_2\text{Et}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ or $\text{CH}_2\text{Cl}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{OH}$ is produced, but the authors after repeating this experiment have confirmed Kling's statement (*Bull. Soc. chim.*, 1904, 31, 14) that only the chlorobromohydrin of glycerol is produced in this reaction. This substance is also obtained as a by-product in the following reactions. *Phenylchloroisopropyl alcohol*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, b. p. 153—154°/27 mm., 254—257°/760 mm., D_4^{20} 1.172, is obtained by treating magnesium phenyl bromide with epichlorohydrin in ether. It is converted by potassium hydroxide into allylbenzene oxide (Abstr., 1905, i, 591). With dry oxalic acid, it yields the *formyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{O}\cdot\text{COH})\cdot\text{CH}_2\text{Cl}$, b. p. 250—245°(?), D_4^{20} 1.203, and with acetic anhydride the *acetyl* derivative, b. p. 147—148°/15 mm., D_4^{20} 1.162, and this, when warmed with lead acetate, gives the diacetin of benzylglycol, b. p. 163—166°/13 mm., 282—286°/760 mm., D_4^{20} 1.128. The parent chlorohydrin on oxidation with chromic acid yields a mixture of benzaldehyde, benzoic acid, chloroacetaldehyde, and chloroacetic acid. With cold nitric acid, *p*-nitrobenzoic acid is formed, and, on the first addition of nitric acid, spangles separate, probably of the nitric ester of the chlorohydrin, but this rapidly disappears. *Anisylchloroisopropyl alcohol*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, b. p. 188—190°/24 mm., similarly obtained from magnesium *p*-anisyl bromide, yields, by treatment with potassium hydroxide, estragole oxide (Abstr., 1905, i, 591, this vol., i, 19), b. p. 149—151°/18 mm., D_4^{20} 1.109. *Benzylchloroisopropyl alcohol*, $\text{CH}_2\text{Bz}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, b. p. 156°/22 mm., is similarly obtained from magnesium benzyl chloride.

All these chlorohydrins on treatment with dimethylamine yield amino-alcohols, identical with those obtained from the corresponding iodohydrins (Fournau, Abstr., 1905, i, 57; Daufresne, this vol., i, 19), and, since in these two reactions the same amino-alcohols are produced, it follows that the constitution of the iodohydrins, formed by the action of iodine and yellow mercuric oxide on allylbenzene and on estragole, must be analogous to those of the chlorohydrins mentioned previously, since of the possible formulæ these alone account for the formation of the same amino-alcohols in the two cases. T. A. H.

Hexahydrotriphenylcarbinol [*cyclo*Hexyldiphenylcarbinol]. JULIUS SCHMIDLIN and ROBERT VON ESCHER (*Ber.*, 1908, 41, 447—450).—*Hexahydrotriphenylcarbinol* (*cyclohexyldiphenylcarbinol*), $\text{C}_6\text{H}_{11}\cdot\text{CPh}_2\cdot\text{OH}$, m. p. 71—72° (corr.), prepared from ethyl hexahydrobenzoate and magnesium phenyliodide in ethereal solution, exhibits halochromy, dissolving in concentrated sulphuric acid to a yellow solution (compare Sabatier and Mailhe, Abstr., 1904, i, 809; Hell and Schaal, Abstr., 1907, i, 1049).

cycloHexyl-*p*-dimethylaminophenylcarbinol,



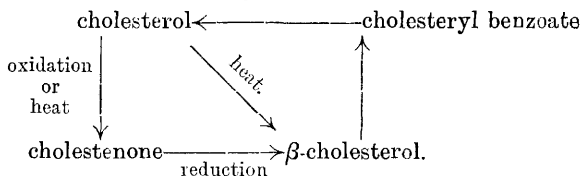
m. p. 86—87° (corr.), is prepared by the action of *p*-dimethylaminobenzaldehyde on magnesium cyclohexyl bromide in ethereal solution.

C. S.

Cholesterol. V. OTTO DIELS and KARL LINN (*Ber.*, 1908, **41**, 260—266).—Although the ketone cholestenone differs markedly from cholesterol, the unsaturated, secondary alcohol from which it is derived, towards oxidising agents (Windaus, *Abstr.*, 1906, i, 174), or towards reduction with sodium and amyl alcohol, the ketone giving rise to β -cholestanol and the alcohol to the α -cholestanol (Diels and Abderhalden, *Abstr.*, 1906, i, 272), they both possess the same ring system, and are very closely related. This has been established by studying the behaviour of cholesterol when heated at 310—315°. The change does not occur with pure cholesterol, only occurring in the presence of a catalyst, such as an iron or zinc compound. During the change, hydrogen is evolved. On extraction of the mass with acetone and cooling, the isomeric β -cholesterol separates, and on recrystallisation forms white needles, m. p. 160°. It is probably a *cis-trans*-modification, as it is very similar to cholesterol in solubility, and forms dibromocholesterol on treatment with bromine; reduction with sodium and amyl alcohol gives α -cholestanol, and on benzylation, cholesteryl benzoate is formed. From the acetone mother liquor cholestenone can be isolated.

If absolute alcohol is used in the reduction of cholestenone with sodium, β -cholesterol is obtained probably mixed with β -cholestanol.

The relationships existing amongst these various compounds must be a very close one, as shown by the scheme :



A comparison of the m. p.'s and rotatory powers of cholesterol from biliary calculi, yolk of egg, and brain, gave 146.5, 147.5, and 148°, and $[\alpha]_D^{20}$ - 24.92, - 24.92, and - 25.65°.

W. R.

Fluorene Series. Spontaneous Formation of an Ozonide.

MAURICE DAUFRESNE (*Bull. Soc. chim.*, 1907, [iv], 1, 1233—1238).—

9-Methylfluorene alcohol, $\text{C}_6\text{H}_4 > \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{OH}$, prepared by Ullmann and

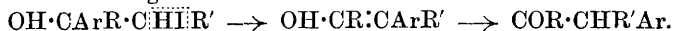
Wurstemberger's method (*Abstr.*, 1906, i, 76), when heated below its melting point, passes into a colourless substance, m. p. 330° (decomp.), which is insoluble in the usual organic solvents, and appears to be an ether. The alcohol on treatment with hydrochloric acid gives a colourless, amorphous substance, m. p. 160° (decomp.), which may be Manchot and Kriesche's diphenylene-ethylene (*Abstr.*, 1905, i, 143). When dissolved in ether and treated with hydrogen chloride, the

alcohol yields a crystalline *substance*, $C_{14}H_{12}O$, m. p. $85-86^{\circ}$, in which the oxygen atom is not present in a hydroxyl or carbonyl group. 9-Ethylfluorene alcohol, similarly prepared (*loc. cit.*), furnishes with aqueous or gaseous hydrogen chloride, diphenylenepropylene, $C_{15}H_{12}$ (*loc. cit.*), the *dibromide* of which melts at 94° . The hydrocarbon oxidises spontaneously in the air, forming an *ozonide*, $C_{15}H_{12}O_3$, which is colourless, amorphous, insoluble, and explodes at 160° . It decomposes spontaneously in air, evolving aldehyde and forming fluorenone. All the ozonides yet described (Harries, *Abstr.*, 1904, i, 361) contain only three atoms of oxygen in place of four atoms as in this compound, and this appears to be the first instance of the spontaneous formation of an ozonide.

T. A. H.

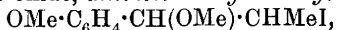
Mechanism of Transposition of Phenyl in Aromatic Iodo-hydrins MARC TIFFENEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 1205—1220).—A theoretical paper, dealing with the changes accompanying the elimination from an aromatic iodohydrin of hydrogen and iodine from (1) the same carbon atom, and (2) from different carbon atoms.

The first case comprises iodohydrins derived from α -glycols by the substitution of an iodine atom for the stronger of the two alcohol functions, and includes the types $Ar \cdot CH(OH) \cdot CH_2I$, $Ar \cdot C(OH)R \cdot CH_2I$, $Ar \cdot CH(OH) \cdot CHI \cdot R$, and $Ar \cdot C(OH)R \cdot CHR'$, in which the change proceeds according to the scheme



Until recently, this view has rested wholly on negative evidence (*Abstr.*, 1907, i, 39), only the aldehydes or ketones forming the end products being known, but the intermediate products (homologues of vinyl alcohol) have recently been isolated in some cases, thus affording experimental proof of the accuracy of this view (*Abstr.*, 1907, i, 922; this vol., i, 19).

When anethole, dissolved in methyl alcohol, is treated with iodine and yellow mercuric oxide, *anethole methyl iodohydrin*,



is formed; this, on treatment with potassium hydroxide in alcohol, yields α -methoxyanethole, and, when dissolved in ether and shaken with yellow mercuric oxide, gives the corresponding vinyl ether, $OMe \cdot C_6H_4 \cdot CMe : CH \cdot OMe$, already described (*loc. cit.*). *isoSafrole* furnishes under analogous conditions a methyl iodohydrin, which is hydrolysed by potassium hydroxide in alcohol to form α -methoxy-*isosafrole*, b. p. 269° , and, on agitation with yellow mercuric oxide in ether, yields the *vinyl ether*, $CH_2O_2 \cdot C_6H_3 \cdot CMe : CH \cdot OMe$, b. p. $280-282^{\circ}$, which is hydrolysed by dilute acids to the methylene ether of dihydroxyhydratropaldehyde, $CH_2O_2 \cdot C_6H_3 \cdot CHMe \cdot CHO$.

The second case comprises iodohydrins derived from the α -glycols by the substitution of an iodine atom for the weaker alcohol function, and includes the types $Ar \cdot CHI \cdot CH(OH) \cdot R$, $Ar \cdot CH(OH) \cdot CRR'I$, and $R \cdot CH(OH) \cdot CArR'I$, which behave like the glycols (*Abstr.*, 1906, i, 662, 724, 965; 1907, i, 130, 404; Faworsky, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 741), probably forming first, by the elimination

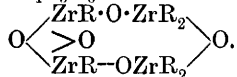
of hydrogen and iodine, diethylenic oxides, $2\text{Ar}\cdot\text{CH}(\text{OH})\cdot\text{CRR}'\text{I} \rightarrow \text{RR}'\text{C} \begin{array}{c} \text{CHAr}\cdot\text{O} \\ \text{O}\cdot\text{CHAr} \end{array} \text{CRR}'$, which undergo asymmetrical fission, forming unstable, intermediate compounds of the type $-\text{CRR}'\cdot\text{CR}''\text{R}'''\cdot\text{O}-$, that in turn undergo transformation in various ways, depending on the position and nature of the substituent groups, forming ultimately aldehydes or ketones.

T. A. H.

Mechanism of the Transposition of Phenyl in Iodohydrins and Aromatic Glycols. MARC TIFFENEAU (*Compt. rend.*, 1908, 146, 29—32).—The author has put forward the view (Abstr., 1907, i, 404) that only (1) the α -glycols, α -chlorohydrins, and tetra-substituted ethylene oxides, and (2) the poly-substituted aromatic glycols of the general formulæ $\text{OH}\cdot\text{CHAr}\cdot\text{CRR}'\cdot\text{OH}$ and $\text{OH}\cdot\text{CHAr}\cdot\text{CHAr}'\cdot\text{OH}$, and the aromatic halohydrins of the general formulæ $\text{OH}\cdot\text{CHAr}\cdot\text{CHXR}'$ and $\text{OH}\cdot\text{CHAr}\cdot\text{CRR}'\text{X}$, are capable of undergoing intramolecular change when transformed into aldehydes or ketones, not as Houben and Führer (this vol., i, 73) have assumed, that these compounds always undergo such change. The author has previously emphasised the fact that the molecular transpositions are conditioned by the nature of the reagent employed (Abstr., 1907, i, 39), some reagents (HgO , AgNO_3 , Ag_2O) effecting the migration of the aromatic radicle, whilst others (alcoholic potash and the alkali ethoxides) withdraw a molecule of hydracid without producing intramolecular change (Abstr., 1907, i, 922, this vol., i, 19). $\alpha\beta$ -Triphenylethane- $\alpha\beta$ -diol, when heated with sulphuric acid, gives, not triphenylacetaldehyde, but a compound, $\text{C}_{20}\text{H}_{16}\text{O}$, m. p. 136° , identical with Biltz's triphenylvinyl alcohol (Abstr., 1899, i, 439).

E. H.

Glucinum and Zirconium Benzoates. SEBASTIAN M. TANATAR and E. K. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1630—1632. Compare Abstr., 1907, i, 888).—Glucinum benzoate is formed by the action of an aqueous solution of sodium benzoate on an acid solution of glucinum acetate. It is a white, amorphous substance, similar in properties to compounds of the type Gl_4OR_6 , and yields non-conducting solutions in benzene and acetone. Its structural formula is probably $\text{R}_3\text{Gl}\cdot\text{O}\cdot\text{GlR}_2\cdot[\text{OGlR}_2]\cdot\gamma\text{OGlR}_3$ (where $\text{R} = \text{C}_7\text{H}_5\text{O}_2$). The zirconium salt, $\text{Zr}_4\text{O}_5\text{R}_6$, is similar to the glucinum salt, and can be represented thus:



Z. K.

Esterification of Benzoic Acid. ISAAC K. PHELPS, M. A. PHELPS, and R. W. OSBORNE (*Amer. J. Sci.*, 1908, [iv], 25, 39—48. Compare Abstr., 1907, i, 823; Fischer and Speier, Abstr., 1896, i, 201; Taylor, Abstr., 1905, i, 852).—The method described previously for the preparation of ethyl succinate has been applied to the preparation of ethyl benzoate. The amount obtained varies with the proportion of alcohol and hydrochloric acid used, and is increased by the addition of fused zinc chloride. By passing the vapour of 400 c.c. of absolute alcohol, containing 5 grams of hydrogen chloride, into 50 grams of

benzoic acid and 10 grams of zinc chloride maintained at 100—110° for four hours, the theoretical yield of ester was obtained. Complete esterification could also be attained by treating 50 grams of benzoic acid and 2 grams of sulphuric acid with 200 c.c. of absolute alcohol.

R. J. C.

Preparation of Benzoylalkylamino-alcohols. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 187209).—The benzoyl derivatives of the alkylamino-alcohols, which have valuable anæsthetic properties, can be prepared by heating the alkyl benzoates with an alkylamino-alcohol.

β-Diethylaminoethyl benzoate, $\text{Ph}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{Et})_2$, a colourless oil, b. p. 132°/5 mm., prepared by heating together methyl benzoate and *β*-diethylaminoethyl alcohol, when treated with alcoholic hydrogen chloride, yields a soluble *hydrochloride*, needles, m. p. 124°.

β-Dimethylaminoethyl benzoate, $\text{Ph}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{Me})_2$, uncrystallisable oil; *hydrochloride*, lustrous needles, m. p. 148°, was obtained by heating phenyl benzoate and *β*-dimethylaminoethyl alcohol at 170—180°.

β-Diamylaminoethyl benzoate, $\text{Ph}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, an oil obtained from ethyl benzoate and *β*-diamylaminoethyl alcohol at 190°, furnishes a *hydrochloride*, needles, m. p. 107—108°, and soluble in water, alcohol acetone, and ethyl acetate, and an acid *oxalate*, m. p. 158°, soluble in dilute alcohol.

Diethylaminoisopropyl benzoate, $\text{Ph}\cdot\text{CO}_2\cdot\text{CH}(\text{Me})\cdot\text{CH}_2\cdot\text{N}(\text{Et})_2$, an uncrystallisable oil obtained from methyl benzoate and diethylaminoisopropyl alcohol, gives rise to a very soluble *hydrochloride* and *oxalate*, and a *picrate*, crystallising from dilute alcohol in yellow spicules.

G. T. M.

Nitration of Methyl 3-Nitro-4-dimethylaminobenzoate. FRÉDÉRIC REVERDIN and A. DE LUC (*Bull. Soc. chim.*, 1908, [iv], 3, 126—133; *Ber.*, 1908, 41, 501—502; *Arch. Sci. phys. nat.*, 1908, 25, 133—145).—In attempting to nitrate 3-nitro-4-dimethylaminobenzoic acid (Abstr., 1907, i, 620), a small quantity of a substance was obtained which was believed to be a polynitro-derivative of the acid, but has since been found to be a mixture of products, and further experiments have shown that it is impossible to obtain polynitro-derivatives of this acid.

Methyl 3-nitro-4-dimethylaminobenzoate (Abstr., 1906, i, 273), when treated with nitric acid (D 1.52) in presence of acetic acid, yields *methyl 3:5-dinitro-4-nitrosomethylaminobenzoate*, m. p. 88°, which crystallises in leaflets from dilute alcohol or acetic acid, or a mixture of benzene with light petroleum. It gives Liebermann's reaction, and its solution in alcohol gives with solution of sodium hydroxide a reddish-violet colour. When boiled with mineral acids, it yields *3:5-dinitro-4-methylaminobenzoic acid*, m. p. 223—224°, which crystallises in lemon-yellow, prismatic needles, and is coloured reddish-brown by sodium hydroxide in alcohol. *Methyl 3:5-dinitro-4-methylaminobenzoate*, m. p. 123—124°, obtained as a by-product in the same reaction, or when the parent ester is heated with phenol, crystallises in orange-yellow spangles.

When boiled with sodium carbonate solution, or when merely moistened with sodium hydroxide solution in alcohol and set aside, methyl 3:5-dinitro-4-nitrosomethylaminobenzoate furnishes, first, 3:5-dinitro-4-methylaminobenzoic acid and, finally, 3:5-dinitro-4-hydroxybenzoic acid, m. p. about 245°, which forms yellow needles from acetic acid.

When methyl 3-nitro-4-dimethylaminobenzoate is treated with nitric acid in presence of sulphuric acid at 16°, methyl 3:5-dinitro-4-nitromethylaminobenzoate, m. p. 126°, crystallising in almost white, nacreous spangles from a mixture of benzene and light petroleum, is formed, together with some 3-nitro-4-methylaminobenzoic acid. The first of these products gives a fine reddish-violet colour with sodium hydroxide in alcohol, and when boiled with dilute hydrochloric acid or with sodium carbonate solution is, in part, converted into the free acid, m. p. 200°, which crystallises in lemon-yellow spangles.

When nitric acid (D 1.52) is added to the parent ester, dissolved in sulphuric acid, and the temperature raised to 35–40°, methyl 3-nitro-4-methylaminobenzoate, m. p. 145°, crystallising in lemon-yellow prisms from a mixture of benzene and light petroleum, is formed.

If the nitration is effected with nitric acid (D 1.52) alone at -2° to 4° , methyl 3:5-dinitro-4-nitromethylaminobenzoate is formed, whereas with acid of D 1.2–1.4, at the ordinary temperature, or on warming for a short time at 100°, methyl 3:5-dinitro-4-nitrosomethylaminobenzoate is produced.

T. A. H.

Addition of Halogens to Cinnamic Acid and Some of its Derivatives. ARTHUR MICHAEL and HOWARD D. SMITH (*Amer. Chem. J.*, 1908, 39, 16–28).—It has been shown previously (Abstr., 1896, i, 130, 133) that in the case of stereoisomeric dibasic acids, the application of the addition-elimination principle provides a means of expressing the relationship between their physical and chemical properties. Thus, of two such stereoisomerides, the unstable maleinoid form should have a lower m. p. and a greater solubility than the fumaroid form. The stereoisomeride of higher m. p. is the form which is produced by the addition of hydrogen halide or halogen to the corresponding acetylenecarboxylic acid, and also loses the added atoms more easily with regeneration of the original acid.

These generalisations were applicable to the cinnamic acids until Liebermann and Finkenbeiner (Abstr., 1905, i, 663) observed that, when cinnamic acid is treated with chlorine in the dark, a dichloride is produced of m. p. 86° instead of the stereoisomeric form, of m. p. 168°. From this, it would appear as if the dichloride of higher m. p. were the primary addition product of *allocinnamic* acid instead of that of cinnamic acid. On the other hand, it has been shown by Liebermann (Abstr., 1891, 832; 1896, i, 526) that both *allocinnamic* acid and its methyl ester react in the dark with excess of bromine, with formation of 30–40% of a dibromide of lower m. p., together with the ordinary form, and that the products of lower m. p. are not obtained from cinnamic acid and its ester under the same conditions.

It is now found that when a cold solution of cinnamic acid and

chlorine in carbon tetrachloride is exposed to direct sunlight, the chloride of higher m. p. is formed together with a relatively small amount of the stereoisomeride, but that a much larger proportion of the latter form is produced if the light is passed through solutions capable of absorbing the ultra-violet rays. It is therefore concluded that the conversion of the *allodichloride* into the ordinary form is due to absorption of energy from the actinic rays. It has also been observed that a considerable quantity of the *allo*-form is produced if the reaction takes place in diffused light. Methyl cinnamate and cinnamyl chloride behave in a similar manner. *allo*Cinnamic acid, however, yields the dichloride of higher m. p. as the primary additive product together with a small quantity of an oily dichloride which may be the dichloride of lower m. p. It is considered, however, that the latter compound is probably formed from some cinnamic acid produced by the transformation of *allocinnamic* acid by the action of the halogen.

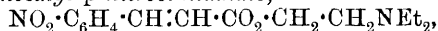
Experiments on the action of bromine on methyl and ethyl cinnamates have shown that, under the conditions in which a quantitative yield of the *allodichloride* is obtained, only a small quantity of the *allodibromide* is produced, and that the yield of this substance depends largely on the solvent employed. It is evident that these additive reactions are governed by subtle conditions, which vary with the reagent to an extent quite unknown in other groups of unsaturated acids. These results confirm those of Michael and Whitehorne (Abstr., 1902, i, 32), but do not agree with those of Sudborough and Thompson (Trans., 1903, 83, 671), who were unable to obtain more than a trace of ethyl cinnamate *allodibromide*. E. G.

Preparation of Alkylaminoalkyl Aminocinnamates.

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 187593).—The alkylaminoalkyl esters of the aminocinnamic acids may be prepared by the following methods: (1) Reduction of an alkylaminoalkyl nitrocinnamate, (2) alkylation of the aminocinnamic acids with an alkylaminocarbonol in the presence of hydrochloric or sulphuric acid, and (3) warming together an alkylaminocarbonol and an alkylaminocinnamate.

These new alkylamino-esters are valuable anaesthetics, greatly surpassing in this respect the alkylaminoalkyl benzoates.

β-Diethylaminoethyl *p*-nitrocinnamate,



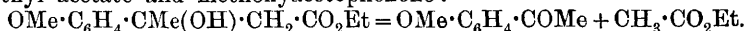
reddish-yellow crystals, m. p. 44°, prepared by condensing *p*-nitrocinnamyl chloride with *β*-diethylaminoethyl alcohol on reduction with tin and hydrochloric acid, yields *β*-diethylaminoethyl *p*-aminocinnamate, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2$, pale yellow spicules, m. p. 89°.

The patent contains references to seven other alkylamino-esters derived from the three aminocinnamic acids. G. T. M.

β-Alkylcinnamic Acids. III. GEORG SCHROETER [with OTTO BUCHHOLZ] (*Ber.*, 1908, 41, 5—12. Compare Abstr., 1904, i, 415; 1907, i, 530).—A 90% yield of *β*-methylcinnamic acid from acetophenone and ethyl bromoacetate is considered to be unattainable

and incorrect (compare Rupe and Busolt, this vol., i, 23). In the case of substituted β -methylcinnamic acids where the substitution occurs in the nucleus, the yields obtained are similar to that of β -methylcinnamic acid itself. The yields of side-chain homologues, however, are almost quantitative.

p-Methoxy- β -methylcinnamic acid, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$, m. p. 156.5° , obtained from *p*-methoxyacetophenone, ethyl iodoacetate, magnesium, and benzene, heating the crude ethyl anisylmethylhydracrylate formed, first at 100 – 120° and then at 150° , distilling, and subsequently hydrolysing the ester, crystallises from alcohol. Should the hydracrylic ester be distilled, it is decomposed into ethyl acetate and methoxyacetophenone:



The corresponding *p*-ethoxy-derivative, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$, separates from carbon disulphide or alcohol in well-formed crystals, and also forms a liquid, crystalline phase (compare Vorländer, Abstr., 1907, ii, 70, 337), m. p., I, 122.2 – 122.8° , m. p. II, 159.2 – 159.4° ; *p*- β -dimethylcinnamic acid forms two solid phases and one liquid crystalline phase.

β -Phenyl- β -*n*-propylhydracrylic acid, $\text{OH} \cdot \text{CPrPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, obtained when the crude ester is hydrolysed first and distilled afterwards, separates from benzene in crystals, m. p. 121.5 – 122° ; its silver salt, $\text{C}_{12}\text{H}_{15}\text{O}_3\text{Ag}$, is white. When the hydracrylic acid is dissolved in sulphuric acid and ice added, solid β -*n*-propylcinnamic acid is obtained (Abstr., 1907, i, 531). If, however, the crude hydracrylic ester is distilled and subsequently hydrolysed, a mixture of two possibly stereoisomeric propylcinnamic acids results.

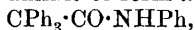
β -Phenyl- β -*n*-butylhydracrylic acid, $\text{OH} \cdot \text{CPh}(\text{C}_4\text{H}_9) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, from *n*-valerophenone, crystallises from carbon disulphide, m. p. 106 – 107° , and gives β -*n*-butylcinnamic acid, $\text{CPh}(\text{C}_4\text{H}_9) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which crystallises from petroleum, m. p. 48 – 49° , on solution in sulphuric acid.

The β -ethyl-, β -*n*-propyl-, and β -*n*-butyl-phenylhydracrylic acids were compared as regards their stability, by heating the acids in tubes connected with flasks containing baryta water. The *n*-propyl acid gave a regular stream of carbon dioxide at 135° , the *n*-butyl at 145° , and the ethyl at 150° . The quantities of carbon dioxide evolved, after heating for thirty minutes at that temperature, were approximately ethyl : propyl : butyl = $2 : 5 : 3$. W. R.

Triphenylacetic and Tritolylacetic Acids. JULIUS SCHMIDLIN and HERBERT H. HODGSON (*Ber.*, 1908, 41, 438–447).—The authors use the theory advanced by Werner to explain the mobility of the atom or group attached to the triphenylmethyl complex in triphenylmethane derivatives (Abstr., 1906, i, 436), to account for the stability of the halogen in triphenylacetyl chloride. By the theory, the carbonyl group must have a residual affinity which, exerted on the halogen atom, endows the latter with its exceptional stability. The theory is extended to include the cases of picryl chloride and *s*-trinitrobenzoyl chloride, the halogen atom in the former being, as is well known, very easily displaced, whilst the latter is affected only slightly by boiling water (compare V. Meyer, Abstr., 1895, i, 91).

Triphenylacetyl chloride, $\text{CPh}_3\cdot\text{COCl}$, prepared by Fischer's method (Abstr., 1905, i, 263), separates from benzene in colourless needles or prisms, m. p. $116-118^\circ$ (decomp.), but after repeated crystallisation the m. p. rises to 128° (decomp.), carbon monoxide being evolved in both cases. The acid chloride is unaffected by moist air, can be crystallised from alcohol, and is only slowly attacked by hot 10% potassium hydroxide. It yields the following esters after being heated for eight hours with the corresponding alcohol: *methyl* ester, m. p. 186° (corr.), distils without decomposition, but after prolonged heating at the b. p. loses carbon dioxide; *ethyl* ester, m. p. $120-121^\circ$ (corr.), distils unchanged, but after twenty minutes' heating at the b. p. loses carbon dioxide and ethylene, and yields triphenylmethane; *isoamyl* ester, m. p. $78.5-79.5^\circ$ (corr.). The *phenyl* ester, obtained from the acid chloride and phenol after four hours on the water bath, has m. p. $124.5-125^\circ$ (corr.), and carbonises on distillation.

Triphenylacetyl chloride reacts in benzene with dry ammonia to form triphenylacetamide, m. p. $246-247^\circ$ (corr.) (E. and O. Fischer give m. p. 210°), and with aniline to form *triphenylacetanilide*,



m. p. $173.5-174.5^\circ$ (corr.).

p-Tritolylacetic acid, $\text{C}(\text{C}_7\text{H}_7)_3\cdot\text{CO}_2\text{H}$, m. p. $226-228^\circ$ (corr.), is ultimately obtained when carbon dioxide is passed into an ethereal solution of magnesium *p*-tritolylmethyl chloride at the time of its formation. It loses carbon dioxide above 250° . C. S.

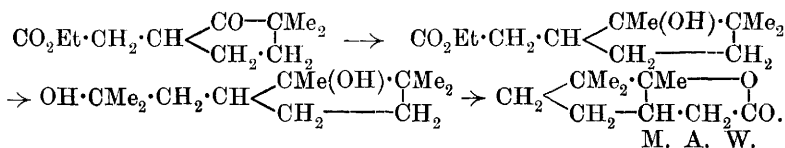
Syntheses in the Camphor Series. Complete Synthesis of β -Campholenolactone. GUSTAVE BLANC (*Compt. rend.*, 1908, 146, 77-79).—The author has synthesised β -campholenolactone from *aa*-dimethyladipic acid through a similar series of reactions to those whereby the lactone of 1:3-dimethylcyclopentane-3-ol-4-acetic acid was obtained from β -methyladipic acid (this vol. i, 20).

Ethyl aa-dimethyladipate, b. p. $148^\circ/18\text{ mm.}$, when treated with sodium, yields a sodium derivative, $\text{CO}_2\text{Et}\cdot\text{CNa}\begin{matrix} \text{CO-CMe}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix}$, which condenses

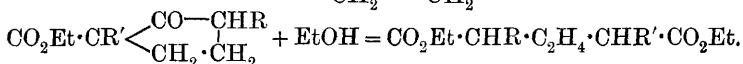
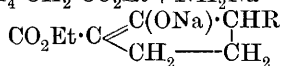
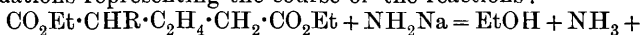
with ethyl bromoacetate to form 3-carbethoxy-1:1-dimethylcyclopentane-2-one-3-acetic acid, $\text{CO}_2\text{Et}\begin{matrix} \text{CO-CMe}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix}\text{CH}_2\text{CO}_2\text{Et}$, a colourless, oily liquid, b. p. $165^\circ/12\text{ mm.}$, which on hydrolysis yields 1:1-dimethyl-

cyclopentane-2-one-3-acetic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}\begin{matrix} \text{CO-CMe}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix}$, m. p. 85° , identical with the acid already described (Abstr., 1905, i, 680); it forms an *oxime*, m. p. 160° , a semicarbazone, m. p. 210° , and is reduced by sodium and alcohol to form 1:1-dimethylcyclopentane-2-ol-3-acetic acid, $\text{C}_9\text{H}_{16}\text{O}_3$, m. p. $109-110^\circ$, together with a small quantity of the lactone, $\text{C}_9\text{H}_{14}\text{O}_2$.

The *methyl* ester of the ketonic acid has b. p. $120^\circ/14\text{ mm.}$; the *ethyl* ester, b. p. $129^\circ/13\text{ mm.}$, is converted by the action of magnesium methyl iodide and subsequent hydrolysis into a *glycol*, b. p. $130^\circ/15\text{ mm.}$, which yields β -campholenolactone when treated with acids; the following scheme represents the last three stages of the synthesis:



Synthesis of Racemic Dihydrocamphoric Acid. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1908, 146, 82—84).—When the esters of α -alkyladipates (Abstr., 1900, i, 171) are treated with sodamide, then corresponding ester of 3-alkyl-2-cyclopentanone-carboxylic acid is formed, and the 1:3-dialkyl substituted derivative of this acid by the action of sodium ethoxide at 140—150° yields the corresponding ester of α : δ -dialkyladipic acid, the following equations representing the course of the reactions:

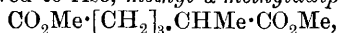


By means of this method, the authors have prepared α -methyl- δ -isopropyladipic acid and δ -methyl- α -isopropyladipic acid; the two products, however, were identical, and consisted of a crystalline acid, m. p. 110—111°, and an isomeric liquid, which was probably the eutectic mixture of the two stereoisomerides (compare Crossley and Perkin, *Trans.*, 1898, 73, 23; Martine, *Abstr.*, 1902, i, 629; Blanc, *Abstr.*, 1905, i, 681).

M. A. W.

Syntheses by means of Methyl and Ethyl Adipates. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1908, 146, 138—139).—Methyl adipate is transformed by sodamide into the sodium derivative of methyl cyclopentanonecarboxylate, $\begin{array}{l} \text{CH}_2 \text{---} \text{CH}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Me}) \end{array} > \text{CO}.$

The latter ester is a colourless liquid with a sweetish odour, b. p. 105°/19 mm., D_4^{20} 1.145. Its semicarbazone forms colourless crystals, m. p. 167°. The sodium compound, when treated with methyl iodide, gives methyl methylcyclopentanone-1-carboxylate, $\begin{array}{l} \text{CH}_2 \text{---} \text{CH}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CMe}(\text{CO}_2\text{Me}) \end{array} > \text{CO}$, a liquid having b. p. 105—106°/15 mm., D_4^{20} 1.103, which is insoluble in alkalis, and does not form a copper derivative, but forms a semicarbazone, brilliant spangles, m. p. 187°. If in the preparation of methyl methylcyclopentanonecarboxylate the temperature is allowed to rise, methyl α -methyladipate,



a liquid, b. p. 112—114°/10 mm., D_4^{20} 1.054, is formed. This is converted by cold aqueous ammonia into α -methyladipodiamide, which forms small white crystals, m. p. 186.5°. By the action of sodamide on methyl α -methyladipate, methyl methylcyclopentane-2-one-3-carboxylate, $\begin{array}{l} \text{CH}_2 \text{---} \text{CHMe} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Me}) \end{array} > \text{CO}$, is formed. This is a liquid, b. p. 113—114°/19 mm., which forms a semicarbazone, m. p. 118°.

Ethyl methylcyclopentanone-1-carboxylate (Bouveault, Abstr., 1900, i, 171), when heated with sodium ethoxide, is converted into *ethyl α-methyladipate*, a liquid, b. p. 132—134°/15 mm., D_4^{20} 1.010, which reacts with sodamide giving *ethyl methylcyclopentane-2-one-3-carboxylate*, a colourless liquid, b. p. 105°/12 mm., D_4^{20} 1.057; this gives a non-crystallisable semicarbazone. The sodium compound of the latter ester, on treatment with an isopropyl halide, forms *ethyl methyl-3-isopropylcyclopentane-2-one-3-carboxylate*,

$$\begin{array}{c} \text{CH}_2 \text{---} \text{CHMe} \\ | \\ \text{CH}_2 \cdot \text{CPr}^\beta (\text{CO}_2\text{Et}) \end{array} > \text{CO}, \text{ b. p. } 123\text{---}124^\circ/10 \text{ mm.},$$
 which, when heated with alcoholic potash, gives

methyl-3-isopropylcyclopentane-2-one,
$$\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 \cdot \text{CHPr}^\beta \end{array} > \text{CO}, \text{ a liquid, b. p. } 181^\circ,$$

of a camphor-like odour. This forms a *semicarbazone*, m. p. 210°, and an *oxime*, b. p. 127°/22 mm., and is found to be identical with dihydrophorone. But by heating ethyl methyl-3-isopropylcyclopentanonecarboxylate with sodium ethoxide (1 mol.) dissolved in absolute alcohol, at 150° in an autoclave, *ethyl α-methyl-δ-isopropyladipate*, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot [\text{CH}_2]_2 \cdot \text{CHPr}^\beta \cdot \text{CO}_2\text{Et}$, b. p. 144—146°/14 mm., is formed, and on saponification gives the corresponding *acid*, m. p. 110—111°, b. p. 215—220°/14 mm. *Ethyl 1-isopropylcyclopentanonecarboxylate*, prepared by the method used for the methyl compound, is difficult to obtain pure; it is a liquid, b. p. 141—143°/27 mm., which gives a *semicarbazone*, m. p. 141—142°. The ester, when saponified by alcoholic potash, gives a small quantity

of 1-isopropylcyclopentane-2-one,
$$\begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CHPr}^\beta \end{array} > \text{CO}, \text{ a liquid, b. p. } 174^\circ,$$

with a pleasant camphor-like odour, which forms a *semicarbazone*, m. p. 200—201°, but the chief product consists of Blanc's *α-isopropyladipic acid* (Abstr., 1905, i, 681), b. p. 222°/12 mm., m. p. 66—67°. The *ethyl ester*, a liquid having b. p. 148—149°/17 mm., D_4^{20} 0.9876, when condensed by sodamide, gives *ethyl isopropylcyclopentane-2-one-3-carboxylate*,

$$\begin{array}{c} \text{CH}_2 \text{---} \text{CHPr}^\beta \\ | \\ \text{CH}_2 \cdot \text{CH} (\text{CO}_2\text{Et}) \end{array} > \text{CO}, \text{ b. p. } 132\text{---}136^\circ/14 \text{ mm.}, D_4^{20} 1.028.$$

The latter is easily methylated, giving *ethyl 1-methyl-3-isopropylcyclopentane-2-one-1-carboxylate*, a liquid, b. p. 128—129°/12 mm., D_4^{20} 1.027, which behaves like its isomeride towards alcoholic potash and sodium ethoxide. *α-Methyladipic* and *α-methyl-δ-isopropyladipic* acids have been characterised by Locquin's method (Abstr., 1904, i, 644). *Methyl-α-ketol α-methyladipate*,

$\text{COMe} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{CHMe} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, b. p. 230°/12 mm., forms a *disemicarbazone*, m. p. 157—160° (decomp.).

Methyl-α-ketol α-methyl-δ-isopropyladipate,

$\text{COMe} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{CHMe} \cdot [\text{CH}_2]_2 \cdot \text{CHPr}^\beta \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, b. p. 230°/12 mm. (approx.), gives a *disemicarbazone*, m. p. 162° (decomp.).
E. H.

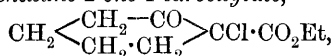
Transitions from Hydroaromatic to Aromatic Compounds.

I. Phenol and Salicylic Acid from Hydrobenzene Derivatives. ARTHUR KÖTZ and C. GÖTZ (*Annalen*, 1907, 358, 183—204). —A study of the relation of the hydroaromatic to the aromatic

derivatives of the six carbon atom ring. The work of previous authors has shown that these hydroaromatic compounds are converted into the corresponding benzene derivatives by intramolecular change, as that of triketohexamethylene into trihydroxybenzene, or by dehydrogenation, when the hydrogen may be removed as a hydrohaloid, as water, or as hydrogen sulphide. The present paper gives an account of the gradual conversion of *cyclohexanol* (hexahydrophenol) and *cyclohexane-2-ol-1-carboxylic acid* (hexahydrosalicylic acid) into phenol and salicylic acid respectively. Schemes are given showing the various intermediate substances transformable into each other by intramolecular change and formed in the stages of the gradual dehydrogenation by means of halogens. This transformation of hydroaromatic into aromatic compounds is a reversal of Sabatier and Senderens' reduction of phenol and of the reduction of salicylic acid by means of sodium and alcohol, but differs from these in that it permits of the isolation of the intermediate products.

The action of 1 mol. of bromine or chlorine on 1 mol. of *cyclohexanol* in presence of water and calcium carbonate leads to the formation of *cyclohexanone*, whilst if 2 mols. of the halogen are employed, 2-bromocyclohexane-1-one, C_6H_9OBr , is formed. This is obtained also in a 60—65% yield by the action of bromine on *cyclohexanone*, as a strongly refracting oil, b. p. 89—90°/14 mm., and gradually decomposes, evolving hydrogen bromide on exposure to air. When treated with aniline in anhydrous ethereal solution, 2-bromocyclohexanone loses hydrogen bromide and yields Δ^2 -cyclohexenone, $CH_2 < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH = CH \end{smallmatrix} > CO$, which is obtained as a mobile oil, b. p. 63°/14 mm., decolorises permanganate instantaneously, and forms a *semicarbazone*, crystallising in prisms, m. p. 161°. The action of 1 mol. of bromine on the unsaturated ketone in carbon disulphide solution leads to the formation of hydrogen bromide and phenol.

Ethyl 1-chlorocyclohexane-2-one-1-carboxylate,



formed by the action of chlorine on ethyl *cyclohexane-2-one-1-carboxylate* (Kötz and Michels, Abstr., 1906, i, 666), cooled by ice, is obtained as an oil, b. p. 138—139°/13 mm., which has a sharp odour and does not give a blue coloration with ferric chloride. The corresponding *bromo-ester*, $C_9H_{15}O_3Br$, is obtained as a light yellow oil, b. p. 144°/13 mm., has a suffocating odour, and on distillation under the ordinary pressure yields *ethyl 2-hydroxy- $\Delta^{2:6}$ -cyclohexadiene-carboxylate* ($\Delta^{2:6}$ -dihydrosalicylate), $CH_2 < \begin{smallmatrix} CH : C(OH) \\ CH_2 - CH \end{smallmatrix} > C \cdot CO_2Et$, b. p. 104—105°/13 mm., which decolorises potassium permanganate and gives a brown coloration with ferric chloride. The *acid*, $C_7H_8O_3$, crystallises in white leaflets, and sublimes in needles, m. p. 128°.

Ethyl 1-bromo-2-hydroxy- $\Delta^{2:5}$ -cyclohexadienecarboxylate, $C_9H_{11}O_3Br$, formed by the action of bromine on ethyl dihydrosalicylate in carbon disulphide solution cooled with ice, is obtained as a yellow oil, b. p. 155°, under reduced pressure, and, when distilled under the ordinary pressure, evolves hydrogen bromide and yields ethyl salicylate.

The action of 2 mols. of bromine on ethyl *cyclohexane-2-one-1-carboxylate* and hydrolysis of the product leads to the formation of *3-bromosalicylic acid*, $C_7H_5O_3Br$, which sublimes in needles, m. p. 184° .
G. Y.

Substances which play a Part in the Synthesis of Salicylic Acid. JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1908, 27, 58—77).—The theory is put forward that in the synthesis of sodium salicylate, sodium phenoxide (2 mols.) and carbon dioxide (1 mol.) first form an additive product of the type $C(OPh)_2(ONa)_2$, which, after a molecular transposition into a salicylic derivative, decomposes into sodium salicylate and sodium phenoxide, or basic sodium salicylate and phenol (compare Claisen, *Abstr.*, 1905, i, 258). This view is supported by the formation of sodium salicylate and phenetole when ethyl phenyl carbonate is heated with sodium phenoxide (Hentschel, *Abstr.*, 1883, 588), and the production of sodium salicylate by heating sodium phenoxide and sodium ethyl carbonate in sealed tubes at 200° (Schmitt, *Abstr.*, 1885, 982). The author confirms the observations of Hentschel, that phenyl carbonate, when heated at 180° — 190° with sodium phenoxide (2 mols.) in a current of dry hydrogen, gives neither diphenyl ether nor salicylic acid, and of Schmitt, that sodium phenyl carbonate is converted quantitatively into sodium salicylate when heated in a sealed tube at 120° , but, having repeated Bruyn and Tymstra's experiments, fails to confirm their results (*Abstr.*, 1905, i, 209, 439). According to the theory of these authors, after heating sodium phenyl carbonate at 100° , there should be no excess pressure within the tube, whereas this is invariably observed.

When sodium phenyl carbonate is treated with dry acetone in an apparatus arranged to prevent access of atmospheric moisture (a detailed description is given in the paper), carbon dioxide is evolved, and the residue contains phenol and sodium (as normal and basic carbonate) in the proportions required by the equation $3ONa \cdot CO \cdot OPh + 2H_2O = 3Ph \cdot OH + CO_2 + Na_2CO_3 + NaHCO_3$. All external water having been excluded, that used in the reaction probably arises from condensation of the acetone, but no such condensation product was detected. Sodium phenoxide dissolves in boiling acetone, from which it crystallises on cooling in needles containing $1\frac{1}{2}$ mols. of acetone, which is lost in a vacuum over sulphuric acid. Sodium salicylate dissolves in about 21 parts of acetone at 16° , but the basic salt is insoluble. In acetone, sodium salicylate has the abnormally high molecular weight 282.

When sodium phenyl carbonate is heated in a sealed tube in a boiling water-bath for 100 hours and the product treated with acetone in the above apparatus, carbon dioxide is evolved corresponding with 50—60% of unchanged sodium phenyl carbonate, and the residue contains about 14% of phenol and about 10% of sodium salicylate. No basic sodium salicylate and no additive product were observed, the latter possibly having been decomposed by the acetone. The suggestion is made that the sodium phenoxide *o*-carboxylic acid described by Bruyn and Tymstra is really an additive compound of the nature proposed by the author.
E. H.

Preparation of Alkylaminoalkyl Esters of Salicylic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 188571).—The alkylaminoalkyl salicylates, which combine anæsthetic properties with those of salicylic acid, may be prepared by the following three methods: esterification of salicylic acid with alkylamino-alcohols, interaction of alkylamines and the salicylates of the chlorohydrins, interaction of alkylamino-alcohols and the salicylides.

β-Diethylaminoethyl salicylate, $C_6H_4(OH) \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot NEt_2$, a colourless oil, results from the interaction of diethylaminoethyl alcohol and salicylic acid or salicylide, the former condensation being effected with hydrogen chloride at 115—120°, and the latter with the two reagents alone at 160°; it is also produced by heating salicylic acid and ethyleneglycolchlorohydrin with a small amount of sulphuric acid and then boiling the resulting *β*-chloroethyl salicylate with diethylamine; its *hydrochloride* separates from acetone as a white, crystalline mass, m. p. 146°.

Piperidylethyl salicylate, obtained by condensing salicylic acid and *β*-hydroxyethylpiperidine with hydrogen chloride at 115—120°, yields a *hydrochloride*, m. p. 174°, which separates from acetone in white crystals. G. T. M.

The Supposed Phenylhydrazone of Salicylic Acid. HANS MEYER (*Monatsh.*, 1907, 28, 1381—1384).—It was shown previously (Abstr., 1904, i, 251) that salicylaldehyde neutralises 75% of a molecular proportion of alkali. This influence of an ortho-substituting group on the acidity of a phenol has been studied in other similar cases, and some of the results obtained are now published. As is well known, the phenolic hydroxyl of salicylic acid is almost neutral, salicylic acid neutralising only one equivalent of alkali. This must be ascribed to the influence of the group, $\cdot CO_2M'$, which is positive, not negative as is that of the carboxylic group. Hence the acidity of the phenolic hydroxyl must increase as the $\cdot OM'$ in the group CO_2M' is substituted by a less positive group. In agreement with this view, it is found that whilst methyl salicylate is almost neutral, the following derivatives of salicylic acid neutralise varying amounts of alkali, as indicated by the figures given, which are percentages of an equivalent of base: phenylsalicylate (salol), 30; α -naphthyl salicylate (alphenol), almost 40; saligenin, 20; salicylamide, over 90; salicylanilide, about 95.

Schrötter and Flooh's supposed phenylhydrazone of salicylic acid (Abstr., 1907, i, 929) is salicylphenylhydrazide, m. p. 131°, which is best prepared by heating wintergreen oil with phenylhydrazine and phenylhydrazine hydrochloride; it neutralises almost one equivalent of alkali. G. Y.

Formation of Organic Nitro-compounds by the Action of Ammoniacal Silver Oxide Solution. HEINRICH BRUNNER and RUDOLF MELLET (*J. pr. Chem.*, 1908, [ii], 77, 25—33. Compare Brunner, Abstr., 1902, i, 452; 1905, i, 59).—It is now found that the action of ammoniacal silver oxide solution on salicylaldehyde in presence of sodium hydroxide leads to the formation of two nitrosalicylic acids, which are separated by means of their barium salts.

3-Nitrosalicylic acid, $C_7H_5O_5N$, crystallises in white needles containing water of crystallisation, m. p. 144° (when anhydrous), and gives a blood-red coloration with ferric chloride. The *barium* salt forms orange-yellow needles.

5-Nitrosalicylic acid crystallises in anhydrous needles, m. p. 228° , and gives a red coloration with ferric chloride, and the indophenol reaction with soda-lime. The *barium* salt crystallises in yellow prisms, and is more soluble than its isomeride in water.

Under similar conditions, *m*-methoxysalicylic, *p*-hydroxybenzoic and dibromosalicylic acids, and dibromosalicylaldehyde form nitro-derivatives, but in quantities too small to permit of their isolation. Phenol, benzaldehyde and dextrose, on the other hand, are not nitrated in this manner. The mechanism of the reaction is discussed.

G. Y.

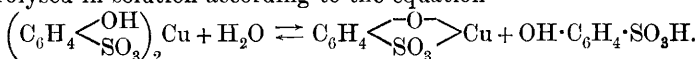
Preparation of Thiosalicylic Acid. LEOPOLD CASSELLA and Co. (D.R.-P. 189200).—Thiosalicylic acid, $SH \cdot C_6H_4 \cdot CO_2H$, is obtained in almost quantitative yield by heating *o*-chlorobenzoic acid with strong aqueous sodium hydroxide (1 mol. NaOH) and potassium hydrosulphide at 150 – 200° in the presence of a small amount of copper sulphate or finely divided copper. As the water evaporates, the temperature of the mixture is raised to 250° until the mass becomes solid. The product is then dissolved in water, and thiosalicylic acid precipitated by mineral acids as a yellowish-white, crystalline precipitate.

This reaction may also be effected in closed vessels by heating the mixture at 200 – 250° for six to twelve hours.

G. T. M.

Formation of Salts and Complex Salts with Organic Acids containing the Hydroxyl Group. HEINRICH LEY and O. ERLER (*Zeitsch. anorg. Chem.*, 1908, 56, 401–421).—The authors have investigated by physico-chemical methods the copper salts of the phenolsulphonic, *o*-cresolsulphonic and hydroxybenzoic acids, and the compounds formed by the action of ammonia and pyridine on these salts. Evidence has been obtained that the phenolic hydroxyl group has a tendency to salt-formation, more particularly in the compounds containing ammonia and pyridine.

The aqueous solution of *copper p*-phenolsulphonate is deep blue in colour, and is highly dissociated into Cu^{++} and phenolsulphonate ions. Solutions of the corresponding salt of *o*-phenolsulphonic acid are yellowish-green in colour, which seems to indicate a different constitution from the *p*-compound. It was found, however, that the Cu^{++} ion concentration is much the same in both cases, but the *o*-salt is hydrolysed in solution according to the equation



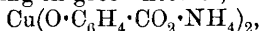
The basic salt is brown in colour, and, although present only in small concentration, masks the blue colour of the Cu^{++} ions. It has been isolated by the action of dilute ammonia on the solution of the copper salt, and crystallises in needles with $2H_2O$.

The copper salts of *o*-cresol-*o*-sulphonic and *p*-sulphonic acids behave similarly; the basic *o*-cresol salt, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{SO}_3 \end{smallmatrix} \text{Cu}$, forms small, yellowish-green leaflets.

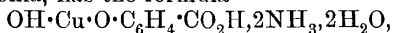
Of the copper salts of the hydroxybenzoic acids, only copper salicylate was sufficiently soluble for investigation in aqueous solution. The solution is intensely green in colour, probably owing to some extent to partial hydrolysis with production of the greenish-yellow basic salt,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{smallmatrix} \text{Cu}$, already isolated by Piria (1855).

By the action of ammonia on copper salicylate, two compounds were obtained. One, occurring in green needles, has the formula



the copper being present as complex anion; the other, obtained with more dilute ammonia, has the formula

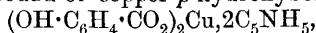


but its constitution has not been established with certainty. A pyridine compound of copper salicylate, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_2\text{Cu} \cdot 2\text{C}_5\text{NH}_5$, has been obtained in small, light-blue, columnar needles; its constitution has not been elucidated.

When ammonia is added in considerable excess to a solution of copper *p*-hydroxybenzoate, the solution finally becomes blue, and then contains the copper as complex $\text{Cu}(\text{NH}_3)_2^{++}$ and $\text{Cu}(\text{NH}_3)_4^{++}$ ions. From the solution, the compound, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_2\text{Cu} \cdot 2\text{NH}_3$, was isolated in dark-blue leaflets.

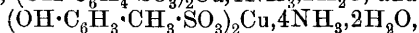
The behaviour of copper *m*-hydroxybenzoate with ammonia is between that of the ortho- and para-compounds; with very concentrated ammonia, a solution containing complex copper cations is obtained.

The pyridine compound of copper *p*-hydroxybenzoate,



occurs in bluish-violet needles.

Corresponding results were obtained for the action of ammonia and pyridine on the copper phenolsulphonates and *o*-cresolsulphonates. From the solutions of the *p*-sulphonates, treated with ammonia in excess, the salts, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Cu} \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$, and



were obtained in bluish-violet needles. Migration experiments showed that the copper in these solutions is present as a complex cation, probably $\text{Cu}(\text{NH}_3)_4^{++}$. The pyridine salts, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Cu} \cdot 4\text{C}_5\text{NH}_5$, and $(\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_3 \cdot \text{SO}_3)_2\text{Cu} \cdot 4\text{C}_5\text{NH}_5$, also occur in blue needles.

The *o*-sulphonates, with excess of ammonia, only give green solutions, from which the two salts, $\text{OH} \cdot \text{Cu} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$, and $\text{OH} \cdot \text{Cu} \cdot \text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{Me} \cdot \text{SO}_3\text{H} \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$, were obtained in dark green needles. Their constitution has not been elucidated, but migration experiments show that at least one ammonia group is present as an NH_4^+ ion. The corresponding pyridine salts,

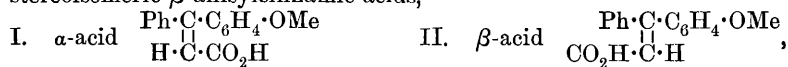
$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{SO}_3 \end{smallmatrix} \text{Cu} \cdot 2\text{C}_5\text{NH}_5 \cdot \text{H}_2\text{O}$, and $\text{OH} \cdot \text{Cu} \cdot \text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{Me} \cdot \text{SO}_3\text{H} \cdot 2\text{C}_5\text{NH}_5$, form olive-green needles.

The green anions containing copper are much more stable in the ortho- than in the para-compounds, which is probably due to the fact that

the phenolic hydroxyl group is more acidic when the carboxyl or sulphonic group is in the para- than when in the ortho-position. G. S.

Action of Nascent Hypoiodous Acid (Iodine and Sodium Carbonate) on Some Acids of the General Formula $\text{CHR}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (R being Phenyl more or less substituted). J. BOUGAULT (*Compt. rend.*, 1908, 146, 140—142).—It has been shown previously (Abstr., 1905, i, 9; 1906, i, 848) that the unsaturated acids having a single double linking in the $\beta\gamma$ or $\gamma\delta$ position give iodo-lactones when their alkali salts are treated in aqueous solution with iodine. The yield of iodo-lactone is diminished by the presence of sodium carbonate, and a large excess of this salt totally inhibits its formation. Phenylisocrotonic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, in dilute aqueous solution, with a large excess of sodium carbonate, gives von Pechmann's benzoylacrylic acid, $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (Abstr., 1882, 1074), when treated with iodine dissolved in potassium iodide solution. Benzoylacrylic acid, on oxidation with alkaline permanganate, gives benzoic and oxalic acids, and, on reduction with sodium amalgam, γ -hydroxyphenylbutyric acid, $\text{OH}\cdot\text{CHPh}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$. It combines with hydrogen bromide and chloride, giving bromo- and chloro-phenylbutyric acids, the first of which is reduced by zinc and acetic acid to benzoylpropionic acid. The action of hypoiodous acid on phenylisocrotonic acid differs from that on anethole (Abstr., 1902, i, 452) in that twice as much oxygen is absorbed in the former as in the latter case. Application of the reaction to *p*-methoxyphenylisocrotonic acid gives a yellow acid, m. p. 131° , which is probably *p*-methoxybenzoylacrylic acid. E. H.

Stereoisomeric β -Arylcinnamic Acids. RICHARD STOERMER and E. FRIDERICI (*Ber.*, 1908, 41, 324—343).—*o*-Methoxybenzophenone reacts with ethyl bromoacetate in the presence of zinc yielding ethyl β -phenyl- β -*o*-anisylhydracrylate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which reacts with a mixture of acetyl chloride and acetic anhydride yielding ethyl β -*o*-anisyleinnamate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$; the ester thus obtained appears to be homogeneous, and has the configuration corresponding with formula II. When hydrolysed with alcoholic potash and precipitated with dilute mineral acid, a mixture of the two stereoisomeric β -anisyleinnamic acids,



is obtained. These may be separated by fractional crystallisation from benzene. The two acids are stereoisomeric, as their esters have the same b. p.; both acids yield β -phenyl- β -anisylpropionic acid, m. p. 131° , when reduced, and the β -acid is readily transformed into the α -acid when exposed to sunlight or ultra-violet light. The acids do not combine with bromine, and when solutions of their sodium salts are treated with bromine water, carbon dioxide is evolved, and α -phenyl-*o*-anisylbromoethylene (m. p. $78\cdot5^\circ$, Stoermer and Simon, Abstr., 1905, i, 53) is obtained. The silver salts, when treated with iodine, yield phenylanisyliodoethylene, m. p. 84° , which appears to exist in one modification only. The configurations of the two acids have

been deduced from the relatively positive and negative nature of the substituents, from their relative strengths, and also from the action of acetyl chloride on the two acids. The acetyl chloride hydrolyses the methoxy-group; the α -acid is hydrolysed more readily, and yields the anhydride, phenylcoumarin. The β -acid is also hydrolysed, but less readily; it is shown that the hydrolysis is preceded by molecular rearrangement, and the final product is also phenylcoumarin. *Ethyl β -phenyl- β -o-anisylhydracrylate* has b. p. 190—196°/7 mm., and solidifies to a crystalline mass, m. p. 57·5—58°. When distilled under higher pressures, it shows a tendency to lose water, and then does not solidify readily. The corresponding acid has m. p. 139°, and when melted evolves carbon dioxide and water. The barium salt dissolves in alcohol, and has m. p. 225°. *Ethyl β -o-anisylcinnamate* has b. p. 215—220°/20 mm., and dissolves in concentrated sulphuric acid to an intense olive-green solution.

β -o-Anisylcinnamic acid (α -acid) crystallises from benzene in slender, colourless needles containing a molecule of benzene. It melts at 146°, but if previously heated at 80—95° to remove the benzene it melts at 153°. The stereoisomeric acid also crystallises with benzene, but when heated previously at 80—95° melts at 118°.

The solubilities in alcohol are α , 1·33; β , 3·75; in benzene, α , 0·67; β , 3·3, and in carbon disulphide, α , 0·51; β , 2·4; the numbers indicating % of dissolved material.

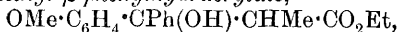
The sodium salt of the α -acid is readily soluble in alcohol or water, is hygroscopic, and has m. p. 255°; the isomeric β -salt can be crystallised from water, in which it is somewhat sparingly soluble, and has m. p. 105° in the hydrated, or 282° in the anhydrous, state. Both salts, when decomposed with acetic, carbonic, or hydrochloric acids, yield the α -acid; the β -acid can, however, be obtained from the β -sodium salt if it is finely divided and mixed with $N/10$ solution of hydrogen chloride or oxalic acid in ether. The β -silver salt is crystalline, and has m. p. 170° (decomp.); the α -salt amorphous, and is solid at 300°. Both are unaffected by light. The α -pyridine salt, obtained by boiling the acid with water and pyridine, has m. p. 62°, and readily loses pyridine. The β -pyridine salt, m. p. 83°, is more stable. Aniline yields a salt with the β -acid only. The α -piperidine salt has m. p. 54—55°; the β -piperidine salt is less soluble, has m. p. 194°, and is very stable.

When esterified by saturating their alcoholic solutions with hydrogen chloride, both acids yield the same ester, and this, on hydrolysis, yields mainly the β -acid, the small amount of α -acid being due to the transforming action of the mineral acid used in precipitating the acids. The α - and β -esters are best prepared by the action of methyl sulphate on the sodium salts. The α -methyl ester crystallises from methyl alcohol in compact prisms, m. p. 58°, and, on hydrolysis, yields the α -acid. The β -methyl ester has been obtained as an oil only, and when hydrolysed gives a mixture of both acids. In the presence of aqueous ammonia, the β -ester is transformed into the α -compound.

β -Phenylcoumarin, $C_{15}H_{10}O_2$, crystallises from alcohol in slender, colourless needles, m. p. 105°. It does not give a coloration with ferric chloride, and dissolves in sodium hydroxide solution, the addition

of acids precipitating the unaltered coumarin. The solution of the sodium salt reacts with methyl sulphate, yielding the methyl ester of the methoxy-acid, m. p. 58°.

α -Methoxybenzophenone, ethyl α -bromopropionate, and zinc yield ethyl β -anisyl- α -methyl- β -phenylhydracrylate,

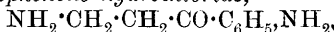


m. p. 65°, and from this two stereoisomeric β -o-anisyl- α -methylcinnamic acids, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$, m. p. 139° and 110°, have been prepared. The chief product of hydrolysis is, however, β -phenyl- α -methylcoumarin, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{CPh} \cdot \text{CMe}$, m. p. 79°. Ethyl β -o-hydroxyphenyl-

α -methylhydracrylate, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, obtained from o-hydroxybenzophenone, zinc, and ethyl α -bromopropionate, crystallises from alcohol, and has m. p. 136°. J. J. S.

Derivatives of the Amino-acids Applicable for Synthetical Purposes. SIEGMUND GABRIEL (*Ber.*, 1908, 41, 242—250. Compare *Abstr.*, 1907, i, 625).—Phthalylglycyl chloride and α -bromo- β -phthalyl alanine are very reactive, and can be used for synthetical purposes. Phthalylglycyl chloride (*loc. cit.*) can be distilled in vacuum without change, but decomposes at atmospheric pressure, forming carbon monoxide and chloromethylphthalimide.

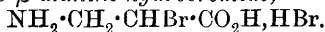
β -Phthalylalanyl chloride, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \\ \diagdown \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{Cl}$, obtained from phthalylalanine and phosphorus pentachloride, forms a bright yellow oil, solidifying to a crystalline mass, m. p. 107—108°. It reacts with benzene in presence of aluminium chloride to form β -phthaliminopropiophenone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \\ \diagdown \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, crystallising in faint yellow, rhombic plates, m. p. 130—131°. When heated at 150° under pressure with acetic and hydrochloric acids, this forms β -aminopropiophenone hydrochloride,



which crystallises in large, flat prisms, m. p. 128°, does not reduce Fehling's solution, and forms a *picrate*, long needles, m. p. 155°, and a *platinichloride*, separating in concentrically-arranged yellow needles, which sinter at 200°, m. p. 215° (decomp.).

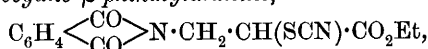
β -Aminopropiophenone reacts with potassium cyanate to form propiophenonylcarbamide, $\text{CPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, consisting of long needles, m. p. 129°. When heated with sulphuric acid, it is probably converted into an anhydro-compound, *oxyphenyldihydropyrimidine*, $\text{CPh} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \diagup \text{CH} \cdot \text{CH}_2 \end{smallmatrix} \text{NH}$, forming three- and four-sided plates, and giving a *platinichloride*, which darkens about 260°. Propiophenonylphenylthiocarbamide, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$, forms flat, six-sided plates, m. p. 90°.

α -Bromo- β -phthalylalanine is converted by heating with hydrogen bromide into α -bromo- β -alanine hydrobromide,



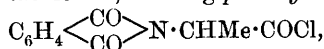
Of the phthalyl compound, the methyl ester has m. p. 52—53°; the

ethyl ester, 48—50°. These, on heating with potassium thiocyanate, form ethyl α -thiocyano- β -phthalylalanine,



m. p. 83—85°, which, when heated with hydrogen chloride, is converted into *isocysteine*.

α -Phthalylalanine reacts with bromine and phosphorus to form tribromoethylphthalimide (compare Sachs, Abstr., 1898, i, 476), and with phosphorus pentachloride, forming *phthalylalanyl chloride*,



m. p. 73°. This reacts with benzene and aluminium chloride, forming α -phthaliminopropiophenone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$,

separating in colourless, stellar, aggregates of needles and prisms, m. p. 87—88° (compare Schmidt, Abstr., 1890, 372), and yields α -aminopropiophenone, previously described by Behr-Bregowski (Abstr., 1897, i, 459). The picrate is now found to have m. p. 164—165°; the platinichloride, m. p. 205—206°.

Phenacylphthalimide has m. p. 167°, and not 155° as previously given. E. F. A.

Phenylmalononitrile. II. JOHN C. HESSLER (*Amer. Chem. J.*, 1908, 39, 63—80).—In the first paper on this subject (Abstr., 1904, i, 830), an account was given of the preparation of phenylmalononitrile, and it was stated that the silver salt rapidly decomposes with formation of a white, amorphous substance, m. p. 147—148°. It has now been found that at least three compounds are formed by the decomposition of this salt, namely, bisphenylmalononitrile, trisphenylmalononitrile, and a substance, m.p. about 210—230°.

Bisphenylmalononitrile, probably $\text{CN} \cdot \text{CPh}(\text{CH}:\text{NH}) \cdot \text{CPh}(\text{CN})_2$, m. p. 87—88°, forms nearly colourless crystals, and separates from benzene in large, white plates, $(\text{C}_9\text{H}_6\text{N}_2)_2 \cdot \text{C}_6\text{H}_6$, m. p. 67—68°. The *silver* salt, $\text{C}_{18}\text{H}_{11}\text{N}_4\text{Ag}$, is stable at the ordinary temperature, but decomposes at 90°. The *ethyl* derivative, $\text{CN} \cdot \text{CPh}(\text{CH}:\text{NEt}) \cdot \text{CPh}(\text{CN})_2$, m. p. 101—102°, crystallises in plates. The *n-butyl* derivative has m. p. 80—81°.

The compound (m. p. 147—148°) described previously is probably trisphenylmalononitrile, $(\text{C}_9\text{H}_6\text{N}_2)_3$.

The third compound formed by the decomposition of the silver salt is an amorphous *substance*, $(\text{C}_9\text{H}_6\text{N}_2)_x$, m. p. 210—230° (decomp.), which can also be obtained by the oxidation of phenylmalononitrile or either of its polymerides with chromic acid. It also formed together with small quantities of another *substance*, m. p. 117—118°, by the action of bromine on the sodium derivative of the nitrile.

Phenylmethylmalononitrile, $\text{CPhMe}(\text{CN})_2$, b. p. 125—130°/16 mm., is obtained as an oil by the action of methyl iodide on the sodium derivative.

When the sodium derivative of phenylmalononitrile is treated with a solution of diazobenzene chloride, an unstable product is obtained,

which is decomposed by ether with evolution of nitrogen and formation of a white substance, m. p. 107°.

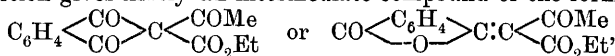
α-Cyanophenylacetanilide, m. p. 136°, crystallises in needles. The *o*-, *m*-, and *p*-toluidides melt at 139°, 131°, and 139° respectively. The *phenylhydrazide* has m. p. 224°.

When an alcoholic solution of phenylmalononitrile is treated with hydrochloric acid, cyanophenylacetic acid, amide, and ethyl ester are produced, together with ammonium chloride.

Attempts were made to prepare ethyl cyanophenylacetate by the elimination of carbon monoxide from ethyl cyanophenylpyruvate (Erlenmeyer, Abstr., 1893, i, 37), but without success. E. G.

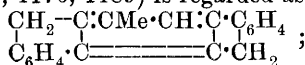
Santonin. X. Bromination of Santonin. EDGAR WEDEKIND [with MARTIN RÖDIGER] (*Ber.*, 1908, 41, 359—366. Compare Abstr., 1907, i, 137).—The bromination of santonin has been again studied, and the cause of the differences in the observations of Klein (Abstr., 1893, i, 112; 1907, i, 421) and of Wedekind and Koch (Abstr., 1905, i, 212) determined. Klein's colourless product, obtained on bromination of santonin in acetic acid in presence of 5—10% of water, is santoninoxonium dibromide, $C_{13}H_{16}O_2 \begin{smallmatrix} <CH_2 \\ <CO:Br_2 \end{smallmatrix}$, and if freshly prepared yields santonin on treatment with an alkali. When mixed with santonin and hydrogen bromide in molecular proportions in glacial acetic acid or chloroform solution, it forms a red solution resembling that of Wedekind and Koch's hydroperebromide, which is formed on bromination of santonin in glacial acetic acid solution. The formation of bromosantonin by the action of aniline on santonin dibromide is confirmed. When exposed to light for three days in aqueous bromine solution, santonin forms a product, decomposing about 100°, which is a mixture of santonin and santonin dibromide. G. Y.

Structure of Phthalacene. GIORGIO ERRERA (*Gazzetta*, 1907, 37, ii, 624—636).—Ethyl phthalaceneconecarboxylate, $C_{21}H_{11}O_2 \cdot CO_2Et$, prepared by the action of sodium acetate on a mixture of phthalic anhydride and ethyl acetoacetate, is accompanied by tribenzoylenebenzene (compare Michael, Abstr., 1906, i, 518). According to the author, this reaction gives firstly an intermediate compound of the form:

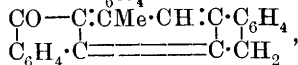


from which diketohydrindene is formed, 2 mols. of this then condensing to anhydrobisdiketohydrindene. One mol. of the latter may then condense with either a third mol. of diketohydrindene, giving tribenzoylenebenzene, or a mol. of ethyl acetate, yielding ethyl phthalaceneconecarboxylate, $CO-C \begin{smallmatrix} <COMe \\ <CO_2Et \end{smallmatrix} C(CO_2Et):C \begin{smallmatrix} <C_6H_4 \\ <CO \end{smallmatrix}$. It has, however,

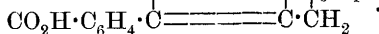
not been found possible to obtain the latter from either ethyl phthalylacetoacetate, ethyl sodiohydrindenecarboxylate, diketohydrindene, or anhydrobisdiketohydrindene. Phthalacene (compare Gabriel, Abstr., 1884, 1176, 1189) is regarded as



the oxide of phthalacene as $\begin{array}{c} \text{CH}_2 - \text{C} : \text{CMe} : \text{CH} : \text{C} \cdot \text{C}_6\text{H}_4 \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C} = = = = \text{C} \cdot \text{CO} \end{array}$, or



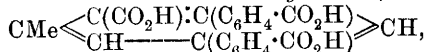
and phthalacenic acid as $\begin{array}{c} \text{CH}_2 - \text{C} : \text{CMe} : \text{CH} : \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C} = = = = \text{CH} \\ | \\ \text{HC} : \text{CMe} : \text{CH} : \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$, or



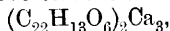
Phthalacone, $\begin{array}{c} \text{CO} - \text{C} : \text{CMe} : \text{CH} : \text{C} \cdot \text{C}_6\text{H}_4 \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C} = = = = \text{C} \cdot \text{CO} \end{array}$, prepared by the action of

excess of potassium dichromate on phthalacene in acetic acid solution or by dry distillation of phthalaconecarboxylic acid either alone or mixed with zinc dust, crystallises from acetic acid in minute, yellow needles, m. p. 257—259°, and dissolves sparingly in the ordinary solvents.

3 : 5-Diphenyltoluene-2 : 2' : 2''-tricarboxylic acid,



prepared by fusing phthalaconecarboxylic acid with potassium hydroxide, exists in two modifications, one amorphous and readily soluble in alcohol, acetic acid, or ethyl acetate, whilst the other crystallises from acetic acid in granules, m. p. 212—215°, and is sparingly soluble in the above solvents. The calcium salt,



also exists in an amorphous and a crystalline (+14H₂O) condition. The diethyl ester, CO₂H·C₆H₂Me(C₆H₄·CO₂Et)₂, m. p. 189—190°; triethyl ester, C₂₈H₂₈O₆, m. p. 152—153°; trimethyl ester, C₂₅H₂₂O₆, m. p. 198°, and the monoethyl ester, CO₂Et·C₆H₂Me(C₆H₄·CO₂H)₂, m. p. 258°, were prepared. The action of concentrated sulphuric acid on this acid yields another acid, the ethyl ester of which, $\begin{array}{c} \text{CO} - \text{C} : \text{CMe} : \text{C} \cdot \text{CO} \\ | \qquad \qquad | \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} - \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{Et} \end{array}$ or $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} : \text{CMe} : \text{C} \cdot \text{CO} \\ | \qquad \qquad | \\ \text{CO} - \text{C} = = = = \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{Et} \end{array}$, crystallises from xylene in minute, golden-yellow needles, m. p. 295—297°.

T. H. P.

Onocerin (Onocol). II. FRANZ VON HEMMELMAYR (*Monatsh.*, 1907, 28, 1385—1399. Compare Abstr., 1906, i, 356).—When titrated with potassium hydroxide in alcoholic solution with phenolphthalein as indicator, onocerinic acid requires for neutralisation about 20 per cent. more alkali than calculated for a monobasic acid of the formula C₂₀H₃₀O₄, whilst the methoxyl determination with the methyl ester, m. p. 68—80°, prepared by the action of methyl alcohol and hydrogen chloride or concentrated sulphuric acid on onocerinic acid, gives results about 2 per cent. less than that required for the formula C₂₁H₃₂O₄. When heated with acetic anhydride and sodium acetate, onocerinic acid yields a white, amorphous product, C₄₀H₅₈O₇, which gradually melts when heated, and forms onocerinic acid when boiled with dilute alkalis. The action of bromine on onocerinic acid in cold glacial acetic acid solution leads to the formation of a white, amorphous product,

m. p. 125—130°, containing an amount of bromine lying between $C_{28}H_{30}O_4Br_2$ and $C_{20}H_{29}O_4Br_3$. A *product*, $C_{20}H_{28}O_4Br_4$, is formed by the action of bromine on onocerin acid in boiling glacial acetic acid solution.

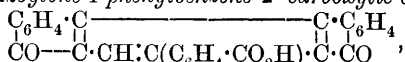
When oxidised by means of potassium permanganate in cold glacial acetic acid solution, onocerin yields *dihydroxyonoketone*, $C_{26}H_{40}O_4$, which is obtained as a white, amorphous mass, m. p. 65—70°, and forms a *diacetate*, $C_{30}H_{44}O_6$, and a *diphenylhydrazone*, $C_{38}H_{52}O_2N_4$, m. p. 120° (decomp.). On oxidation with potassium permanganate in boiling glacial acetic acid solution, onocerin yields an amorphous *acid*, $C_{26}H_{38}O_6$, which melts gradually above 90°, and forms an amorphous *silver salt*, $C_{26}H_{37}O_6Ag$.

On treatment with bromine in cold glacial acetic acid solution, onocerin yields a mixture of *products*, m. p. 100—130°, which contain amounts of bromine varying between those required for the formulæ $C_{26}H_{44}O_2Br_4$ and $C_{26}H_{48}O_2Br_5$. G. Y.

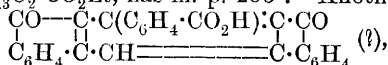
Structure of Phenyltribenzoic [1 : 3 : 5-Triphenylbenzene-2' : 2' : 2'''-tricarboxylic] Acid. GIORGIO ERRERA (*Gazzetta*, 1907, 37, ii, 618—623).—The author finds that phenyltribenzoic acid (compare Gabriel and Michael, *Abstr.*, 1878, 734) is readily esterified by Fischer's method, an observation which supports the structure suggested by the above authors. If it were triphenyltrimelic acid, $C_6Me_3(CO_2H)_3$ (Lanser, *Abstr.*, 1899, i, 916), it would not be esterified by alcohol in presence of sulphuric acid. The author also confirms Michael's refutation (*Abstr.*, 1906, i, 518) of Manthey's statement (*Abstr.*, 1901, i, 31) that the acid is 2 : 4-diphenylcyclobutadiene-1 : 3-dicarboxylic acid.

Triethyl phenyltribenzoate, $C_6H_3(C_6H_4 \cdot CO_2Et)_3$, was obtained only as an uncrystallisable gum.

3 : 4 : 5 : 6-Dibenzoylene-1-phenylbenzene-2'-carboxylic acid,



obtained by the action of concentrated sulphuric acid on phenyltribenzoic acid, crystallises from alcohol in golden-yellow, silky needles containing 1Et·OH; m. p. of alcohol-free substance, 349—350°; the *ethyl ester*, $C_{26}H_{13}O_2 \cdot CO_2Et$, has m. p. 253°. Another *acid*,



m. p. 321°, is also formed by the interaction of concentrated sulphuric acid and phenyltribenzoic acid. T. H. P.

[Condensation Products of Tannic Acid and Formaldehyde with the Phenols.] HERMANN HILDEBRANDT (D.R.-P. 188318).—Condensation products of tannic acid, formaldehyde, and the phenols result when an alcoholic solution of the phenol, mixed with an aqueous solution of tannic acid, is treated successively with excess of formaldehyde and concentrated hydrochloric acid.

Tanninphenolmethane, a flocculent, white powder, insoluble in alcohol but dissolving in alkaline solutions, does not melt below 240°

Tanninthymolmethane and *bromotanninthymolmethane* are slightly coloured powders, soluble in alcohol, and decomposing respectively at 235° and 200°. Similar products are obtained from bromotannic acid and formaldehyde with phenol, *o*-cresol, and β -naphthol. G. T. M.

Methyl Tannin. JOSEF HERZIG (*Ber.*, 1908, 41, 33).—Dekker's contention (Abstr., 1906, i, 686) that the author's analytical data for methyl tannin agree better for a hexamethyl derivative, is due to an arithmetical error. A methoxyl determination, moreover, shows it to be pentamethyl tannin. W. R.

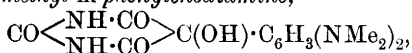
Coffee. I. K. GORTER (*Annalen*, 1908, 358, 327—348).—The account given of the author's study of the constituents of coffee extract is prefaced by a résumé of the work of previous investigators. On evaporation, the alcoholic extract of Liberian coffee yields crystalline potassium-caffeine chlorogenate, $C_{32}H_{36}O_{19}K_2(C_8H_{10}O_2N_4)_2 \cdot 2H_2O$ (Payen, *Annalen*, 1846, 60, 286), in amounts equivalent to 3.3% of the coffee. This substance crystallises in almost white prisms, becomes yellow at 150°, and brown at 225°, but does not melt, yields an alkaline ash on incineration, and loses caffeine when shaken with moist chloroform. *Chlorogenic acid*, $C_{32}H_{38}O_{19}$, is obtained by action of lead acetate on the aqueous solution of the double compound and treatment of the precipitated basic lead salt with hydrogen sulphide, or by addition of sulphuric acid to convert the potassium into the sulphate and extraction of the caffeine with chloroform. The acid crystallises in needles, m. p. 206—207°, $[\alpha]_D - 33.1^\circ$, can be titrated with alkalis as a dibasic acid, reduces silver nitrate when heated, but has only a slight action on Fehling's solution, gives colour reactions with the alkalis and alkaline earths, ferric chloride, uranyl acetate, and zinc chloride, and does not react with semicarbazide or phenylhydrazine. The *calcium*,

magnesium, $(5H_2O)$, *zinc*, $(5H_2O)$, *lead*, $(2H_2O)$, *basic lead*,

$C_{32}H_{36}O_{19}Pb, 2PbO$, *benzidine*, *basic benzidine*, $C_{32}H_{38}O_{19}(C_{12}H_{12}N_2)_2 \cdot 10H_2O$, and *strychnine*, $(C_{32}H_{38}O_{19})_2(C_{21}H_{22}O_2N_2)_3 \cdot 2H_2O$, salts are described. G. Y.

Tetramethyl-2:4-diaminobenzaldehyde. FRANZ SACHS and ERNST APENZELER (*Ber.*, 1908, 41, 91—108).—The only polyamino-benzaldehyde hitherto known, obtained by Sachs and Kempf (Abstr., 1902, i, 682) by the reduction of 2:4-dinitrobenzaldehyde, showed neither the properties of an aldehyde nor of a *m*-diamine, owing to internal condensation to an aldehyde ammonia compound. To prevent such condensation, a diaminobenzaldehyde has been prepared, in which all the amine hydrogens were replaced. Starting from *m*-phenylene-tetramethyldiamine, attempts were made to obtain an aldehyde by heating it with formaldehyde and *p*-nitrosodimethylaniline (Ullmann and Frey), or with formaldehyde and an aromatic hydroxylamine or its sulphonic acid (Geigy), but without success. Formaldehyde does not even condense with the base in presence of hydrogen chloride to a diphenylmethane derivative.

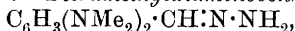
Alloxanyltetramethyl-m-phenylenediamine,



prepared by Pellizari's method, forms colourless, glistening crystals, which darken at 180° , soften at 205° , and decompose at 223° . When decomposed with hot sulphuric acid, a small quantity of tetramethyldiaminobenzaldehyde is formed. This is more conveniently obtained by condensing the diamine with chloraldehyde to *tetramethyldiaminophenylhydroxytrichloroethane*, $\text{C}_6\text{H}_3(\text{NMe}_2)_2 \cdot \text{CH}(\text{OH}) \cdot \text{CCl}_3$, which, without being isolated, is hydrolysed by alkali.

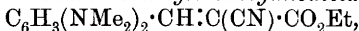
Tetramethyl-2 : 4-diaminobenzaldehyde is a yellow, oily liquid of a resin-like odour and biting, bitter taste, b. p. $203^\circ/14$ mm., and solidifies to a yellow, hard, crystalline mass, m. p. 8° .

The *mercurichloride* crystallises in pale greenish-yellow tablets; the *sodium hydrogen sulphite* compound is a grey powder, m. p. 105° . It does not react with hydroxylamine or phenylhydrazine, nor is it attacked by concentrated alcoholic ammonia. The *picrate* sinters at 145° , m. p. $161-162^\circ$; the *semicarbazone*, a yellowish-white mass of needles, has m. p. 215° . *Tetramethyldiaminobenzylidenedehydrazine*,



separates from alcohol in glistening, yellow crystals, m. p. 212° .

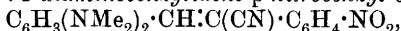
Ethyl tetramethyl-m-diaminobenzylidenecyanoacetate,



prepared by condensation of the acid with ethyl cyanoacetate, forms yellow, glistening crystals, m. p. $110-112^\circ$. *Tetramethyl-2 : 4-diaminobenzylidenecetophenone*, $\text{C}_6\text{H}_3(\text{NMe}_2)_2 \cdot \text{CH} : \text{CH} \cdot \text{COPh}$, is a reddish-yellow oil, of which the *picrate* crystallises in orange needles, which sinter at 158° , m. p. 163° .

Tetramethyldiaminobenzylidenemalonitrile, $\text{C}_6\text{H}_3(\text{NMe}_2)_2 \cdot \text{CH} : \text{C}(\text{CN})_2$, crystallises in orange-yellow needles, m. p. 166° .

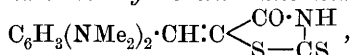
Tetramethyl-2 : 4-diaminobenzylidene-p-nitrobenzyl cyanide,



forms glistening, red needles, m. p. 170° .

4 - *Tetramethyl-2' : 4'-diaminobenzylidene - 1 - phenyl - 3 - methyl - 5-pyrazolone*, $\text{C}_6\text{H}_3(\text{NMe}_2)_2 \cdot \text{CH} : \text{C} \begin{array}{c} \text{CO} \\ \text{CMe} : \text{N} \end{array} \text{NPh}$, prepared by condensation of the aldehyde with phenylmethylpyrazolone, forms minute, matted, reddish-yellow needles, m. p. 181° .

Tetramethyl-2 : 4-diaminobenzylidenetherhodanic acid,



separates in microscopic, red needles, which sinter at 198° , and slowly melt at 208° .

On mixing the dilute hydrochloric acid solution of the components and warming, the aldehyde gives with phloroglucinol a very characteristic, red *hydrochloride*, $\text{C}_6\text{H}_3(\text{NMe}_2)_2 \cdot \text{CH}[\text{C}_6\text{H}_2(\text{OH})_3]_2 \cdot 2\text{HCl}$, which has no melting point, and is insoluble in all solvents but pyridine or acetic acid, but dissolves in alkali hydroxides to a red solution with green fluorescence. The free *base* is a brown, indistinctly crystalline substance, which becomes lighter in colour when dried, and analysis indicates partial elimination of water, forming $\text{C}_{23}\text{H}_{24}\text{O}_5\text{N}_2$.

The aldehyde reacts with a diazotised solution of *m*-nitroaniline, forming *m*-nitrobenzeneazotetramethyl-2:4-diaminobenzaldehyde,



a brownish-yellow powder, m. p. 158°.

By reaction with magnesium ethyl bromide, *tetramethyldiaminophenylethylcarbinol* is formed as an oil, which on distillation yields *propenyltetramethyl-m-phenylenediamine*, a yellow oil which crystallises when cooled, but melts at the room temperature. The *picrate* forms intensely yellow, microscopic crystals, which sinter at 138°, m. p. 142°.

Tetramethyl-2:4-diaminotriphenylmethane forms pale brown tablets, m. p. 122—123°. E. F. A.

p-Tolylacetaldehyde and its Derivatives. K. KLING (*Bull. Acad. Sci. Cracow*, 1907, 448—453. Compare Auwers and Keil, *Abstr.*, 1903, i, 100, 620).—*p*-Tolylacetaldehyde, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}_2 \cdot \text{CHO}$, is obtained on distilling barium *p*-tolylacetate with barium formate under 17—50 mm. pressure. It forms a white, crystalline substance, m. p. about 40°, b. p. 221—222°/760 mm. (partial decomp.) or 109°/17 mm., has a characteristic odour, gives Tollens' aldehyde reaction, is oxidised slowly on exposure to air, forming *p*-tolylacetic acid, and forms an *additive* compound with sodium hydrogen sulphite. The *aldoxime*, $\text{C}_9\text{H}_{11}\text{ON}$, crystallises in colourless prisms, m. p. 126—126.5°. The *thiosemicarbazone*, $\text{C}_9\text{H}_{10} \cdot \text{N} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$, crystallises in colourless, rhombic scales, and forms a *silver* salt, $\text{C}_{10}\text{H}_{12}\text{N}_3\text{SAg}$, which was analysed. Reduction of the aldehyde or the acid in alcoholic sulphuric acid solution, with a lead cathode and an electric current of 2.6 amperes per sq. dm. density, at 20—40° leads to the formation of primary *p*-tolylethyl alcohol, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, b. p. 244—245°. Ciesielski's product, b. p. 220—221° (*Abstr.*, 1907, i, 409), was probably a mixture of the primary and secondary alcohols. G. Y.

A Method of Preparation of Cyclic Aldehydes. SAVARIAU (*Compt. rend.*, 1908, 146, 297—298).—Blaise and Bagard (*Abstr.*, 1904, i, 369) have shown that acyclic acid-alcohols are decomposed by heat, giving aldehydes. The author has applied this method to the preparation of cyclic aldehydes. Aryl organo-magnesium compounds condense with chloral, giving trichloro-secondary aryl alcohols, which are transformed by alkalis into acid-alcohols, or, in some cases, into the aldehydes themselves. Joritsch's $\beta\beta\beta$ -trichloro- α -phenylethyl alcohol, $\text{CCl}_3 \cdot \text{CHPh} \cdot \text{OH}$, when boiled with a saturated solution of potassium carbonate, gives benzaldehyde, chloroform, and phenylglycollic acid (65%). The latter when heated gives 47% of benzaldehyde, and leaves a residue containing diphenylmaleic anhydride, formed by condensation, and phenylacetic acid, probably resulting from the reduction of phenylglycollic acid by the formic acid produced in its decomposition.

Chloral condenses with the magnesium derivative of bromo-*p*-xylene, giving $\beta\beta\beta$ -trichloro- α -xylylethyl alcohol, $\text{CCl}_3 \cdot \text{CH}(\text{C}_6\text{H}_3\text{Me}_2) \cdot \text{OH}$, a light yellow, viscous liquid, b. p. 158°/10 mm., which on prolonged

boiling with potassium carbonate solution gives xylylaldehyde, $C_6H_3Me_2 \cdot CHO$ (compare Bouveault, Abstr., 1899, i, 286; Harding and Cohen, Abstr., 1901, i, 725). The following derivatives of this aldehyde are described: *semicarbazone*, fine, white needles, m. p. 217° ; *p-nitrophenylhydrazone*, small, red crystals, m. p. 182° ; *phenylbenzylhydrazone*, small, light yellow needles, m. p. 103° ; *p-xylylidene- β -naphthylamine*, nacreous lamellæ, m. p. $86-87^\circ$, and *p-xylylidene-cyanoacetic acid*, m. p. 174° .
E. H.

Friedel and Crafts' Reaction. VIII. Successive Substitution of the Atoms of Chlorine in Carbon Tetrachloride by Aromatic Groups. JACOB BÖESEKEN (*Rec. trav. chim.*, 1908, 27, 5—9).—The fact that the chief product of the action of benzene on carbon tetrachloride in the presence of aluminium chloride is dichlorodiphenylmethane and that no trace of trichlorophenylmethane can be detected (Abstr., 1905, i, 423, 583) can be explained either by the simultaneous substitution of the first two atoms of chlorine, or by the rapidity of the second of the two reactions: $CCl_4 + C_6H_6 = CPhCl_3 + HCl$; $CPhCl_3 + C_6H_6 = CPh_2Cl_2 + HCl$.

By reacting with carbon tetrachloride in the presence of aluminium chloride and subsequent heating of the product with a mixture of sulphuric and glacial acetic acids, *o*-dichlorobenzene gives 3:4-dichlorobenzoic acid and 3:4:3':4'-*tetrachlorobenzophenone*, m. p. 142° ; *m*-dichlorobenzene gives 2:4-dichlorobenzoic acid and 2:4:2':4'-*tetrachlorobenzophenone*, m. p. 78° ; *p*-dichlorobenzene gives 2:5-dichlorobenzoic acid and Norris and Green's 2:5:2':5'-*tetrachlorobenzophenone* (Abstr., 1902, i, 379); whilst *p*-dibromobenzene gives 2:5-dibromobenzoic acid. The yields of the acids are small. The conclusion is drawn that the second explanation is correct, and this is in accordance with many other reactions of carbon tetrachloride (compare Besson, Abstr., 1894, i, 481; Goldschmidt, Abstr., 1881, 707; Radziszewski, Abstr., 1884, 1133; Klason, Abstr., 1887, 1015).
E. H.

Friedel and Crafts' Reaction. IX. Condensation of the Dihalogen Derivatives of Benzene with Acetyl and Benzoyl Chlorides under the Influence of Aluminium Chloride. JACOB BÖESEKEN (*Rec. trav. chim.*, 1908, 27, 10—15).—When a mixture of a benzene derivative with an acyl chloride is acted on by aluminium chloride, two distinct reactions may take place: (1) Friedel and Crafts' reaction; (2) Combe's condensation (Abstr., 1887, 127), thus:



These two reactions generally have very different velocities; in the case of the benzene derivatives, in which the substituting group increases the activity of the remaining hydrogen atoms of the benzene nucleus, the second reaction is so slow as to be practically non-existent, but, when the substituting group diminishes the activity of the hydrogen atoms, the velocity of Friedel and Crafts' reaction may become equal to, or less than, that of the second condensation. The condensation of polyhalide derivatives of benzene with acetyl chloride

is an instance of the latter kind, the second reaction having the greater velocity, in consequence of which only very small quantities of the ketones are formed. *o*-Dichlorobenzene gives 2% of *o*-dichloroacetophenone, whilst *m*-dichlorobenzene gives only 0.4% of the corresponding ketone, and other polyhalogenbenzenes give no trace of ketone (identifiable by oxidation). On the other hand, benzoyl chloride, which does not react with aluminium chloride below 170°, condenses with *o*- and *m*-dichloro- and dibromo-benzenes, giving 80—90% yields of the dichloro- and dibromo-benzophenones. *p*-Dichloro- or dibromo-benzene is not attacked below 200°, at which temperature a black, tarry product results. E. H.

Hydrolysis of Phenolic Ethers. RICHARD STOERMER and, in part, E. FRIDERICI and H. ALTGELT (*Ber.*, 1908, 41, 321—324. Compare Auwers, *Abstr.*, 1907, i, 919, 1033).—*o*-Hydroxybenzophenone cannot be obtained by boiling the methyl ether with concentrated hydrochloric acid (Edelstein and Kostanecki, *Abstr.*, 1905, i, 460), and even at 120° only a small amount is formed. The hydroxy-ketone may be obtained quite readily by dissolving the methoxy-compound in four times its weight of glacial acetic acid, adding concentrated hydrobromic acid (48%) so long as the ketone is not precipitated, and then boiling the mixture for 1.5 hours. The product is diluted, neutralised with sodium carbonate, and extracted with ether. *p*-Methoxybenzophenone, *o*-*p*-dianisyl ketone, anisole, *p*-bromoanisole, *o*-bromoanisole, anisic acid, and phenyl-*p*-anisylpropylene are readily hydrolysed; *p*-methoxybenzophenone yields 28.6% of the hydroxy-compound after two hours. Vanillin yields 38% of protocatechualdehyde, and *m*-methoxybenzophenone only a small amount of hydroxybenzophenone, whereas *o*-methoxybenzaldehyde and dianisylethylene yield resins. J. J. S.

2:5-Dihydroxybenzophenone. JOSEF HERZIG and BR. HOFMANN (*Ber.*, 1908, 41, 143—145).—2:5-Dimethoxybenzophenone is pure white, as recorded by Hantzsch and Blackler (*Abstr.*, 1906, i, 857), and not yellow as stated by Kauffmann and Grombach (*Abstr.*, 1906, i, 283); the latter authors' statement that this compound cannot be converted by hydriodic acid into 2:5-dihydroxybenzophenone is incorrect. The monomethyl ether obtained by the partial hydrolysis of 2:5-dimethoxybenzophenone and described by Kauffmann and Grombach (*loc. cit.*) as 5-hydroxy-2-methoxybenzophenone may also be prepared by the action of diazomethane on 2:5-dihydroxybenzophenone. Since it is formed in this manner and is, moreover, yellow and but sparingly soluble in alkalis, the authors consider it probable that this compound is really 2-hydroxy-5-methoxybenzophenone (compare Herzig, *Abstr.*, 1891, 1349; Graebe and Eichengrün, *Abstr.*, 1892, 1224).

W. H. G.

Preparation and Purification of Tetrachlorobenzoquinone (Chloroanil) and Tetrachloroquinol (Hydrochloroanil). LOUIS BOUVEAULT (*Ann. Chim. Phys.*, 1908, [viii], 13, 142—144. Compare *Abstr.*, 1899, i, 790).—When commercial chloroanil (Schuchardt) dis-

solved in fuming nitric acid is treated with potassium chlorate, the lower chloro-derivatives of quinone, which constitute the chief impurity, are converted into higher chloro-derivatives, and a mixture of tri- and tetra-chlorobenzoquinones containing traces of the mono- and di-chloro-derivatives is obtained. After removing the latter by distillation in steam, the mixture is dissolved in acetic acid and saturated with dry hydrogen chloride; this converts the trichlorobenzoquinone into tetrachloroquinol, and the resulting mixture of tetrachloroquinol and tetra-chlorobenzoquinone can be converted into the quinol derivative by reduction with stannous chloride, or into the quinone derivative by oxidation with nitric acid, the final product in each case weighing more than the original crude substance. M. A. W.

Tribromomethoxy-*o*-benzoquinone Methylhemiacetal. C. LORING JACKSON and H. A. FLINT (*Amer. Chem. J.*, 1908, **39**, 80—87).—It was shown by Jackson and MacLaurin (*Abstr.*, 1907, i, 856) that tetrachloro- and tetrabromo-*o*-quinones behave differently towards methyl alcohol, and this was attributed to the chlorine of the former substance being attacked whilst the bromine of the latter was not. It is now found, however, that, although the halogen of the tetrabromo-compound is much less liable to attack than that of the tetrachloro-compound, it is affected to a very small extent. This has been proved by the observation that when the tetrabromo-compound is treated with cold methyl alcohol, a small quantity of *tribromomethoxy-*o*-benzoquinone methylhemiacetal*, $\text{OH} \cdot \text{C}_6\text{Br}_3\text{O}(\text{OMe})_2$, m. p. 138° , is produced and crystallises in yellow plates. This substance is obtained as the main product when tetrabromo-*o*-benzoquinone is boiled with methyl alcohol for one and a-half to two hours. The *acetyl* derivative, m. p. 158° , forms pale yellow crystals, and yields a *phenylhydrazone*, m. p. 205° , which crystallises in nearly white needles. When the hemiacetal is heated with hydrobromic acid, it is converted into *tribromohydroxy-*p*-benzoquinone*, $\text{C}_6\text{Br}_3\text{O}_2 \cdot \text{OH}$, m. p. 205° , which forms red plates. If hydrochloric acid is used instead of hydrobromic acid, a mixture of trichloro- and tribromo-hydroxy-*p*-quinones is produced. E. G.

[**Direct Production of Alizarin from Anthraquinone.**] BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 116526).—In the technical production of alizarin from anthraquinone, the sulphonation sometimes proceeds to the extent of forming a certain proportion of disulphonic acid which either entails a separation of the sulphonic acids or leads to the contamination of the final product with trihydroxyanthraquinones.

It has now been found that anthraquinone may be converted readily into alizarin by one operation, the product being free from by-products and furnishing a remarkably blue shade of alizarin-red. One hundred parts of anthraquinone are mixed with a solution of 300 parts of sodium or potassium hydroxide and 20 to 30 parts of sodium chlorate in 100 parts of water, and heated to 200° either in an open vessel or in an autoclave until the oxidising agent is expended. The mass must be stirred until the operation is complete. The product is dissolved in water, and the hydroxyanthranol present re-converted into anthra-

quinone by a current of air. The alizarin is then precipitated by milk of lime, the calcium salt decomposed with hydrochloric acid, and the alizarin freed from anthraquinone by dissolving in dilute aqueous sodium hydroxide.

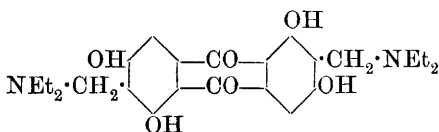
In this operation, sodium chlorate may be replaced by other oxidising agents, such as the peroxides of sodium, barium, manganese, or lead.

G. T. M.

Preparation of Dichloroanthraflavic Acid. R. WEDEKIND & Co. (D.R.-P. 187685).—Anthraflavic acid cannot be chlorinated in dilute acid solution, but when suspended in a mixture of 160 parts of 50% sulphuric acid heated at 120°, it is readily converted into a new *dichloroanthraflavic acid* (m. p. 362—364°), which yields a *diacetate*, m. p. 292°, and *dibenzoate*, m. p. 318—320°. Although these constants agree with the data obtained for the dichloroanthraflavic acid and its derivatives produced by the action of alkaline hypochlorite on anthraflavic acid, yet the solubilities of the two series of substances are quite different (compare Abstr., 1904, i, 813).

G. T. M.

[Preparation of Amino-derivatives of Anthrachrysone.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 188189).—Anthrachrysone (110 parts) dissolved in 180 parts of 30% diethylamine and 1500 parts of water, and treated with 60 parts of 40% formaldehyde at the ordinary temperature, rapidly undergoes trans-



formation into the *diamine* (annexed formula), which separates as a mass of orange-red crystals with a blue reflex. The diethylamine may be replaced by ammonia,

methylamine, ethylamine, dimethylamine, or benzylamine. The diamines thus produced are all of the above type, and have the same general properties; they are orange-red, crystalline powders, scarcely soluble in water or the volatile organic solvents, but dissolving in aqueous alkali hydroxides or acids, or in concentrated sulphuric acid, to yellow solutions. They crystallise in well defined forms from chlorobenzene, but have no definite melting point.

G. T. M.

[Thio-derivatives of Anthraquinone.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 188605).—4:8-Dithiol-1:5-dihydroxyanthraquinone, when heated with aromatic amines, such as aniline or *p*-toluidine in the presence of boric acid, gives rise to a green, crystalline condensation product, which contains the original sulphur entirely in the sulphide condition, and has the empirical formula

$\text{OH} \cdot \text{C}_6\text{H}_3\text{S} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3\text{S} \cdot \text{OH}$. This substance on sulphonation with fuming acid (10% SO_3) gives rise to a soluble colouring matter, which furnishes very fast shades of green on unmordanted wool.

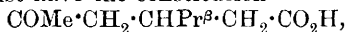
G. T. M.

Preparation of Hydroxybenzanthrones. BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 187495. Compare Abstr., 1906, i, 889; 1907, i, 324).—Further examination of the benzanthrone condensation has shown that the mono- and poly-anthraquinones and their hydrogenated derivatives, such as β -hydroxyanthranol and leucoquinizarin, condense with glycerol to furnish hydroxybenzanthrones. The condensation is conveniently effected in sulphuric acid, and proceeds most readily with the hydrogenated derivatives of the hydroxy-anthraquinones; when, however, the latter are employed, it is preferable to introduce reducing agents, such as ferrous sulphate, zinc, tin, or aniline sulphate.

1-Hydroxybenzanthrone, yellow needles, m. p. 179.5° , was obtained by heating together, at 150° , 1-hydroxyanthraquinone, glycerol, aniline sulphate, and concentrated sulphuric acid. 2-Hydroxybenzanthrone, small yellow crystals, m. p. 291° , was prepared from 2-hydroxyanthranol, glycerol, and concentrated sulphuric acid at 150° , or with zinc chloride as the condensing agent at 180° . G. T. M.

[Chlorination of Dianthraquinonyl Derivatives.] BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 186596. Compare Abstr., 1907, i, 226).—The condensation product of 2:2'-dimethyl-1:1'-dianthraquinonyl can be chlorinated either with free chlorine or sulphonyl chloride when nitrobenzene is employed as a diluent at the ordinary temperature. G. T. M.

Establishment of the Constitutional Formula of Fenchone. LOUIS BOUVEAULT and LEVALLOIS (*Compt. rend.*, 1908, 146, 180—183).—Since fenchone is a saturated ketone derived from the hydrocarbon $C_{10}H_{18}$, which is therefore dicyclic, whilst Semmler's dihydrofencholenamide (Abstr., 1906, i, 681) is the amide of the acid $C_9H_{17}\cdot CO_2H$ derived from the saturated hydrocarbon C_9H_{18} , necessarily monocyclic, the fixation of ammonia in the action of sodamide on fenchone has resulted in the rupture of one of the two chains in the ketone. When dihydrofencholenamide is treated with bromine and alkali, instead of the expected amine, $C_9H_{17}\cdot NH_2$, for which the name aminoapofenchane is proposed, *diapofenchylcarbamide*, $CO(NH\cdot C_9H_{17})_2$, crystals, m. p. 168 — 169° , is formed. This, when heated with boiling 50% sulphuric acid, decomposes, thus: $CO(NH\cdot C_9H_{17})_2 + H_2SO_4 = CO_2 + (NH_4)_2SO_4 + 2C_9H_{16}$, giving the hydrocarbon apofenchene, C_9H_{16} , H_2O , a liquid, b. p. 143° , $D_4^{20} 0.812$, $n_D^{20} 1.462$, with a terpenic odour, which forms a *hydrochloride*, b. p. $60^\circ/8$ mm., $D_4^{18} 0.9275$. The separation of ammonia in this decomposition suggests that the NH_2 is attached to a tertiary carbon atom. When oxidised with neutral potassium permanganate solution, apofenchene gives a ketonic acid, $C_9H_{16}O_3$, which forms a *semicarbazone*, m. p. 175 — 177° . The ketonic acid contains the acetyl group, and when treated with alkali and bromine is transformed into bromoform and β -isopropylglutaric acid. Since the latter is symmetrical, the ketonic acid must have the constitution



whence the formula of apofenchene is deduced as $\begin{matrix} CMe\cdot CH_2 \\ | \\ CH-CH_2 \end{matrix} > CHPr^s$,

The *benzylidene* derivative of π -norcamphor (Abstr., 1907, i, 1062), $C_{16}H_{18}O$, has b. p. 182—184°/10 mm., D^{20} 1·041, n_D 1·57516; on oxidation with permanganate in acetone solution, π -norcamphoric acid, $C_9H_{14}O_4$, is obtained, m. p. 170—171°. The *dimethyl* ester has b. p. 120—123°/9 mm., D^{20} 1·078, n_D 1·46459; the *anhydride* separates in plates, m. p. 107°. π -Norcamphor oxime has b. p. 116—120°/9 mm., D^{20} 1·012, n_D 1·49856; it is reduced by sodium in ethyl alcohol to π -norbornylamine, $C_9H_{17}N$, b. p. 69°/10 mm., D^{20} 0·9163, n_D 1·47642, which becomes solid when cooled, but melts again at the temperature of the hand. The *picrate* has m. p. 208°; the *oxalate* decomposes at 280°, and the *hydrochloride* has m. p. 272° (decomp.). π -Norcampholenic acid nitrile, $C_9H_{13}N$, prepared by heating norcamphoroxime with sulphuric acid, has b. p. 82—83°/9 mm., D^{20} 0·95, n_D 1·472; the *acid*, $C_9H_{14}O_2$, has b. p. 132—134°/10 mm., D^{20} 1·014, n_D 1·47936.

Norborneol with phosphorus pentachloride yields a *chloride*, b. p. 72—73°/10 mm., D^{20} 1·010, n_D 1·48422, m. p. 59—61°. Alcoholic potassium hydroxide eliminates hydrogen chloride from this with ease, forming norcamphene, b. p. 33—35°/10 mm., D^{18} 0·8677, n_D 1·46658, which is identical with santene, as proved by the oxidation to the diketone, $C_9H_{14}O_2$, b. p. 119—124°/10 mm., D^{18} 1·031, n_D 1·47250, whereby an *acid*, m. p. 149—151°, is also formed. When heated with formic acid, santene gives the π -norborneol formate already described (*loc. cit.*), but differing from this in being optically inactive. This formate, on hydrolysis, yields π -norborneol. There is a close analogy between the interconversion of camphene and isoborneol, and of santene and π -norborneol. The santenol described by Aschan (this vol., i, 94) is regarded as identical with π -norborneol. E. F. A.

Constituents of Essential Oils. Elucidation of the Constitution of Santene, C_9H_{14} . FRIEDERICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, 41, 385—389).—The results obtained on progressive oxidation of santene confirm the constitution previously suggested for this hydrocarbon (this vol., i, 37, 92). When treated with bromine in sodium hydroxide solution, the diketone, formed on oxidation of santene with ozone or potassium permanganate (*loc. cit.*), yields *cyclopentanetransdicarboxylic acid*, m. p. 86° (Pospischill, Abstr., 1898, i, 636). The *methyl* ester of the *cis*-acid has b. p. 118—120°/9 mm., n_D 1·4576, D^{20} 1·137. It follows that the diketone must be represented by the formula $CH_2 \begin{smallmatrix} \text{CHAc} \cdot \text{CH}_2 \\ \text{CHAc} \cdot \text{CH}_2 \end{smallmatrix}$,

and is derived from santene, $\begin{smallmatrix} \text{CMe} \cdot \text{CH} - \text{CH}_2 \\ || \quad | \\ \text{CH}_2 \\ || \quad | \\ \text{CMe} \cdot \text{CH} - \text{CH}_2 \end{smallmatrix}$, by resolution of the ethylene linking. Structural formulæ are given showing the relation of santene to teresantallic acid, π -norborneol, π -norborneol chloride, and the diketone with its oxidation product. G. Y.

Thujene and Carvestrene Dihydrohaloids. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1908, [ii], 77, 135—140. Compare Abstr., 1904, i, 438, 755, 756; 1907, i, 329).—The nature of the

dihydrohaloids obtained from thujene is discussed in the light of the results obtained by Wallach (Abstr., 1907, i, 64, 227, 228, 229, 1058, 1061) and by Semmler (Abstr., 1907, i, 145, 329, 714). These substances, previously conceived as dipentene dihydrohaloids, are now considered to be derivatives of terpinene. The liquid dihydrochloride and dihydrobromide are the *cis*-, and the solid isomerides the *trans*-, modifications. Terpinene, prepared from the *trans*-dihydrochloride, has b. p. 174—178°, D^{20}_D 0.8444, n_D 1.4798, and is optically inactive (compare Abstr., 1904, i, 438). Tschugaeff's and Wallach's terpinenes, obtained by treating the dihydrohaloids with quinoline and aniline respectively, are probably partially isomerised (Abstr., 1900, i, 104). The dihydrobromide prepared from carvestrene is found to be identical with that obtained from thujene. G. Y.

Essential Oil of *Brassica rapa* var. *rapifera*. MAX KUNTZE (Arch. Pharm., 1907, 245, 660—661).—Treatment with alcoholic ammonia yielded phenylethylenethiocarbamide, already observed in other *Cruciferae* and in *Reseda*. G. B.

Essential Oil of *Cardamine amara*. MAX KUNTZE (Arch. Pharm., 1907, 245, 657—659).—A slightly impure thiocarbamide, obtained from this oil by treatment with alcoholic ammonia, was identified as *d*-butylthiocarbamide, already described by Urban (Abstr., 1904, i, 376). G. B.

Essential Oil of *Magnolia kobus*. EUGENE CHARABOT and G. LALOUÉ (Compt. rend., 1908, 146, 183—185).—From a specimen of the essential oil of *Magnolia kobus* having $\alpha - 1.20'$ (100 mm.), D^{15}_D 0.9432, the authors have isolated citral (about 15%) and anethole, which is the chief constituent. They suspect the presence of a small quantity of estragole. E. H.

A False Euphorbium Resin. ALEXANDER TSCHIRCH and CARL LEUCHTENBERGER (Arch. Pharm., 1907, 245, 690—700).—A commercial specimen described as "Gummi Euphorbium" yielded ψ -euphorbone, $C_{15}H_{24}O$, colourless crystals, m. p. 116°, $[\alpha]_D + 48.18^\circ$. This substance is closely related to euphorbone from *Euphorbia*, and is either an aldehyde or a ketone. It unites with two atoms of iodine. When fused with potassium hydroxide, it yields phloroglucinol; oxidation with nitric acid gave picric acid, and with alkaline potassium permanganate, a substance, $C_{18}H_{28}O$, m. p. 100°. Treatment with sodium and alcohol furnishes a crystalline substance, $C_{14}H_{22}O$, m. p. 60°.

The following amorphous substances were also obtained from the resin: ψ -Euphorbic acid, $C_{24}H_{26}O_6$, m. p. 108—109°; α - ψ -euphorbonic acid, $C_{14}H_{22}O_{10}$, m. p. 112—113°; β - ψ -euphorbonic acid, $C_{18}H_{28}O_{12}$, m. p. 81°, and ψ -euphorboresen, $C_{25}H_{64}O_{10}$, m. p. 54—55°. Acid calcium maleate was also present. G. B.

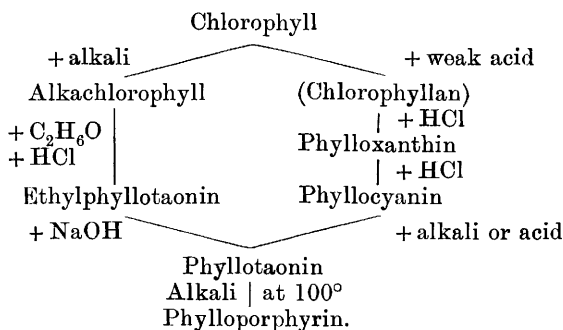
Resin of *Pinus Jeffreyi*. ALEXANDER TSCHIRCH and CARL LEUCHTENBERGER (Arch. Pharm., 1908, 245, 701—707).—The following

amorphous monobasic acids were obtained from the resin of the Californian Nut Pine (Digger Pine): α -jeffropinic acid, $C_{10}H_{14}O_2$, m. p. 160—161°; β -jeffropinic acid, $C_{12}H_{18}O_2$, m. p. 80—82°; α -jeffropinolic acid, $C_{14}H_{20}O_2$, m. p. 117—118°, and β -jeffropinolic acid, $C_{14}H_{20}O_2$, m. p. 77—78°. The first two acids were obtained by extracting the ethereal solution of the resin with ammonium carbonate, the second two with sodium carbonate. G. B.

Amygdalin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1908, 245, 684—685).—Since emulsin does not hydrolyse maltose, and since no maltose is formed when emulsin acts on amygdalin, the latter substance cannot be a maltoside, but must be derived from an unknown disaccharide, as suggested by Auld (*Proc.*, 1907, 23, 72). G. B.

Verbenalin, a New Glucoside from *Verbena officinalis*. L. BOURDIER (*J. Pharm. Chim.*, 1908, [vi], 27, 49—57, 101—112).—The alcoholic extract of the flowering tops of the common Vervein, when extracted with ethyl acetate, yielded the glucoside *verbenalin*, $C_{17}H_{25}O_{10}$, which separates from ethyl acetate in needles, m. p. 181.5° (corr.), $[\alpha]_D - 180.52^\circ$. It is not racemised by baryta at 18°, reduces Fehling's solution, forms crystalline compounds with phenylhydrazine and hydroxylamine, is non-toxic, and is slowly hydrolysed by 2—5% sulphuric acid at 100° and by emulsin to dextrose and an optically inactive, amorphous substance, which is soluble in ether and in sodium hydroxide, reduces Fehling's solution, and gives a violet coloration with ferric chloride. *Verbena officinalis* contains emulsin and invertase. G. B.

The Absorption Spectra of Chlorophyll and its Derivatives. WILHELM MÜLLERMEISTER (*Chem. Zentr.*, 1907, ii, 1522; from *Zeitsch. wiss. Photochemie*, 1907, 5, 339—348).—The spectra of crude chlorophyll, pure chlorophyll, phylloxanthin, phyllocyanin, alkachlorophyll, phyllo-taonin, and ethylphyllo-taonin have been photographed and measured. The manner in which these chlorophyll derivatives are related to chlorophyll is shown in the annexed scheme :



The results obtained are very different to those described by previous authors (compare Schunck and Marchlewski, *Abstr.*, 1896, i, 574; Kozniewski and Marchlewski, *Abstr.*, 1907, i, 866). G. Y.

Chlorophyll. V. Rhodophyllin. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Annalen*, 1907, 358, 205—265. Compare Abstr., 1907, i, 69, 71, 784, 865).—When heated with alcoholic potassium hydroxide on the water-bath, chlorophyllin salts become strongly fluorescent, at about 140° are transformed into crystalline substances which form blue solutions with intense, red fluorescence, and at about 200° yield deep red products. These derivatives of chlorophyll are magnesium compounds. The reaction product of each stage is a mixture of closely related, similarly coloured substances, which can be separated by the differences in their acid and basic properties.

The red products are termed *rhodophyllins*, and the blue intermediate substances, *glaucophyllins*; of the former, one, which is usually the chief product of the action and is distinguished by its tendency to crystallise and by its solubilities, has been studied specially.

To prepare the rhodophyllin, the chlorophyllin salt is heated with alcoholic potassium hydroxide in an autoclave at 140° and then at 200°, and the *potassium rhodophyllin* precipitated by addition of water. If the chlorophyllin and alkali are heated in a glass tube, the chlorophyll derivatives absorb mineral constituents of the glass; in an experiment in a zinc-glass tube, the magnesium of the chlorophyll was substituted by zinc.

Rhodophyllin, $C_{33}H_{34}O_4N_4Mg(?)$, purified by extraction of the ethereal solution with dilute ammonia, crystallises in glistening, monoclinic prisms containing ether of crystallisation, is stable in air, but becomes hygroscopic after being heated at 105°, forms bluish-red solutions with blood-red fluorescence, and is readily decomposed by acids. The same rhodophyllin is obtained from a number of cryptogamic and phanerogamic plants. In its empirical formula, rhodophyllin approaches Zaleski's formula for hæmin, $C_{34}H_{32}O_4N_4FeCl$ or $C_{34}H_{34}O_4N_4FeCl$ (Abstr., 1903, i, 217), or $C_{88}H_{32}O_4N_4FeCl$, which agrees with the results of Nencki and Zaleski (Abstr., 1901, i, 434) and Küster and Haas (Abstr., 1905, i, 647). The potassium and magnesium salts are described.

Alloporphyrin, $C_{33}H_{36}O_4N_4$, the product of the action of acids on rhodophyllin, separates from ether in microscopic needles or leaflets, and dissolves only slowly in concentrated hydrochloric acid when crystalline, but is extracted from its ethereal solution by 8% hydrochloric acid. The *potassium* and *sodium* salts and the *hydrochloride* are described. When heated in acetic anhydride, alloporphyrin forms an *anhydride*, $C_{33}H_{34}O_3N_4$, which crystallises in needles or rhombic leaflets, m. p. above 300° (decomp.), yields a *potassium* salt crystallising in blue prisms, and is extracted from its ethereal solution by 6—7% or, after conversion into the potassium salt and liberation, by 4% hydrochloric acid. Alloporphyrin belongs to the porphyrin group, and has the same composition as mesoporphyrin (Nencki and Zaleski, *loc. cit.*), but is not identical with that substance, as it is insoluble in very dilute hydrochloric acid, but dissolves in the concentrated acid, forms a sodium salt insoluble in aqueous sodium hydroxide, can be regained from its alkaline solutions by acidification and extraction with ether, crystallises on neutralisation of its alkaline or acid solutions in presence of ether, and gives an absorption spectrum differing from that

of hæmatoporphyrin both in the intensity and in the position of the bands. G. Y.

Chlorophyll. VI. Crystalline Chlorophyll. RICHARD WILLSTÄTTER and MAX BENZ (*Annalen*, 1908, 358, 267—287. Compare preceding abstract).—The work of Borodin (*Bot. Zeit.*, 1882, 608) and Monteverde (*Acta Horti Petropolitani*, 1893, 13, 123) on crystalline chlorophyll has been repeated and confirmed. Details are given of an improved method by which 2·4 grams of crystalline chlorophyll are obtained from 1 kilo. of dried leaves. The colour of the solutions, the spectrum, and the indifference towards dilute acids and alkalis show the crystalline substance to be unchanged chlorophyll; the results obtained on analysis agree best with the formula $C_{38}H_{42}O_7N_4Mg$, and differentiate Borodin's product from the supposed chlorophylls of Hoppe-Seyler (*Abstr.*, 1880, 53), Gautier (*Abstr.*, 1880, 267), Rogalski (*Abstr.*, 1880, 561), and Etard (*La Biochimie et les Chlorophylles*, Paris, 1906), which in their composition approach phaeophytin.

On treatment with oxalic acid, chlorophyll yields magnesium oxalate and *phaeophorbin*, which crystallises, forms olive-brown solutions, yields complex metallic derivatives, and differs from phylloxanthin in forming a zinc compound, which is bluish-green with strong red fluorescence in cold, and becomes a deep-green in hot, glacial acetic acid solution. When heated with methyl-alcoholic potassium hydroxide, *phaeophorbin* is hydrolysed, yielding chiefly phytochlorin-*e* and phytorhodin-*g* (Willstätter and Hocheder, *Abstr.*, 1907, i, 784).

These results confirm the view expressed by previous authors that there are two chlorophylls. Crystalline chlorophyll does not yield phytol, whereas the amorphous compound is a phytol ester. G. Y.

The Chlorophyll Group. LEON MARCHLEWSKI (*Ber.*, 1908, 41, 453—455).—Phaeophytin (Willstätter and Benz, preceding abstract) is identical with the black precipitate obtained on treating chlorophyll dissolved in 80% alcohol with hydrogen chloride (Schunck and Marchlewski, *Abstr.*, 1894, i, 341). When prepared at the ordinary temperature, it does not contain free phyllocyanin or phylloxanthin, but yields these substances when treated with concentrated hydrochloric acid. Chlorophyllan, which is formed by more energetic action of hydrogen chloride on chlorophyll, contains probably both phyllocyanin and phylloxanthin. G. Y.

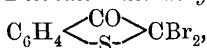
Cacao Butter, Especially its Non-hydrolysable Constituents. HERMANN MATTHES and O. ROHDICH (*Ber.*, 1908, 41, 19—23).—An attempt to isolate the flavouring constituent of cacao butter was not successful. Thirteen kilograms of the butter, after hydrolysis with potassium hydroxide and extraction with ether, gave 28 grams of material which consisted partly of oil and partly of crude phytosterol. The oil, resembling hyacinth in odour, after purification had the following constants: n_D , in 10% benzene, $+0.37^\circ$; n_D 1.492; iodine number after four and a-half hours, 68.58, and after twenty-four hours, 77.69; and composition C=80.33, H=11.77%. The solid consisted of amyrlene, stigmaterol, and phytosterol. The "crude phytosterol"

on acetylation gave white leaflets, m. p. 130°, which on bromination gave stigmasterol acetate tetrabromide, of m. p. 180° (decomp.), and phytosterol acetate dibromide, of m. p. 135°. The stigmasterol obtained had m. p. 146°, and phytosterol, m. p. 135—136° [compare Windaus and Hauth, Abstr., 1907, i, 129, who give for stigmasterol, m. p. 170°, and for stigmasterol acetate tetrabromide, m. p. 212° (decomp.)]. W. R.

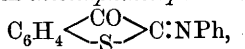
Derivatives of Thionaphthen. A. BEZDRIK, PAUL FRIEDLÄNDER, and P. KOENIGER (*Ber.*, 1908, 41, 227—242. Compare Abstr., 1906, i, 378; 1907, i, 334).—The definite proof that the compounds previously described contained the thionaphthen complex is now given by the reduction of the synthetical hydroxythionaphthen to thionaphthen. A further series of derivatives has been prepared, of which the products of reaction with the halogens and with nitrous acid demand special attention, substitution here taking place in the thionaphthen nucleus. The action of alkali hydroxides leading to the preparation of thionaphthendicarboxylic acid has also been investigated.

Thionaphthen, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \text{---S---} \end{smallmatrix} CH$, has hitherto been very difficult to prepare in quantity (Gattermann and Lockhardt, Abstr., 1894, i, 92). It is, however, easily obtained by the reduction of hydroxythionaphthen or other thionaphthen derivatives with zinc dust and acetic acid; it has m. p. 221—222°, and forms a crystalline, sparingly soluble mercuriacetate, $C_8H_5S \cdot HgC_2H_3O_2$. By means of this, thionaphthen was sought for in the products of tar distillation, but without success.

1-Bromo-2-hydroxythionaphthen, $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{---S---} \end{smallmatrix} CBr$, forms colourless crystals, m. p. 88°; the corresponding *chlorohydroxythionaphthen* is an oil. Both compounds very readily lose hydrogen bromide and form thioindigotin. 1:1-Dibromo-2-ketodihydrothionaphthen,



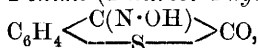
forms brownish-yellow, thick, prismatic plates, m. p. 132°; this is more stable than the monobromide, but gives thioindigotin when heated. It reacts with aniline to form *thionaphthenquinoneanilide*,



consisting of yellowish-red, glistening plates, m. p. 150—151°. The corresponding *p-toluidide* separates in long, thin, brownish-red needles, m. p. 159°. Both compounds when heated with acids give *thionaphthenquinone*,

$C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{---S---} \end{smallmatrix} CO$; this can also be prepared directly from the dibromide by the action of lead acetate, or from 1-nitrosohydroxythionaphthen. It crystallises in well-formed, compact, intensely yellow prisms, m. p. 121°, and distils almost unchanged at 247°. It dissolves in concentrated sulphuric acid with an orange-yellow coloration, and the solution turns intensely blue when shaken with benzene containing thiophen.

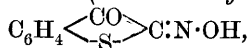
Thionaphthenquinone-2-oxime (2-nitroso-1-hydroxythionaphthen),



crystallises in long, bright yellow needles, m. p. 186° , and gives rise to an *amino-oxy*-compound which turns red in the air on reduction. The quinone reacts with phenylhydrazine to form the 2-phenylhydrazone, of which the orange-yellow crystals have m. p. $165-166^{\circ}$. With *o*-phenylenediamine, a *quinoxaline* derivative, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C}:\text{N} \\ \text{S} \text{---} \text{C}:\text{N} \end{array} > \text{C}_6\text{H}_4$, crystallising in colourless needles, m. p. $166-167^{\circ}$, is formed.

Thionaphthenquinone reacts in sodium carbonate solution with chloroacetic acid to form the yellow *sodium salt* of *phenylthioglycollic-o-glyoxalic acid*, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{H}$, which is converted by sulphuric acid into the free acid; this forms yellow crystals, m. p. $168-169^{\circ}$, gives a yellow *phenylhydrazone*, and forms *o*-carboxyphenylthioglycollic acid when heated with sulphuric acid. Heating with strong alkali hydroxides converts it into *thionaphthen-1:2-dicarboxylic acid*, $\text{C}_6\text{H}_4 \langle \text{C}(\text{CO}_2\text{H}) \rangle \text{S} \rangle \text{C} \cdot \text{CO}_2\text{H}$, crystallising in small, colourless needles, m. p. $249-251^{\circ}$.

Thionaphthenquinone-1-oxime (1-nitroso-2-hydroxythionaphthen),



prepared by the action of sodium nitrite on hydroxythionaphthen, crystallises in yellow to brownish-red needles, m. p. 172° (decomp.). It forms a crystalline, orange-yellow *sodium salt* and a *methyl ether*, $\text{C}_6\text{H}_4 \langle \text{CO} \rangle \text{S} \rangle \text{C}:\text{N} \cdot \text{OMe}$, crystallising in glistening, reddish-yellow needles, m. p. 125° . The *acetate* separates in yellow needles, m. p. 174° ; the *benzenesulphonyl* compound likewise forms yellow needles, m. p. 231° .

When reduced in acetic acid solution with zinc dust, nitrosohydroxythionaphthen yields, in the first place, 1-*amino-2-hydroxythionaphthen*; this rapidly decomposes, but the *acetate* was obtained in the form of colourless needles, m. p. 189.5° . Both the methyl ether and acetyl derivative of nitrosohydroxythionaphthen yield thiosalicylic acid; when heated with sodium carbonate, however, the acetate gives rise to *o*-thiocyanobenzoic acid, $\text{CNS} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ (Abstr., 1907, i, 335), melting at 166° , and not at $154-155^{\circ}$ as stated previously. Alcoholic sodium hydroxide causes the formation of a blue dye, which becomes a dirty red after a time.

E. F. A.

Action of Sulphur on Hydrocarbons. GEORGES CAPELLE (*Bull. Soc. chim.*, 1908, [iv], 3, 150-154).—The author proposes to make a general study of the action of sulphur on hydrocarbons.

When acetylene is passed over melted sulphur in the absence of air, hydrogen sulphide, carbon disulphide, and thiophthen (Abstr., 1886, 1032) are the principal products. Thiophthen crystallises when cooled in a bath of ether and solid carbon dioxide. These compounds seem to be decomposition products of more complex substances first formed in this reaction.

T. A. H.

Dibromothiophthen. GEORGES CAPELLE (*Bull. Soc. chim.*, 1908, [iv], 3, 154-155).—Thiophthen, dissolved in carbon disulphide, reacts

with bromine in the same solvent to form *dibromothiophthen*, $C_6H_2Br_2S_2$, m. p. 122.5° , which crystallises from alcohol in pearly needles, grouped into tufts, and can be distilled without decomposition. By the prolonged action of bromine on thiophthen, Biedermann and Jacobson's tetrabromo-compound is formed (Abstr., 1886, 1032) in addition to a third *bromo*-derivative, m. p. 223° , which may be a polymeride of the tetrabromo-compound.

T. A. H.

Double Salts of Alkaloids and Iron. MAX SCHOLTZ (*Ber. deut. pharm. Ges.*, 1908, 18, 44—52. Compare Christensen, Abstr., 1906, i, 875).—For the purpose of identifying the alkaloids, the complex compounds of the following alkaloid hydrochlorides, with ferric chloride, have been prepared and described. Strychnine forms $C_{21}H_{22}O_2N_2 \cdot HCl \cdot FeCl_3$, ruby-red, hexagonal crystals, having no definite m. p. Atropine, $C_{17}H_{23}O_3N \cdot HCl \cdot FeCl_3 \cdot H_2O$, pale yellow crystals, m. p. 167 — 168° . Cocaine, $C_{17}H_{21}O_4N \cdot HCl \cdot FeCl_3$, pale yellow, transparent needles, m. p. 165 — 166° . Caffeine, $C_8H_{10}O_2N_4 \cdot HCl \cdot FeCl_3$, small, canary-yellow, hexagonal crystals, m. p. 77° . Narcotine, $C_{22}H_{23}O_7N \cdot HCl \cdot FeCl_3$, orange, microcrystalline powder, which slowly melts from 75° . Codeine, $C_{18}H_{21}O_3N \cdot HCl \cdot FeCl_3 \cdot 2H_2O$, minute, yellowish-brown crystals, which slowly melt above 80° . Papaverine, $C_{20}H_{21}O_4N \cdot HCl \cdot FeCl_3 \cdot 2H_2O$, microscopic, orange grains, m. p. 195° ; $C_{20}H_{21}O_4N \cdot HCl \cdot FeCl_3 \cdot H_2O$, microscopic, red plates, m. p. 195° . Thebaine, $C_{19}H_{21}O_3N \cdot HCl \cdot FeCl_3 \cdot 3H_2O$, reddish-brown powder, m. p. 115° . Quinine, $C_{20}H_{24}O_2N_2 \cdot 2HCl \cdot FeCl_3 \cdot H_2O$, small, bright yellow plates, m. p. 170 — 171° . Cinchonine, $C_{19}H_{22}ON_3 \cdot 2HCl \cdot FeCl_3 \cdot \frac{1}{2}H_2O$, bright yellow, rhombic plates, m. p. 189° . Quinidine, $C_{20}H_{24}O_2N_2 \cdot 2HCl \cdot FeCl_3 \cdot 6H_2O$, minute, orange plates, m. p. 220 — 222° ; $C_{20}H_{24}O_2N_2 \cdot 2HCl \cdot FeCl_3 \cdot 2H_2O$, dark orange crystals, m. p. 220 — 222° . Cinchonidine,

$C_{19}H_{22}ON_3 \cdot 2HCl \cdot FeCl_3 \cdot 2H_2O$
and $C_{19}H_{22}ON_3 \cdot 2HCl \cdot FeCl_3$, microscopic, brilliant yellow crystals, m. p. 209 — 210° . From coniine and theobromine, no salt could be obtained; nicotine gave an oil, and brucine a dark flocculent precipitate.

J. V. E.

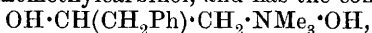
Arecaidine and Arecoline. HANS MEYER (*Ber.*, 1908, 41, 131).—A claim for priority over Wohl and Johnson (this vol., i, 49), who have overlooked the previous determination of the formulæ of these alkaloids (Abstr., 1902, i, 390).

E. F. A.

Cheiroline, an Alkaloid containing Sulphur. PH. WAGNER (*Chem. Zeit.*, 1908, 32, 76—77. Compare Reeb, Abstr., 1900, i, 186).—*Cheiroline*, $C_9H_{16}O_7N_2S_2$, is obtained by extracting with ether powdered wallflower seeds moistened with 5% sodium carbonate solution, and shaking the ethereal extract with 5% sulphuric acid. The filtered acid solution is rendered alkaline with sodium carbonate and extracted with ether; the alkaloid separates from the ethereal solution on evaporation. It crystallises in colourless prisms, m. p. 46 — 48° , and is similar to quinine in its physiological action. When warmed with water and mercuric oxide, it yields *cheirole*, $C_9H_{20}O_9N_2$, crystallising in colourless needles, m. p. 172.5° .

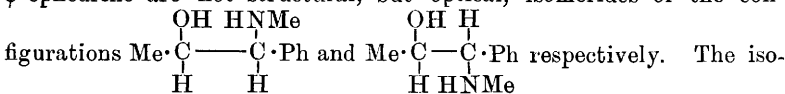
W. H. G.

Ephedrine and ψ -Ephedrine, a case of Asymmetry due to Dissimilar Halves. HERMANN EMDE (*Arch. Pharm.*, 1907, 245, 662—679).—The author agrees with Fournau's conclusion (*Abstr.*, 1907, i, 762) that the quaternary base obtained by Schmidt and Emde from cinnamyltrimethylamine hydrochloride (*Abstr.*, 1906, i, 946) is benzyldimethylaminomethylcarbinol, and has the constitution



and not $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$ as supposed by these authors; the addition of hypochlorous acid here takes place in the opposite way to that in which it unites with cinnamic acid. The aurichloride of the quaternary base described by Schmidt and Flaecher (*Abstr.*, 1905, i, 371) does not melt at 170° , as erroneously stated, but at 150 — 151° , and is thus identical with the aurichloride of the base prepared by means of hypochlorous acid by Schmidt and Emde.

After various speculations, the author concludes that ephedrine and ψ -ephedrine are not structural, but optical, isomerides of the con-



merism would therefore resemble that existing between *l*-arabonic and *l*-ribonic acids, for instance. In the same way that these acids are mutually convertible by heating with pyridine, the two ephedrines can be transformed into each other by heating with hydrochloric acid, for, as Schmidt has found, the change from ephedrine to ψ -ephedrine is reversible. The two alcohols which are formed from the bases by Hofmann's degradation would, on this view, be the two stereoisomeric forms of 1-phenylpropenol, $\text{Ph}\cdot\overset{\text{C}\cdot\text{H}}{\underset{\text{Me}\cdot\text{C}\cdot\text{OH}}{\text{C}}}$ and $\text{Ph}\cdot\overset{\text{C}\cdot\text{H}}{\underset{\text{HO}\cdot\text{C}\cdot\text{Me}}{\text{C}}}$.

By repeated distillation, the boiling point of the alcohol from ψ -ephedrine (197 — 199°) is raised to that of the alcohol from ephedrine (212 — 216°), so that these alcohols are convertible.

The chief reason why the methylimide group in ephedrine and ψ -ephedrine is regarded as attached to the carbon atom adjoining the benzene ring, is the ease with which the carbon-nitrogen linking is broken down by Hofmann's reaction. This linking is regarded as being rendered less stable by the double bonds of the benzene nucleus, in the same way that the group $\text{N}\cdot\text{C}:\text{C}$ is unstable in tetrahydropicoline and other bases having a double bond adjoining the nitrogen atom. But for this consideration, ephedrine and ψ -ephedrine might equally well be represented by the formula $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NHMe}$, previously suggested by Fournau and by Emde for one or other of the two isomerides. G. B.

Crystalline Hydroergotinine Sulphate. FRIEDRICH KRAFT (*Arch. Pharm.*, 1907, 245, 644—645. Compare *Abstr.*, 1906, i, 979).—The preparation, by Barger and Carr (*Trans.*, 1907, 91, 337), of crystalline salts of the amorphous ergot alkaloid ergotoxine (hydroergotinine) has now enabled the author to crystallise the sulphate, which hitherto he had only obtained amorphous.

Hydroergotinine sulphate forms flat, rhombic prisms, from 95% alcohol, of the composition $(C_{35}H_{41}O_6N_5)_2 \cdot H_2SO_4$, confirming the formula $C_{35}H_{41}O_6N_5$ assigned to ergotoxine by Barger and Carr. It was found impossible to prepare a crystalline sulphate from ergotinine; the two ergot alkaloids are distinct, notwithstanding Tanret's view that they are identical. G. B.

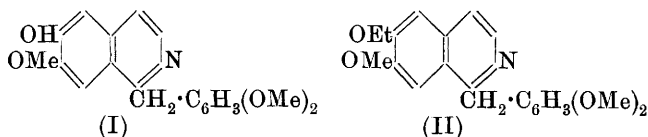
Ergotoxine and other Constituents of Ergot. GEORGE BARGER and HENRY H. DALE (*Bio-Chem.*, *J.*, 1907, 2, 240—299. Compare Abstr., 1907, i, 79).—The alkaloid ergotoxine isolated by Barger and Carr (*Trans.*, 1907, 91, 337) produces in very small doses the effects hitherto described as characteristic of ergot, including gangrene. Ergotinine is but slightly, if at all, active when pure. The relation of Kobert's cornutine and sphacelinic acid and of Jacob's preparations to ergotoxine is discussed; the richest in ergotoxine seems to have been Jacob's sphacelotoxine, which probably contained something like 40%. A list of synonyms of "active principles" is given. Vahlen's clavine (Abstr., 1906, i, 876) is a mixture of leucine and aspartic acid, and was accordingly found to be physiologically inactive. G. B.

Action of Free Alkalis on Morphine and Adrenaline. A Contribution to Sterilisation. M. GRÜBLER (*Chem. Zentr.*, 1907, ii, 1424; from *Pharm. Post.*, 1907, 40, 579—582).—As free alkali may be formed by the action of hot water on glass apparatus during sterilisation, it is recommended to test glass for use with alkaloid salts by heating with phenolphthalein in boiling water or in the steam current of a steriliser for half-an-hour, and to reject all glass giving a red coloration. Free alkali from glass gives a yellow coloration with morphine salts, ψ -morphine being formed in proportion to the amount of the free alkali. Hence morphine salts may serve to indicate the quality of a glass.

Adrenaline can be sterilised only if the glass does not yield free alkali; the sensitiveness of this alkaloid is shown by adding one drop of *N*-sodium hydroxide to 0.5 c.c. of a 1:3000 adrenaline solution, when an intense red coloration is obtained; this changes slowly to yellow, but again appears when the mixture is shaken with air. This reaction is visible with even smaller quantities of adrenaline, and is also given by suprarenine, paranephrine, and epiprenan. G. Y.

Phenolbetaines from Papaverine. HERMAN DECKER and GEORGES DUNANT (*Annalen*, 1908, 358, 288—326).—Decker and Klausner (Abstr., 1904, i, 338) found that the action of alkalis on papaverinium alkyl haloids leads to the formation of isopapaverine bases, which, on oxidation in alkaline solution, yield dimethoxy-*N*-alkylisoquinolones and veratric acid. Hence Goldschmiedt and Stransky's supposed methyl- and ethyl-papaverinium hydroxides (Abstr., 1889, 166; 1890, 179) were considered to have been formed from impure isopapaverine bases. A re-investigation has shown,

however, that the action of alkalis on papaverinium alkyl haloids takes place in three ways, depending on the conditions: (1) with very dilute alkalis, the papaverinium hydroxides are liberated, and undergo gradual condensation to phenolbetaines (Griess, Abstr., 1880, 636, 637); (2) with concentrated alkalis, the quaternary hydroxides are transformed into the isomeric carbinols, which lose water, forming *iso*-papaverine bases, and then, in consequence of oxidation by the air, *iso*quinolones and veratraldehyde. The aldehyde is converted by the alkali into veratryl alcohol and veratric acid, and (3) with alcoholic alkalis, alkylamines are formed together with a phenol, which must result from a far-reaching change in the papaverine nucleus. The constitution of this phenol remains unexplained. Goldschmiedt and Stransky's supposed papaverinium salts were, for at least the most part, salts of phenolbetaines. The terms "norpapaverine" (I) and "homopapaverine" (II) are proposed; the positions of the methoxy- and hydroxy-groups in the former, and the methoxy- and ethoxy-groups in the latter, may be interchanged:



In the following description of the compounds obtained, the m. p.'s in brackets are those given by Goldschmiedt and Stransky.

Derivatives of N-Methylnorpapaverinium.—[With MAX GIRARD.]—

The phenolbetaine, $C_6H_3(OMe)_2 \cdot CH_2 \cdot C \begin{matrix} \nearrow C_6H_2(OMe) \cdot CH \\ \searrow NMe \end{matrix} \begin{matrix} \nearrow O \\ \searrow CH \end{matrix}$, from *N*-methylpapaverinium methosulphate, crystallises in cubes (6—7H₂O), m. p. 60—65°, or, when dried and crystallised from chloroform, yellow crystals, m. p. 251° (215°) (partial decomp.), gives a blue coloration with concentrated sulphuric acid, and when heated with hydriodic acid yields *N*-methylpapaveroline, m. p. 232°. The picrate,

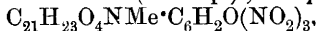
$C_{26}H_{24}O_{11}N_4$, m. p. 215° (205°); the *hydrochloride* (*norpapaverine methochloride*), $C_{20}H_{22}O_4NCl$, colourless crystals, m. p. 222°; the *platinichloride* and *hydrogen chromate*, $C_{20}H_{22}O_4N \cdot HCrO_4$, were analysed; the *mercurichloride* forms colourless crystals. *Norpapaverine methiodide*, yellow crystals (H₂O), m. p. 100°, or, when dried, 180° (decomp.).

Derivatives of N-Ethylnorpapaverinium.—The phenolbetaine,

$C_{21}H_{23}O_4N \cdot 6H_2O$, yellow crystals, m. p. 66—67° (72°), or, when anhydrous, 179—180° (175—180°); the *hydrochloride* (*norpapaverine ethochloride*), crystals (4—5H₂O), m. p. below 100° (80°), or, when anhydrous, 196°; the *hydrobromide*, $C_{21}H_{24}O_4NBr \cdot 4H_2O$, m. p. 61—62°, or, when anhydrous, 195—196°; the *picrate*, m. p. 179—180° (175°); the *dichromate* forms reddish-brown, unstable crystals; the *hydriodide*, yellow crystals, melting in water below 100°.

Derivatives of N-Methylhomopapaverinium.—*Homopapaverine meth-*

iodide, $C_{21}H_{23}O_4NMeI$, C_9H_6O , forms orange, crystalline masses, loses C_2H_6O at 100° , m. p. $187-188^\circ$ (decomp.); the *picrate*,

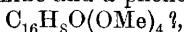


yellow needles, m. p. $133-134^\circ$. The *methobromide*, on treatment with concentrated sodium hydroxide, yields the yellow *isohomopapaverine* base, $C_{21}H_{22}O_4NMe$, which is decomposed by nitric acid, D 1.3, forming a *substance*, crystallising in white needles, m. p. 192° , nitrohomoveratrole, m. p. 117° , and *methoxyethoxy-N-methylisoquinolone*, m. p. $120-123^\circ$; *hydrochloride*, m. p. 86° , or, when anhydrous, 189° , decomp. 191° (compare Pschorr, Abstr., 1904, i, 611).

Derivatives of N-Ethylhomopapaverinium.—The *iodide* (*homopapaverine ethiodide*), $C_{23}H_{28}O_4NI$, m. p. $221-223^\circ$ (decomp.); the *picrate*, $C_{29}H_{30}O_{11}N_4$, yellow crystals, m. p. $126-127^\circ$ (decomp.). The *isobase* forms a yellow, crystalline mass, which, on treatment successively with concentrated nitric acid and an alkali, yields nitrohomoveratrole and *methoxyethoxy-N-ethylisoquinolone*.

The following facts as to the quaternary salts of papaverine are new: they differ from the salts of the phenolbetaines in that they do not give precipitates with ammonia and sodium carbonate. *N*-Methylpapaverinium picrate (Decker and Klauser, *loc. cit.*) melts at $132-133^\circ$, resolidifies, and again melts at $175-176^\circ$; the *methosulphate*, $C_{20}H_{21}O_4NMe \cdot SO_4Me$, is crystalline; the *methiodide*, m. p. $60-65^\circ$, or, when anhydrous, 195° (decomp.). The salts are obtained from the phenolbetaine of *N*-methylnorpapaverinium by the action of methyl sulphate and methyl iodide respectively. The quaternary salts of *N*-ethylpapaverine are formed in the same manner from the phenolbetaine of *N*-ethylnorpapaverinium.

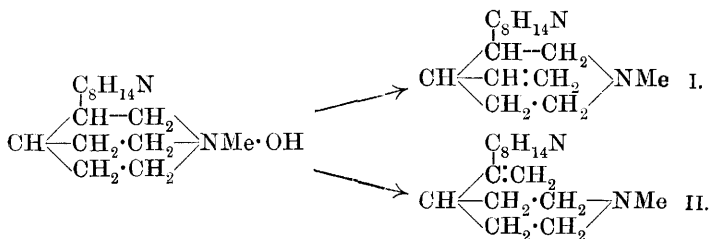
When boiled with alcoholic potassium hydroxide, papaverinium methiodide yields methylamine and a phenol-like *substance*,



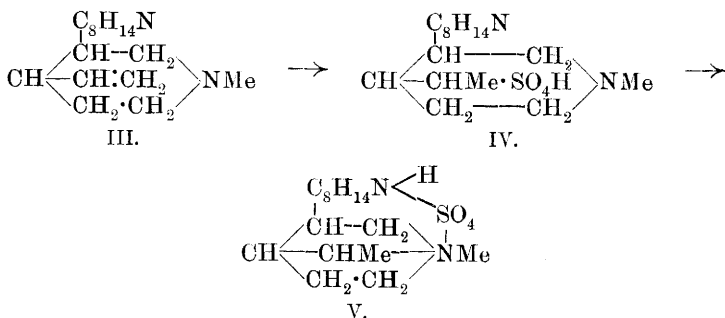
which crystallises in needles, m. p. 180° , and forms *acetyl*, *benzoyl*, and *methyl* derivatives. G. Y.

Constitution of α - and β -Methylsparteine and of *iso*Sparteine.

CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1908, **146**, 79—82. Compare this vol., i, 43, 44, 103).—Accepting the constitutional formula for sparteine suggested by the authors (Abstr., 1905, i, 659, 717), the formation of two isomeric methylsparteines by the decomposition of α -methylsparteinium hydroxide (this vol., i, 44) is readily explained according to the following scheme:



It is not possible at this stage to decide which of these formulæ represents the constitution of α -methylsparteine, but the formation of *isosparteine* derivatives from α -methylsparteine salts is readily explained assuming α -methylsparteine has the constitution I, and the following scheme represents the isomeric changes whereby α -methylsparteine sulphate is converted into *isosparteine* methosulphate :



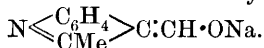
These changes involve the closing of the piperidine ring that was opened by the decomposition of the α -methylsparteinium hydroxide to form a pyrrolidine ring, and *isosparteine* (VII) may be regarded as derived from sparteine (VI) by the conversion of a piperidine into a pyrrolidine ring :



M. A. W.

New Reactions of Indoles and Pyrroles. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 790—795).—The authors describe products obtained by the condensation of 2-methylindole with various carboxylic esters in presence of sodium alkoxide or sodium.

2-Methylindole and amyl formate in presence of sodium amyloxyde or sodium yield the sodium derivative of 2-methylindole-3-aldehyde,

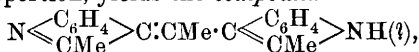


2:2-Dimethylindole reacts with amyl formate giving a compound, the *p*-nitrophenylhydrazone, $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_4$, of which crystallises from acetone or alcohol in red needles, m. p. 210° .

With ethyl oxalate in presence of sodium, 2-methylindole yields the compound, $\text{NH} \ll \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \gg \text{C}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ or $\text{N} \ll \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \gg \text{C}:\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, which crystallises from benzene in yellow needles, m. p. 126° . The corresponding carboxylic acid, $\text{C}_{11}\text{H}_9\text{O}_3\text{N}$, dissolves readily in alcohol

or acetone, decomposes at about 190°, and when boiled with dilute sulphuric acid gives an intense magenta coloration.

The interaction of 2-methylindole, ethyl acetate, and sodium ethoxide in molecular proportion, yields the compound



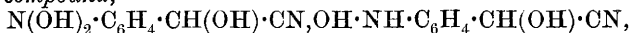
which separates from benzene in shining crystals, m. p. 203°.

T. H. P.

[4-Methylisatin.] RUDOLPH BAUER (*Ber.*, 1908, 41, 450).—4-*p*-Methylisatin has m. p. 187°, not 155° as was incorrectly stated (*Abstr.*, 1907, i, 603).
C. S.

A New Step in the Reduction of the Nitro-group. II. GUSTAV HELLER and APOSTOLOS SOURLIS (*Ber.*, 1908, 41, 373—378).—Further details as to the first product of the reduction of the nitro-group. The properties of Bamberger's agnotobenzaldehyde (*Abstr.*, 1907, i, 163) show it to be a molecular compound of *o*-nitrobenzaldehyde and *o*-hydroxylaminobenzaldehyde, and not a derivative of a dihydroxylamino-compound.

The compound,



previously isolated as the hydrochloride, forms colourless crystals, m. p. 180° (decomp.). When treated with phenylhydrazine in acetic acid solution, it yields 1-hydroxyisatinphenylhydrazone and the α - and β -phenylhydrazones of isatin. The hydrochloride of the double compound is decomposed by water, forming a substance, $\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}_3$, decomp. 175°, and small amounts of isatin or anthroxanic acid, which are formed also by the action of hydrochloric acid on the main product; this is considered to be a molecular compound of isatin and dihydroxylaminomandelonitrile. The action of aqueous potassium hydroxide on the hydrochloride leads to the formation of dibenzoyldioxindol.

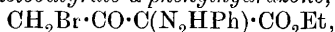
1-Propionoxyisatin, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}(\text{O} \cdot \text{COEt}) \\ \text{CO} \end{smallmatrix} > \text{CO}$, prepared by heating the hydrochloride with propionic anhydride, forms orange-yellow crystals, m. p. 105—106°, and behaves towards alkalis and phenylhydrazine in the same manner as the *l*-acetoxy-compound (*loc. cit.*).
G. Y.

Preparation of a Hydroxyquinolinesulphonic Acid. FRANZ FRITZSCHE & Co. (D.R.-P. 187869).—A new 8-hydroxyquinoline-sulphonic acid, m. p. 310—313°, produced by heating 8-hydroxyquinoline and concentrated sulphuric acid at 90° for about three days, is a lemon-yellow, crystalline powder, sparingly soluble in water and alcohol. Its potassium and sodium salts are soluble; they crystallise respectively in leaflets and needles. Its barium, iron, silver, zinc, and bismuth salts are described. Both the acid and its salts have useful therapeutic properties.
G. T. M.

[Condensation of the Arylsulphonyl- α -naphthylamines with *p*-Aminophenols.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 187823).—*p*-Toluenesulphonyl- α -naphthylamine, when oxidised with alkaline hypochlorite solution in the presence of *p*-aminophenol, furnishes an *indophenol*, $\text{O}:\text{C}_6\text{H}_4:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$, and this product or the corresponding leucoindophenol, when heated at 120° with sulphur, crystallised sodium sulphide, and copper sulphate or copper powder yields a sparingly soluble, greenish-black dye, which gives very fast shades of green on cotton. G. T. M.

Action of Diazo-chlorides on α - and γ -Bromoacetoacetic Esters. G. FAVREL (*Bull. Soc. chim.*, 1907, [iv], 1, 1238—1241).—It has been shown previously (compare Abstr., 1907, i, 796) that the α - and γ -chloroacetoacetates may be readily distinguished by their action on diazo-chlorides; thus ethyl α -chloroacetoacetate yields with diazobenzene chloride, ethyl chloroglyoxylate-phenylhydrazone, whereas the γ -ester furnishes ethyl γ -chloro- $\alpha\beta$ -diketobutyrate-phenylhydrazone and, finally, ethyl diphenylformazylformate (Abstr., 1902, i, 644; 1907, i, 796). It is now shown that the corresponding bromo-esters both behave in the same way with diazo-chlorides.

On adding ethyl γ -bromoacetoacetate to diazobenzene chloride, ethyl γ -bromo- $\alpha\beta$ -diketobutyrate- α -phenylhydrazone,



m. p. $78-80^\circ$, crystallising in yellow needles, is formed together with some ethyl diphenylformazylformate. The corresponding α -*o*-tolylhydrazone, m. p. $108-110^\circ$, crystallises from alcohol, and the isomeric *p*-compound melts at $82-83^\circ$. The methyl esters, corresponding with the first two substances described, are crystalline, and melt at $104-105^\circ$ and $139-140^\circ$ respectively.

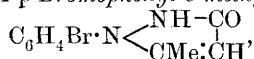
Ethyl α -bromoacetoacetate is very unstable; at temperatures above 0° , it readily passes into the γ -isomeride, and gives with diazo-chlorides the same compounds as the latter. In brominating ethyl acetoacetate at -15 to -20° , ethyl $\gamma\gamma$ -dibromoacetoacetate is formed. T. A. H.

3-Pyrazolones. III. AUGUST MICHAELIS (*Annalen*, 1907, 358, 127—170. Compare Abstr., 1905, i, 377; 1907, i, 154).—In continuation of the study of the 3-pyrazolones, 1-*p*-bromophenyl- and 1-*m*-nitrophenyl-5-methyl-3-pyrazolones and 1:5-diphenyl-3-pyrazolone and a number of their derivatives have been prepared and are now described. The bromo-compound resembles 1-phenyl-5-methyl-3-pyrazolone, forming a green nitroso-derivative, a red benzeneazo-compound, a stable 4-amino-derivative, and a 4-azopyrazolone, which crystallises more readily than the azophenylmethyl-3-pyrazolone. 1-*m*-Nitrophenyl-5-methyl-3-pyrazolone, on the other hand, does not form either a nitroso- or a benzeneazo-derivative, but is comparatively easily converted into 1-*m*-nitroantipyrine; it does not combine directly with methyl iodide, but the methiodide, from which the 3-thiopyrine is readily formed, is obtained by successive treatment of the pyrazolone with methyl sulphate and potassium iodide.

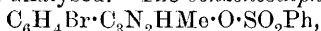
1:5-Diphenyl-3-pyrazolone (Knorr and Klotz, Abstr., 1887, 1121), obtained in good yields by condensation of acetylphenylhydrazide with

ethyl benzoylacetate in presence of phosphorus trichloride, in its reactions resembles 1-*m*-nitrophenyl-5-methyl-3-pyrazolone.

1. 1-*p*-Bromophenyl- and 1-*m*-Nitrophenyl-5-methyl-3-pyrazolone.—[With A. STIEGLER.]—1-*p*-Bromophenyl-5-methyl-3-pyrazolone,



prepared by heating acetyl-*p*-bromophenylhydrazide with ethyl acetoacetate and phosphorus trichloride at 45° and, finally, at 70°, separates from alcohol in white crystals, m. p. 227°, and is soluble in acids and alkalis. The *hydrochloride*, $\text{C}_{10}\text{H}_9\text{ON}_2\text{Br}\cdot\text{HCl}$, crystallises in white needles, m. p. 200°, and is decomposed by water; the *sodium salt*, $\text{C}_{10}\text{H}_8\text{ON}_2\text{BrNa}$, was analysed. The *benzenesulphonate*,

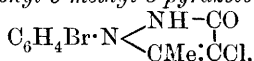


forms white crystals, m. p. 96°; the benzoate, $\text{C}_{10}\text{H}_8\text{ON}_2\text{BrBz}$, crystallises in white needles, m. p. 86°. The 4-*benzylidene* derivative,

$\text{CHPh}\left(\text{C} \begin{array}{l} \text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} \\ \diagup \quad \diagdown \\ \text{CO-NH} \end{array}\right)_2$, forms a white, crystalline powder, m. p.

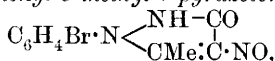
273°. The 4-*benzeneazo*-derivative, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N} \begin{array}{l} \text{NH-CO} \\ \diagup \quad \diagdown \\ \text{CMe}\cdot\text{C}\cdot\text{N}_2\text{Ph} \end{array}$, crystallises in red prisms, m. p. 219°.

4-*Chloro*-1-*p*-bromophenyl-5-methyl-3-pyrazolone,



prepared by heating the pyrazolone with phosphorus pentachloride at 150°, separates from alcohol in small, white crystals, m. p. 220°. The corresponding 4-*bromo*-compound, $\text{C}_{10}\text{H}_8\text{ON}_2\text{Br}_2$, forms colourless crystals, m. p. 231°. The 4-*iodo*-compound, prepared by treating the pyrazolone successively with mercuric chloride in hot saturated solution and an excess of iodine, crystallises in yellow leaflets, m. p. 207° (decomp.).

4-*Nitroso*-1-*p*-bromophenyl-5-methyl-3-pyrazolone,



prepared by treating the 3-pyrazolone with nitrogen trioxide in cooled glacial acetic acid solution, crystallises in emerald-green needles, becoming brown at 180°, m. p. 185°, dissolves unchanged in alkalis and acids, and gives Liebermann's reaction; the *hydrochloride*, $\text{C}_{10}\text{H}_8\text{ON}_2\text{Br}\cdot\text{NO}\cdot\text{HCl}$, crystallises in yellow needles, m. p. 210°, and is stable towards cold water. The 4-*nitro*-derivative,

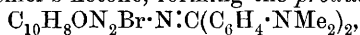


obtained on heating the pyrazolone with concentrated nitric acid, crystallises in white needles, m. p. 211.5°, and forms yellow solutions in alkalis. Reduction of the nitro- or nitroso-compound with zinc and acetic acid leads to the formation of 4-*amino*-1-*p*-bromophenyl-5-methyl-

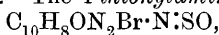
3-pyrazolone, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N} \begin{array}{l} \text{NH-CO} \\ \diagup \quad \diagdown \\ \text{CMe}\cdot\text{C}\cdot\text{NH}_2 \end{array}$, which, after purification by

conversion into its benzylidene derivative and hydrolysis of this with an alkali, separates from chloroform in white crystals, m. p. 238°, is stable when dry, but readily becomes brown on exposure to moist air,

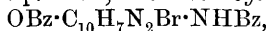
reduces Fehling's solution in the cold or ammoniacal silver solutions when heated, and gives a characteristic, reddish-brown coloration with calcium hypochlorite. The *hydrochloride*, $C_{10}H_8ON_2Br \cdot NH_2 \cdot HCl$, forms white crystals, m. p. 291° ; the *picrate*, $C_{10}H_8ON_3Br \cdot C_6H_3O_7N_3$, crystallises from alcohol in brownish-yellow needles, m. p. 200° . The *benzylidene* derivative, $C_{10}H_8ON_2Br \cdot N \cdot CHPh$, separates from ethyl acetate in white crystals, m. p. 249° , and becomes brown on exposure to air; the *m-nitrobenzylidene* derivative, yellow crystals, m. p. 274° ; the *anisylidene* derivative, yellow plates, m. p. 303° . The base condenses with Michler's ketone, forming the *product*,



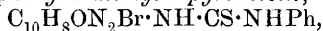
crystallising in silvery leaflets, m. p. 330° , and with ethyl acetoacetate, forming the *product*, $C_{10}H_8ON_2Br \cdot N \cdot CMe \cdot CH_2 \cdot CO_2Et$, crystallising in white needles, m. p. 199° . The 4-*thionylamino*-compound,



obtained by treating the amine with thionyl chloride in hot benzene solution, crystallises in yellow needles, m. p. 168° , decomposes on exposure to moist air, and yields a sulphite and the amino-pyrazolone when treated with an alkali. The *acetyl* derivative, $C_{10}H_8ON_2Br \cdot NHAc$, forms white crystals, m. p. 259° ; the *formyl* derivative is obtained as a crystalline powder, m. p. 240° ; the *dibenzoyl* derivative,



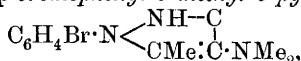
crystallises from alcohol in white needles, m. p. 188° . The 4-*carbamido*-compound, $C_{10}H_8ON_2Br \cdot NH \cdot CO \cdot NH_2$, forms white crystals, does not melt at 350° , and is readily soluble in aqueous alkalis; 4-*phenylthio*-*carbamido*-1-*p*-*bromophenyl*-5-*methyl*-3-*pyrazolone*,



crystallises in white prisms, m. p. 262° , and is decomposed by hot acids; the *s-thiocarbamide*, $CS(NH \cdot C_{10}H_8ON_2Br)_2$, prepared by heating the 4-amino-pyrazolone with carbon disulphide on the water-bath, forms a yellow, crystalline powder, m. p. 289° . The *diazo-chloride*, $C_{10}H_8ON_2Br \cdot N_2Cl$, prepared by the action of sodium nitrite on the amine hydrochloride, forms a light yellow, gelatinous mass, remains unchanged when evaporated with water, is soluble in chloroform, and in aqueous solution couples with amines and phenols; the *dye*, $C_{10}H_8ON_2Br \cdot N_2 \cdot C_{10}H_6 \cdot OH$, formed by coupling the *diazo-chloride* with β -naphthol, crystallises in orange red needles, m. p. 253° . Similar *dyes* are obtained from salicylic acid, resorcinol, aniline, and dimethylaniline.

4-*Azo*-1-*p*-*bromophenyl*-5-*methyl*-3-*pyrazolone*, $N_2(C_{10}H_8ON_2Br)_2$, prepared by coupling the *diazo-chloride* with the *pyrazolone* in alkaline solution, crystallises in reddish-brown needles, m. p. 175° .

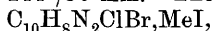
4-*Dimethylamino*-1-*p*-*bromophenyl*-5-*methyl*-3-*pyrazolone*,



prepared by heating the amino-pyrazolone with methyl iodide and potassium hydroxide in methyl-alcoholic solution, forms refracting, yellow crystals, m. p. 190° .

3-*Chloro*-1-*p*-*bromophenyl*-5-*methyl*pyrazole, $C_6H_4Br \cdot N \begin{array}{l} N = CCl \\ \text{CMe} \cdot CH \end{array}$

formed by heating the 3-pyrazolone with phosphoryl chloride at 210°, is obtained as a colourless oil, which gradually solidifies, m. p. 45°, b. p. 200°/15 mm. or 211°/30 mm. The *methiodide*,



prepared by heating the chloropyrazole with methyl iodide at 100—115°, crystallises in white prisms, m. p. 207°. 4-Azo-3-chloro-1-p-bromophenyl-5-methylpyrazole, $\text{N}_2(\text{C}_{10}\text{H}_7\text{N}_2\text{ClBr})_2$, formed by heating 4-azobromophenylmethylpyrazolone with phosphoryl chloride at 125°, crystallises in yellow needles, m. p. 203°, sublimes when highly heated, and cannot be reduced to the azopyrazole.

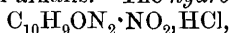
3-p-Bromoantipyridine, $\text{CMe} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NMe} \\ \text{CH} \text{---} \text{C} \end{smallmatrix} \text{O}$, is formed by the action of alkalis on 1-p-bromophenyl-5-methyl-3-pyrazolone methiodide, or by heating the 3-pyrazolone with methyl iodide and methyl alcohol in a sealed tube at 115°, but is best prepared by heating the 3-pyrazolone with methyl sulphate and treating the product with an alkali. It crystallises from chloroform in white prisms, m. p. 150°, distils almost unchanged in a vacuum, gives with ferric chloride a red, with fuming nitric acid a green, coloration becoming reddish-yellow, and does not yield a nitroso-derivative. The *hydrochloride*, $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br}\cdot\text{HCl}$, m. p. 225°; the *picrate*, $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 169°; the *ferrocyanide*, $(\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br})_3\cdot\text{H}_4\text{Fe}(\text{CN})_6$, forms a white, crystalline precipitate, decomp. about 310°. The action of bromine on 3-bromoantipyridine leads to the formation of 4-bromo-1-p-bromophenyl-3:5-dimethylpyrazolone ("4':4-dibromo-3-antipyridine"),



which forms white crystals, m. p. 163°. 4-Nitro-1-p-bromo-3-antipyridine, $\text{CMe} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NMe} \\ \text{C}(\text{NO}_2) \text{---} \text{C} \end{smallmatrix} \text{O}$, formed by the action of sodium nitrite on the antipyridine in glacial acetic acid solution, crystallises in yellow needles, m. p. 221°. 1-p-Bromophenyl-3:5-dimethyl-3-

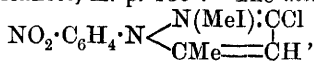
thiopyrazolone, $\text{CMe} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NMe} \\ \text{CH} \text{---} \text{C} \end{smallmatrix} \text{S}$, prepared by the action of potassium hydrogen sulphide on 3-chloro-1-p-bromophenyl-5-methylpyrazole methiodide in alcoholic solution, crystallises in yellow needles, m. p. 236°, and gives an intense yellow coloration with sulphurous acid.

1-m-Nitrophenyl-5-methyl-3-pyrazolone, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{NH-CO} \\ \text{CMe}\cdot\text{CH} \end{smallmatrix}$, prepared by condensation of acetyl-m-nitrophenylhydrazide with ethyl acetoacetate in presence of phosphorus trichloride, separates from alcohol in almost white crystals, m. p. 239°, is soluble in acids, and forms yellow solutions in alkalis. The *hydrochloride*,



yellow crystals, m. p. 235°; the *sodium salt*, $\text{C}_{10}\text{H}_8\text{O}_3\text{N}_3\text{Na}$, yellow needles. The *benzenesulphonate*, $\text{NO}_2\cdot\text{C}_{10}\text{H}_8\text{ON}_2\cdot\text{SO}_2\text{Ph}$, golden leaflets, m. p. 90°; the *benzoate*, $\text{NO}_2\cdot\text{C}_{10}\text{H}_8\text{ON}_2\cdot\text{Bz}$, white needles, m. p. 130°. The *benzylidene* derivative, $\text{CHPh}(\text{C}_{10}\text{H}_8\text{ON}_2\cdot\text{NO}_2)_2$, a white, crystalline powder, m. p. 197°. The 4-chloro-, m. p. 253°, 4-bromo-, m. p. 245°, and 4-iodo-, m. p. 221°, derivatives were analysed.

3-Chloro-1-m-nitrophenyl-5-methylpyrazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{HClMe}$, prepared by heating the pyrazolone with phosphoryl chloride at 190° , crystallises in white leaflets, m. p. 135° . The *methiodide*,



prepared by way of the methosulphate, forms yellow crystals, m. p. 196.5° .

3-Chloro-1-m-aminophenyl-5-methylpyrazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{HClMe}$, is formed by reduction of the nitrophenylpyrazole with tin and hydrochloric acid; it crystallises in white needles, m. p. 94° . The *hydrochloride*, $\text{C}_{10}\text{H}_8\text{N}_2\text{Cl} \cdot \text{NH}_2 \cdot \text{HCl}$, crystallises in needles, m. p. 103° .

1-m-Nitro-3-antipyryne, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{OHMe}$, prepared by heating 1-m-nitrophenyl-5-methyl-3-pyrazolone with methyl iodide at 115° and treating the product with sodium hydroxide, or by heating the pyrazolone with methyl sulphate, forms yellow crystals, m. p. 181° , and behaves towards ferric chloride and fuming nitric acid in the same manner as 1-p-bromo-3-antipyryne. The *picrate*,

$\text{C}_{11}\text{H}_{11}\text{ON}_2 \cdot \text{NO}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, yellow prisms, m. p. 149° ; the *ferrocyanide*,

$(\text{C}_{11}\text{H}_{11}\text{ON}_2 \cdot \text{NO}_2)_2\text{H}_4\text{Fe}(\text{CN})_6$, golden needles, decomp. 330° . The action of bromine on 1-m-nitro-3-antipyryne in glacial acetic acid solution, leads to the formation of 4-bromo-1-m-nitro-3-antipyryne, $\text{CMe} \begin{array}{l} \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{NMe} \\ \text{CBr} \text{---} \text{C} \end{array} \text{O}$, which separates from alcohol in yellow crystals, m. p. 200° .

1:4-Dinitro-3-antipyryne, $\text{CMe} \begin{array}{l} \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{NMe} \\ \text{C}(\text{NO}_2)_2 \text{---} \text{C} \end{array} \text{O}$, prepared by treating the nitropyryne with cooled concentrated nitric acid, separates from dilute acetic acid in yellow crystals, m. p. 271° (explodes).

1-m-Amino-3-antipyryne, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{OHMe}_2$, prepared by reduction of nitro-3-antipyryne with tin and hydrochloric acid, separates from dilute alcohol in white crystals, m. p. 155° . The *acetyl* derivative, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{OHMe}_2 \cdot 2\text{H}_2\text{O}$, m. p. 112° , or, when anhydrous, 199° .

1:4-Diamino-3-antipyryne, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{N}_2\text{OME}_2 \cdot \text{NH}_2$, prepared by reduction of dinitro-3-antipyryne with tin and alcoholic hydrogen chloride, forms white crystals, m. p. 185° .

1-m-Nitro-3-thiopyryne, $\text{CMe} \begin{array}{l} \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{NMe} \\ \text{CH} \text{---} \text{C} \end{array} \text{S}$, formed together with 1-m-amino-3-antipyryne by the action of potassium hydrogen sulphide on 3-chloro-1-m-nitrophenyl-5-methylpyrazole, is obtained as a yellow, microcrystalline powder, m. p. 242.5° , and is only sparingly soluble in hot water. The amino-compound forms white crystals, m. p. 97° , is readily soluble in hot water, and gives an intense yellow coloration with sulphurous acid.

2. 1:5-Diphenyl-3-pyrazolone and its Derivatives.—[With WALTER WILLERT.]—The *sodium* salt of 1:5-diphenyl-3-pyrazolone, $\text{C}_{15}\text{H}_{11}\text{ON}_2\text{Na}$, crystallises in needles, and is decomposed by water.

3-Chloro-1:5-diphenylpyrazole, $\text{NPh} \begin{array}{l} \text{N} = \text{CCl} \\ \text{CPh} \text{---} \text{CH} \end{array}$, crystallises in

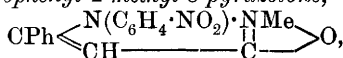
colourless needles, m. p. 64°. The *methiodide*, $C_{15}H_{11}N_2Cl, MeI$, prepared by way of the methosulphate, forms white crystals, m. p. 138°. The *methochloride* ("1:5-diphenylantipyrine chloride"), $C_{15}H_{11}N_2Cl, MeCl$, prepared by the action of silver chloride on the methiodide, or by heating diphenylantipyrine with phosphoryl chloride at 80°, is obtained as a white, hygroscopic powder, m. p. about 145°, decomp. 40° when moist; the *platinichloride*, $(C_{15}H_{11}N_2Cl, MeCl)_2PtCl_4$, crystallises in red needles, m. p. 288°.

1:5-Diphenyl-2-methyl-3-thiopyrazolone, $CPh \begin{array}{c} \text{NPh} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CH} - \text{C} \end{array} \text{S}$, formed by the action of potassium hydrogen sulphide on the methiodide or the methosulphate, or on the product obtained by heating "diphenylantipyrine" with phosphoryl chloride, separates in strongly refracting, yellow crystals, m. p. 185°; the *platinichloride*, $(C_{16}H_{14}N_2S)_2, H_2PtCl_6$, forms a reddish-yellow, microcrystalline powder; the *methiodide*, $C_{16}H_{14}N_2S, MeI$, crystallises in colourless needles, m. p. 213°; the *ethiodide*, m. p. 188°; the *trioxide*, $CPh \begin{array}{c} \text{NPh} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CH} - \text{C} \end{array} \text{SO}_3$, crystallises in white needles, m. p. above 300°.

3-Thiomethyl-1:5-diphenylpyrazole, $NPh \begin{array}{c} \text{N} = \text{C} \cdot \text{SMe} \\ \diagup \quad \diagdown \\ \text{CPh} = \text{CH} \end{array}$, formed on distillation of "diphenylthiopyrine" or its methiodide, crystallises in yellow tablets, m. p. 62°. The 4-nitroso-derivative, $SMe \cdot C_3N_2Ph_2 \cdot NO$, crystallises in green leaflets, m. p. 145° (decomp.). The *sulphone*, $C_3N_2HPh_2 \cdot SO_2Me$, crystallises in glistening needles, m. p. 121°.

5-Phenyl-1-m-nitrophenyl-3-pyrazolone, $NO_2 \cdot C_6H_4 \cdot N \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot \text{CH} \end{array}$ prepared by condensation of acetyl-m-nitrophenylhydrazide with ethyl benzoylacetoacetate in presence of phosphorus trichloride, crystallises in light yellow needles, m. p. 264°, and does not yield a nitroso- or an azo-derivative. The *sodium salt*, $C_{15}H_{10}O_3N_3Na$, forms orange-yellow needles, and detonates and inflames when heated.

5-Phenyl-1-m-nitrophenyl-2-methyl-3-pyrazolone,



crystallises in light yellow needles, m. p. 117°. The corresponding 3-chloropyrazole, $C_{15}H_{10}N_2Cl \cdot NO_2$, forms light yellow needles, m. p. 115°; the *methiodide*, $C_{15}H_{10}N_2Cl \cdot NO_2, MeI$, crystallises in yellow needles, m. p. 169°.

5-Phenyl-1-m-nitrophenyl-2-methyl-3-thiopyrazolone, $C_{16}H_{13}N_2S \cdot NO_2$ is obtained as a yellow, microcrystalline powder, m. p. 112°; the *platinichloride*, $(C_{16}H_{13}N_2S \cdot NO_2)_2, H_2PtCl_6$, orange-red powder; the *methiodide*, $NO_2 \cdot C_{16}H_{13}N_2S, MeI$, crystallises in yellow needles, m. p. 172° (decomp.); the *trioxide*, $C_{16}H_{13}O_5N_3S$, crystallises in yellow needles, decomp. 285°. The action of nitric acid on diphenyl-3-thio pyrine in concentrated sulphuric acid solution leads to the formation of a *trioxide*, $C_{16}H_{12}O_3N_2S(NO_2)_2$, which is obtained as a yellow powder
G. Y.

1 : 3-Diphenyl-5-pyrazolone and its 1-Nitro-derivative.
 AUGUST MICHAELIS and WALTER WILLERT (*Annalen*, 1907, 358, 171—182).—1 : 3-Diphenyl-5-pyrazolone, $\text{NPh} \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$, and some of its derivatives were prepared by Knorr and Klotz (*Abstr.*, 1887, 1121). The present paper contains an account of a number of other derivatives which have not been described previously.

5-Chloro-1 : 3-diphenylpyrazole, $\text{C}_8\text{N}_2\text{HClPh}_2$, prepared by heating diphenyl-5-pyrazolone with phosphoryl chloride at 150—160°, or together with methyl chloride by heating diphenyl-5-antipyrine with phosphoryl chloride, forms colourless crystals, m. p. 49°. The

methiodide, $\text{NPh} \begin{smallmatrix} \text{N}(\text{MeI})\cdot\text{CPh} \\ \text{CC}=\text{CH} \end{smallmatrix}$, formed by conversion of chloro-

diphenylpyrazole into its *methosulphate* and treatment of this with potassium iodide, crystallises in white needles, m. p. 172°. The *methochloride* ("1 : 3-diphenylantipyrine chloride") forms white crystals, m. p. 194°, and is less hygroscopic than the corresponding 1 : 5-diphenyl derivative. The *platinichloride*, $(\text{C}_{15}\text{H}_{11}\text{N}_2\text{Cl})_2\text{PtCl}_4$, crystallises in orange-red needles, m. p. 222°. The action of potassium hydrogen sulphide on the methiodide leads to the formation of 1 : 3-diphenyl-2-methyl-

5-thiopyrazolone, $\text{NPh} \begin{smallmatrix} \text{NMe}\cdot\text{CPh} \\ >\text{S} \mid \\ \text{C}=\text{CH} \end{smallmatrix}$, which crystallises from alcohol in

yellow needles, m. p. 163°, and gives with ferric chloride a transient brown coloration, or an intense yellow coloration with sulphurous acid. The *platinichloride*, $(\text{C}_{16}\text{H}_{14}\text{N}_2\text{S})_2\cdot\text{H}_2\text{PtCl}_6$, forms a crystalline powder, decomp. when heated; the *methiodide*, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}\cdot\text{MeI}$, crystallises in white needles, m. p. 185°; the *ethiodide*, white needles, m. p. 167°; the *trioxide*, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{SO}_3$, nacreous leaflets, decomp. above 300°.

5-Thiomethyl-1 : 3-diphenylpyrazole ("diphenyl-5- ψ -thiopyrpyrine"), $\text{NPh} \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{C}(\text{SMe}) \end{smallmatrix} \text{CH}$, is obtained as a colourless oil, b. p. 225°/11 mm., gradually becomes yellow, and does not form a nitroso-derivative. The *hydrochloride*, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, crystallises in needles, m. p. 80°, and is decomposed by water. The *sulphone*, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{SO}_2$, crystallises in silky needles, m. p. 162°.

4-Benzeneazo-5-chloro-1 : 3-diphenylpyrazole, $\text{N}_2\text{Ph}\cdot\text{C}_8\text{N}_2\text{ClPh}_2$, prepared by heating 4-benzeneazo-1 : 3-diphenyl-5-pyrazolone with phosphoryl chloride at 110—115°, crystallises from alcohol in orange-red needles, m. p. 122°, is insoluble in alkalis, and on reduction with zinc dust and alcoholic potassium hydroxide yields 4-benzeneazo-1 : 3-diphenylpyrazole, $\text{N}_2\text{Ph}\cdot\text{C}_8\text{N}_2\text{Ph}_2$, which crystallises in orange-red needles, m. p. 111°, and gives an intense red coloration when heated with concentrated hydrochloric acid; the *hydrochloride*, $\text{C}_{21}\text{H}_{16}\text{N}_4\cdot\text{HCl}$, crystallises in red needles, decomp. about 100°.

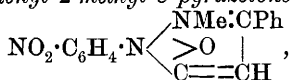
3-Phenyl-1-m-nitrophenyl-5-pyrazolone, $\text{C}_8\text{HON}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared from ethyl benzoylacetate and m-nitrophenylhydrazine, forms light yellow needles, m. p. 174°. The 4-benzeneazo-derivative,



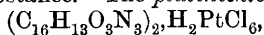
prepared by the action of diazobenzene chloride on the pyrazolone in

aqueous sodium hydroxide solution and acidification of the mixture with acetic acid, crystallises from alcohol in orange-red needles, m. p. 179°, and is soluble in aqueous alkalis. The corresponding 4-benzene-azo-5-chloro-compound, $C_{15}H_9N_2Cl(NO_2) \cdot N_2Ph$, forms reddish-brown crystals, m. p. 152°.

3-Phenyl-1-m-nitrophenyl-2-methyl-5-pyrazolone,



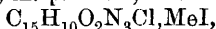
prepared by heating nitrodiphenylpyrazolone with methyl sulphate and liberating the base with a dilute alkali, crystallises from alcohol in light yellow needles, m. p. 178°, and resembles antipyrine in its behaviour towards ferric chloride and nitrous acid, but is much less basic than that substance. The *platinichloride*,



forms orange-red needles, m. p. 230°; the *hydriodide*, $C_{16}H_{13}O_3N_3 \cdot HI$, crystallises from alcohol in yellow needles; the *nitroso*-derivative, $C_{16}H_{12}O_3N_3 \cdot NO$, crystallises in green leaflets, darkens at 215°, m. p. 225° (decomp.).

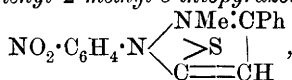
5-Chloro-3-phenyl-1-m-nitrophenylpyrazole, $NO_2 \cdot C_6H_4 \cdot N \begin{array}{l} \swarrow N=CPh \\ >C \\ \searrow CCl:CH \end{array},$

prepared in the same manner as 5-chlorodiphenylpyrazole, crystallises in slightly yellow needles, m. p. 105°; the *methiodide*,



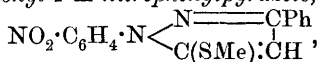
formed by way of the methosulphate, crystallises in dark yellow needles, m. p. 172°.

3-Phenyl-1-m-nitrophenyl-2-methyl-5-thiopyrazolone,



prepared by the action of potassium hydrogen sulphide on the methiodide, is obtained as a yellowish-brown powder, m. p. 158°; the *platinichloride*, $(NO_2 \cdot C_{16}H_{13}N_2S)_2 \cdot H_2PtCl_6$, orange-red powder, decomp. when heated; the *methiodide*, $C_{16}H_{13}N_2S(NO_2)MeI$, yellow needles, m. p. 202°; the *trioxide*, $NO_2 \cdot C_{16}H_{13}N_2SO_3$, yellow crystals, m. p. 300°.

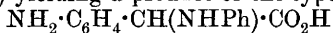
5-Thiomethyl-3-phenyl-1-m-nitrophenylpyrazole,



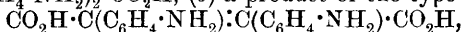
prepared by heating the methiodide in a vacuum, crystallises from alcohol in yellow needles, m. p. 106°; the *sulphone*, $NO_2 \cdot C_{16}H_{13}N_2SO_2$, forms white needles, m. p. 148°. G. Y.

Action of Dichloroacetic Acid on Aniline and its Homologues. II. GUSTAV HELLER (*Annalen*, 1908, 358, 349—373. Compare Abstr., 1904, i, 730).—In amplification of the previous paper, further details are given as to the nitration of stilbenedicarboxylic acid, the preparation of 3:3'-dinitrostilbenedicarboxylic acid is described, and the action of dichloroacetic acid on aniline and its homologues is discussed in the light of results obtained with *m*-toluidine and the xylidines. The first product of the action of dichloroacetic acid on aniline or a homologue is a substance of the type (a) $CH(NHPh)_2 \cdot CO_2H$, (b) $NHPh \cdot CHCl \cdot CO_2H$, or (c) $NHPh \cdot CHCl \cdot CO \cdot NHPh$. These are not

isolated, but immediately undergo isomerisation alone, or followed by condensation, (a) yielding a product of the type (I)



or (II) $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2 \cdot \text{CO}_2\text{H}$, (b) a product of the type (III)



and (c) a product of type (IV) $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}(\text{NHPh}) \\ \text{NH} \end{smallmatrix} \text{CO}$. Products of

type (I) are obtained in the case of *o*-toluidine and *v-m*-xylidine, (II) is obtained from *p*-xylidine, (III) from aniline, *m*-toluidine, and *v-o*-xylidine, whilst products of type (IV) are formed from *p*-toluidine, *as-m*-xylidine, *s*-xylidine, and 1:2:4-xylidine.

The action of nitric acid, D 1.52, on stilbenedicarboxylic anhydride at 0° and, finally at the ordinary temperature, leads to the formation of a mixture of crystalline acids, which on oxidation with permanganate in dilute sodium hydroxide yield *p*-nitrobenzoic acid together with small amounts of *o*- and probably of *m*-nitrobenzoic acids. Reduction of the mixed nitrostilbenedicarboxylic acids leads to the formation of an *acid*, crystallising in needles, decomp. about 180°, and 4:4'-diaminostilbenedicarboxylic acid, together with traces of nitro- or azoxy-compounds.

m-Nitrobenzyl cyanide (Gabriel, Abstr., 1883, 916), formed together with a *substance*, m. p. 149°, insoluble in hot ether, from the chloride and potassium cyanide in aqueous solution at 50–60°, separates from a mixture of ether and light petroleum in crystals, m. p. 61–62°. On successive treatment with iodine and sodium methoxide in methyl alcohol-etheral solution, *m*-nitrobenzyl cyanide yields 3:3'-*dinitrodicyanostilbene*, $\text{C}_{16}\text{H}_8\text{O}_4\text{N}_4$, which crystallises in colourless plates or short prisms, m. p. 233° (decomp.); on reduction with stannous chloride and hydrogen chloride in acetic acid solution, it is converted into the 3:3'-*diamino*-compound, $\text{C}_{16}\text{H}_{12}\text{N}_4$, crystallising in threads, m. p. 187°, and forming a sparingly soluble, colourless *hydrochloride*. 3:3'-*Dinitrostilbenedicarboxylic anhydride*, $\text{C}_{16}\text{H}_8\text{O}_7\text{N}_2$, prepared by heating the dicyanide with hydrogen chloride in glacial acetic acid solution at 185–190°, forms colourless needles, m. p. 249–249.5°. The dinitro-anhydride could not be reduced in acid solution; with zinc dust and ammonia in sodium hydroxide solution, it yields 3:3'-*azoxystilbenedicarboxylic anhydride*, $\text{C}_{16}\text{H}_8\text{O}_4\text{N}_2$, obtained as a yellow powder, decomp. slowly above 245°. 3:3'-*Diaminostilbenedicarboxylic anhydride*, $\text{C}_{16}\text{H}_8\text{O}_4\text{N}_2$, formed from the dicyanide by hydrolysis with alcoholic alkali, is obtained in red, amorphous masses, soluble in ethyl benzoate.

2:2'-*Azoxystilbenedicarboxylic anhydride*, prepared by reduction of the 2:2'-dinitro-acid with stannous chloride and hydrochloric acid or with boiling zinc dust and ammonia, remains unchanged at 270°, and dissolves in dilute sodium carbonate, forming the yellow sodium salt of the dicarboxylic acid. The reduction appears to proceed further if the dinitro-acid is treated with stannous chloride in glacial acetic acid solution.

The action of sodium dichloroacetate on *m*-toluidine in sodium acetate solution leads to the formation of a crystalline *hydrochloride*, decomposing when highly heated; the free *amino*-compound behaves in the same manner as the acids derived from dichloroacetic acid and aniline, or *o*- or *p*-toluidines.

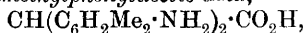
[With P. LEYDEN.]—3-as-m-*Xylidino*-5 : 7-*dimethyloxindole*,



prepared from dichloroacetic acid and 1 : 3 : 4-xylidine, crystallises in needles, m. p. about 234°, forms a *bromo-derivative*, $\text{C}_{18}\text{H}_{19}\text{ON}_2\text{Br}$, m. p. about 215°, and, when treated with bromine in hot glacial acetic acid solution, is oxidised to 5 : 7-*dimethylisatin*, $\text{C}_{10}\text{H}_9\text{O}_2\text{N}$, crystallising in yellow needles, m. p. 243°. The *phenylhydrazone* of this, $\text{C}_{16}\text{H}_{15}\text{ON}_3$, yellow needles, m. p. 272°.

3' : 5'-*Xylidino*-4 : 6-*dimethyloxindole*, prepared from dichloroacetic acid and 1 : 3 : 5-xylidine, crystallises in needles, m. p. 250° (decomp.). 4 : 6-*Dimethylisatin*, yellow needles, m. p. 238—239°; the *phenylhydrazone*, yellow needles, m. p. 238—239°.

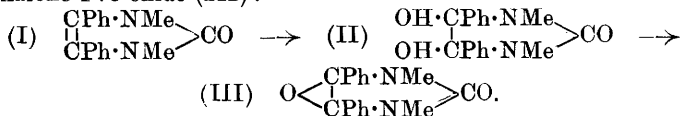
Di-4-*amino*-2 : 5-*dimethylphenylacetic acid*,



formed from dichloroacetic acid and *p*-xylidine, is obtained in granular crystals, m. p. 245° (decomp.); the *hydrochloride*, $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$, needles; the *sulphate* is only very sparingly soluble. The *dibenzoyl* derivative, $\text{C}_{32}\text{H}_{30}\text{O}_4\text{N}_2$, needles, m. p. 182—183°. When diazotised and coupled with β -naphthol, the base forms the *bisazonaphthol*, $\text{CH}(\text{C}_6\text{H}_2\text{Me}_2 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH})_2 \cdot \text{CO}_2\text{H}$, which crystallises in red needles, softens at 195°, and gradually decomposes at the higher temperature.

Ostromisslensky's paper on the same subject (this vol., i, 82) is criticised. G. Y.

Action of Methylcarbamides on Benzil. HEINRICH BILTZ [with P. HORRMANN and RIMPEL] (*Ber.*, 1908, 41, 167—173)—An investigation of the compounds formed by the condensation of methylcarbamide and *s*-dimethylcarbamide with benzil. Unlike glyoxal and diacetyl (Biltz and Horrmann, this vol., i, 62), benzil condenses with only 1 mol. of methylcarbamide or *s*-dimethylcarbamide. The products so formed may also be prepared from glyoxalones; for example, 4 : 5-diphenyl-1 : 3-dimethylglyoxalone (I), when oxidised by potassium permanganate in aqueous acetone, is converted into 4 : 5-dihydroxy-4 : 5-diphenyl-1 : 3-dimethylglyoxalone (II), which compound readily loses water when heated at 180° or boiled with acetic anhydride, being converted into a substance identical with that formed by the condensation of *s*-dimethylcarbamide with benzil, and which, from its mode of formation from the glyoxalone, must be 4 : 5-diphenyl-1 : 3-dimethylglyoxalone-4 : 5-oxide (III):



The condensation of benzil with the substituted carbamide probably takes place in two stages, the compound first formed being the glycol, which then decomposes with the elimination of water.

4 : 5-*Diphenyl*-1-*methylglyoxalone*-4 : 5-*oxide* (4 : 5-*endoxy*-2-*oxy*-4 : 5-*diphenyl*-1-*methyltetrahydroglyoxaline*, $\text{O} < \begin{array}{c} \text{CPh} \cdot \text{NMe} \\ | \\ \text{CPh} \cdot \text{NH} \end{array} > \text{CO}$, results on

heating benzil with methyl carbamide at 145° ; it crystallises in rhombic leaflets, m. p. $216-217^{\circ}$; the acetate, $C_{18}H_{16}O_3N_2$, crystallises in small rhombohedra, m. p. 172° .

4:5-Dihydroxy-4:5-diphenyl-1:3-dimethylglyoxalone, $C_{17}H_{18}O_3N_2$, prepared by the oxidation of 4:5-diphenyl-1:3-dimethylglyoxalone (Biltz and Horrmann, this vol., i, 57), crystallises in long, flat, rectangular plates, m. p. 205° (decomp.). When heated with acetic anhydride or alone at 180° , it loses water, yielding 4:5-diphenyl-1:3-dimethylglyoxalone-4:5-oxide (4:5-endoxy-2-oxy-4:5-diphenyl-1:3-dimethyltetrahydroglyoxaline), $C_{17}H_{16}O_2N_2$, crystallising in flat, six-sided plates, m. p. $197-198^{\circ}$; the same compound is obtained on heating benzil with *s*-dimethylcarbamide at 205° .

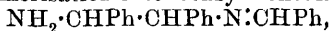
Benzil behaves like benzoin when heated with *as*-dimethylcarbamide, diphenylacetylenediureine being formed (compare Anschütz and Geldermann, Abstr., 1891, 725).

Attempts to prepare 4:5-diphenylglyoxalone-4:5-oxide were unsuccessful. W. H. G.

Interaction of Sodium Sulphide and the Hydroxyphenazines. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 187868).—The hydroxyphenazines derived from the meta-diamines and the chlorinated *p*-aminophenols, containing one or two chlorine atoms in the ortho-positions with respect to the hydroxyl group when heated with crystallised sodium sulphide at $110-140^{\circ}$, give rise to sulphur derivatives which no longer contain chlorine. These sulphur compounds are reddish-brown powders, sparingly soluble in water, alcohol, or dilute acids; they dye cotton only very slightly, and seem to be intermediate products in the formation of sulphide dyes, as they are converted into these substances by further treatment with sodium sulphide and sulphur. The properties of a series of these intermediate sulphur derivatives are tabulated in the patent. G. T. M.

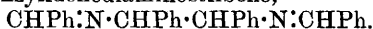
Resolution of the Iminazole Ring in the Case of Amarine and Anisine. OTTO FISCHER and GEORG PRAUSE (*J. pr. Chem.*, 1908, [ii], 77, 125—134).—The resolution of the iminazole ring of amarine and anisine has been studied in extension of the investigations on this subject already published (Abstr., 1906, i, 539; 1907, i, 352).

Amarine, $C_{21}H_{18}N_2 \cdot \frac{1}{2}H_2O$ (Bertagnini, *Annalen*, 1853, 88, 127), crystallises from dilute alcohol in pointed rhombohedra, m. p. 106° , loses $\frac{1}{2}H_2O$ at $100-110^{\circ}$ or when boiled with water (Claus, Abstr., 1885, 1063), and when anhydrous crystallises from benzene-light petroleum in colourless prisms, m. p. 133° . The formation of dibenzylidenediaminostilbene on reduction of amarine with sodium (Grossmann, Abstr., 1889, 1191) is considered to take place in several stages, the amarine, $CPh \begin{smallmatrix} \text{NH} \cdot \text{CHPh} \\ \diagdown \quad \diagup \\ \text{N} \end{smallmatrix}$, being reduced to hydroamarine, which undergoes isomerisation into benzylidenediaminostilbene,



and hydrobenzamide, which is further reduced to benzylideneimine, $CHPh \cdot NH$, and this reacts with the monobenzylidene compound forming

ammonia and dibenzylidenediaminostilbene,

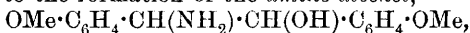


In agreement with this view, it is found that ammonia is evolved during the reduction, and that the yield of the dibenzylidene compound is increased by addition of hydrobenzamide to the reaction mixture.

cis-Diaminostilbene picrate, $\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_8$, has m. p. 239°. The *di*formyl derivative, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$, crystallises in colourless prisms, m. p. 294°.

*iso*Amarine is obtained in an almost quantitative yield by heating amarine with sodium ethoxide in alcoholic solution at 150—160°.

p-Anisine crystallises from dilute alcohol in needles (H_2O), m. p. 118°, or when anhydrous from benzene-light petroleum in prisms, m. p. 148°. On reduction with sodium, it forms ammonia and *dianisylidenedi-p-methoxydiaminostilbene*, $\text{C}_{32}\text{H}_{32}\text{O}_4\text{N}_2$, which crystallises in colourless leaflets, m. p. 183°, and when heated with dilute acids yields anisaldehyde and *di-p-methoxydiaminostilbene*, $\text{C}_{16}\text{H}_{20}\text{O}_2\text{N}_2$, crystallising in needles, m. p. 151°; the *hydrochloride*, $\text{C}_{16}\text{H}_{20}\text{O}_2\text{N}_2\cdot 2\text{HCl}$, needles, decomp. about 260°; the *picrate* (H_2O), yellow prisms, m. p. about 215° (decomp.). The *di*formyl derivative, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, crystallises in leaflets, m. p. 290° (decomp.); the *diacetyl* derivative, $\text{C}_{20}\text{H}_{24}\text{O}_4\text{N}_2$, prisms, m. p. about 330° (decomp.). The action of nitrous acid on the diamine leads to the formation of the *amino-alcohol*,



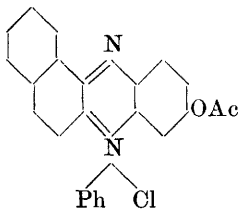
which crystallises from light petroleum in colourless prisms, m. p. 134°. The diamine condenses with anisaldehyde to form *dianisylidenedimethoxydiaminostilbene*, m. p. 183°, or with benzaldehyde, yielding *dibenzylidenedimethoxydiaminostilbene*, $\text{C}_{30}\text{H}_{28}\text{O}_2\text{N}_2$, which crystallises in colourless prisms, m. p. 148°, and is hydrolysed by boiling dilute sulphuric acid, forming benzaldehyde and the diamine.

G. Y.

Constitution of Rosindone and *iso*Rosindone. FRIEDRICH KEHRMANN and K. L. STERN (*Ber.*, 1908, 41, 12—17).—The phenol-betaine formula for *isorosindone*, which has been supported by Decker and Würsch on negative grounds (*Abstr.*, 1906, i, 905), is confirmed by a study of its behaviour towards acetic anhydride and zinc dust.

Leuco-isorosindone diacetate, $\text{C}_{10}\text{H}_6\langle\begin{smallmatrix} \text{N}^{\text{Ac}} \\ \text{N}^{\text{Ph}} \end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{OAc}$, prepared in

this way, crystallises from alcohol in small, colourless, glistening plates, m. p. 215° (decomp.). Ferric chloride oxidises it, yielding the ferrichloride of 3-acetoxyphenylnaphthaphenazonium chloride, annexed formula, which forms yellowish-brown crystals, decomposing slowly in aqueous solution into *isorosindone*. When *isorosindone* is kept in contact with acetic anhydride for two months at the ordinary temperature, and afterwards ferric chloride added to its aqueous solution, the same double salt is formed, a reaction quite analogous to that of naphthaprasindone (*Abstr.*, 1899, i, 528). The conclusion is drawn that addition



of acetic anhydride occurs, forming the phenazonium acetate, this being converted into chloride by the ferric chloride.

Leuco-2-methylisosindone diacetate forms plates, m. p. 242° , and, on oxidation with ferric chloride, yields the ferrichloride of 2-methyl-3-acetoxyphenylnaphthaphenazonium chloride, $C_{25}H_{19}O_2N_2Cl, FeCl_3$. The chloride itself is red; its *platinichloride*, $(C_{25}H_{19}O_2N_2)_2PtCl_6$, fiery-red, and the *nitrate*, brick-red.

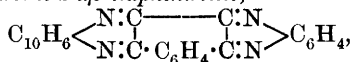
An alcoholic solution of 2-methylisosindone, when treated with ferric chloride, gives a metallic green double salt, which, in contradistinction to the corresponding acetoxy-compound, is insoluble in water.

Leuco-rosindone diacetate is not well characterised; on oxidation with ferric chloride, it gives the ferrichloride of 6-acetoxyphenylnaphthaphenazonium chloride, $C_{24}H_{17}O_2N_2Cl, FeCl_3$, slowly passing back in water to rosindone. W. R.

Oxidation of Naphthazines by Chromic Acid. III. Relation of the Azines to the Quinoxalines. OTTO FISCHER and ERICH SCHINDLER (*Ber.*, 1908, **41**, 390—397. Compare *Abstr.*, 1904, i, 111; 1906, i, 609).—The method of preparing diketonaphthaphenazine by oxidising naphthaphenazine with chromic acid has now been applied to the oxidation of the naphthazines. Progressive degradation to quinoxaline bases has been accomplished in the case of both the naphthazines and naphthaphenazine. The phenazines, quinoxalines, and pyrazines (Gabriel and Sonn, this vol., i, 60) are thus shown to be members of the same group of azines.

Diketo-s- $\alpha\beta$ -naphthazine, $C_{10}H_6 \begin{smallmatrix} \text{N}:\text{C}=\text{CO} \\ \text{N}:\text{C}\cdot\text{C}_6\text{H}_4 \end{smallmatrix} \text{CO}$, crystallises from boiling anisole in yellowish-brown needles, m. p. about 300° (decomp.). In the absence of acetic anhydride, the oxidation leads to the formation of mixed crystals of the diketo-product and unchanged *s- $\alpha\beta$ -naphthazine*. The diketone is reduced by phenylhydrazine in hot glacial acetic acid solution, forming the *dihydroxynaphthazine*, crystallising in brown needles, and gives with alcoholic potassium hydroxide a blue, or with concentrated sulphuric acid a green, coloration. The *diacetyl* derivative, $C_{24}H_{16}O_4N_2$, crystallises in yellow needles, m. p. above 270° (decomp.). The *monoxime*, $C_{20}H_{11}O_2N_3$, crystallises from pyridine in needles, and gives a brown coloration with concentrated sulphuric acid.

$\alpha\beta$ -Naphthaphenazine-s- $\alpha\beta$ -naphthazine,



formed by the action of *o*-phenylenediamine on the diketone at 130° , crystallises in yellow needles, and with mineral acids yields red *salts*, which are hydrolysed by water. When boiled with concentrated sodium hydroxide, the diketone yields 2-phenylnaphthaphenazine-*o*-

carboxylic acid, $C_{10}H_6 \begin{smallmatrix} \text{N}:\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \\ \text{N}:\text{CH} \end{smallmatrix}$, crystallising in yellow needles, m. p. above 300° (decomp.), sublimes partially unchanged, and gives a cherry-red coloration with sulphuric acid. When distilled, it loses carbon dioxide and forms 2-phenylnaphthaphenazine, $C_{18}H_{12}N_2$, which

crystallises in yellow needles, m. p. 153° , sublimes unchanged, and gives a dark red coloration with sulphuric acid.

as- $\alpha\beta$ -Naphthazine give a similar series of derivatives.

Diketo-as- $\alpha\beta$ -naphthazine, $C_{20}H_{10}O_2N_2$, crystallises in red needles, commences to darken at 240° , cokes when highly heated, and is reduced easily by phenylhydrazine in glacial acetic acid-acetic anhydride solution, yielding a blue product, which on exposure to air in presence of alcohol or acetic acid again forms the diketone. The monoxime crystallises in yellow needles.

$\alpha\beta$ -Naphthaphenazine-as- $\alpha\beta$ -naphthazine, $C_{20}H_{14}N_4$, forms yellow needles, m. p. about 284° , and yields dark red salts with concentrated mineral acids. *3-Phenylnaphthaquininoxaline-o-carboxylic acid* sublimes in long needles, m. p. 246° (decomp.). *3-Phenylnaphthaquininoxaline* crystallises in yellow needles, m. p. 163° .

Whilst oxidation of the alkylhydroxides of phenazine and naphthaphenazine in alkaline solution leads to the formation of *N*-alkylaposafranone and rosindone respectively, the quinoxalines under these conditions behave in the same manner as quinolines, yielding quinoxalones. Thus *N-methylnaphthaquininoxalone*, $C_{13}H_{10}ON_2$, which crystallises in yellow prisms, m. p. 214° , is obtained by oxidising *$\alpha\beta$ -naphthaquininoxaline methiodide*, $C_{13}H_{11}N_2I$, red prisms, decomp. above 150° , with alkaline ferricyanide solution. G. Y.

$\alpha\beta$ -Naphthazines. OTTO FISCHER and HEINRICH STRAUS (*Ber.*, 1908, 41, 397—400).—A method of preparing unstable azo-dyes, and a note on the simultaneous formation of α - and β -naphthazines. Azo-dyes, such as benzeneazo- $\beta\beta$ -dinaphthylamine (Matthes, *Abstr.*, 1890, 992), which are readily decomposed by acids, and diazoamino-compounds, which easily undergo isomerisation into aminoazo-compounds, are obtained with ease in a state of purity if prepared in pyridine solution. The following azo-dyes have been prepared in this manner from $\beta\beta$ -dinaphthylamine.

p-Chlorobenzene- $\beta\beta$ -dinaphthylamine, $C_{26}H_{18}N_3Cl$, violet-red needles, m. p. 165° . *p-Tolueneazo- $\beta\beta$ -dinaphthylamine*, $C_{27}H_{21}N_3$, scarlet needles, m. p. 172° . *m-Xyleneazo- $\beta\beta$ -dinaphthylamine*, from 4-amino-*m*-xylene, red prisms, m. p. 130° . *α -Naphthaleneazo- $\beta\beta$ -dinaphthylamine*, $C_{30}H_{21}N_3$, a red, crystalline mass, m. p. 204° . *β -Naphthaleneazo- $\beta\beta$ -dinaphthylamine*, dark violet needles, m. p. 205° . When treated with glacial acetic acid and heated with hydrochloric acid on the water-bath, these azo-dyes are converted into *$\alpha\beta$ -naphthazine*, m. p. 243° .

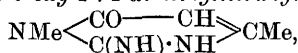
Acetyldihydro-s- $\alpha\beta$ -naphthazine, $C_{10}H_7\begin{smallmatrix} \nearrow NAc \\ \searrow N \end{smallmatrix} C_{10}H_6$, formed by boiling the naphthazine with acetic anhydride and glacial acetic solution, crystallises in yellow prisms, m. p. 228° .

The action of β -naphthaquinone on *$\alpha\beta$ -dinaphthylamine* (Witt, 1887, 153) leads to the formation, not only of *as- $\alpha\beta$ -naphthazine*, but also of the *s*-isomeride, which, in two experiments, was obtained as the chief product. G. Y.

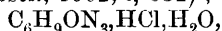
Condensation of Alkylguanidines with Ethyl Acetoacetate, &c. RIKO MAJIMA (*Ber.*, 1908, 41, 176—186).—A continuation of

the investigation on the anhydro-bases derived from aliphatic diamines (Haga and Majima, Abstr., 1903, i, 291). Alkylguanidines condense with unsymmetrical compounds, like ethyl acetoacetate, with the formation of two isomeric dialkyl derivatives of 2-imino-4-oxytetrahydropyrimidines, whereas only one compound is formed when the alkylguanidine condenses with a substance having a symmetrical structure such as ethyl malonate or acetylacetone. The constitution of each compound formed was deduced from its behaviour on decomposition with concentrated hydrochloric acid.

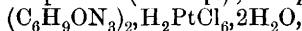
Ethyl acetoacetate, when heated with methylguanidine carbonate in alcohol, yields 2-imino-6-oxy-1 : 4-dimethyltetrahydropyrimidine,



crystallising in needles, m. p. 312° , and 6-oxy-2-methylimino-4-methyltetrahydropyrimidine, $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{CH} \\ \diagdown \quad \diagup \\ \text{C}(\text{NMe}) \cdot \text{NH} \end{array} \text{CMe}$, crystallising in leaflets, m. p. 202° . The former compound was first prepared by Jaeger (Abstr., 1891, 1007) by the methylation of iminomethyluracil, but its constitution was not ascertained; it is converted by concentrated hydrochloric acid under pressure at $170\text{--}180^\circ$ into 1 : 4-dimethyluracil (Behrend and Thurm, Abstr., 1902, i, 832); the *hydrochloride*,



crystallises in prisms, m. p. 265° (decomp.); the *platinichloride*,



forms orange-red, rhombic crystals, m. p. 207° .

6-Oxy-2-methylimino-4-methyltetrahydropyrimidine is converted by concentrated hydrochloric acid under pressure at 220° into 4-methyluracil; its *hydrochloride*, $\text{C}_6\text{H}_9\text{ON}_3 \cdot \text{HCl} \cdot \frac{1}{2}\text{H}_2\text{O}$, m. p. 253° , and *platinichloride*, $(\text{C}_6\text{H}_9\text{ON}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, were prepared.

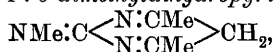
Allylguanidine sulphate, $(\text{C}_4\text{H}_9\text{N}_3)_2 \cdot \text{H}_2\text{SO}_4$, m. p. $220\text{--}222^\circ$, results on heating allylamine sulphate and cyanamide in a sealed tube at $110\text{--}120^\circ$; the *picrate*, $\text{C}_4\text{H}_9\text{N}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, rhombic crystals, m. p. $144\text{--}145^\circ$, and *platinichloride*, $(\text{C}_4\text{H}_9\text{N}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, m. p. 188° (decomp.), were prepared.

2-Imino-6-oxy-4-methyl-1-allyltetrahydropyrimidine, $\text{C}_8\text{H}_{11}\text{ON}_3$, prepared from ethyl acetoacetate and allylguanidine, or by treating iminomethyluracil with allyl iodide in alcohol containing potassium hydroxide, forms crystals, m. p. 182° ; the *picrate* has m. p. 205° . When heated with hydrochloric acid under pressure, it yields 4-methyl-1-chloropropyluracil, $\text{C}_8\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$, crystallising in lustrous leaflets, m. p. $208\text{--}209^\circ$.

6-Oxy-2-allylimino-4-methyltetrahydropyrimidine, $\text{C}_8\text{H}_{11}\text{ON}_3$, is also formed by the interaction of allylguanidine and ethyl acetoacetate; it has m. p. 149° ; the *picrate* forms long prisms, m. p. 182° . It is converted by concentrated hydrochloric acid under pressure at 100° into 2-chloropropylimino-4-methyluracil, $\text{C}_8\text{H}_{12}\text{ON}_3\text{Cl} \cdot \text{H}_2\text{O}$, crystallising in leaflets, m. p. about 90° , whilst at 150° it is converted into a third isomeride, named provisionally γ -isomeride, $\text{C}_8\text{H}_{11}\text{ON}_3$, forming rhombic crystals, m. p. $184\text{--}185^\circ$; the *picrate* has m. p. $200\text{--}201^\circ$.

[With KOBAYASKI.]—Acetylacetone and methylguanidine react,

yielding 2-methylimino-4 : 6-dimethyldihydropyrimidine,



which crystallises in long, glistening prisms, m. p. 98°; it is converted by hydrochloric acid at 160°, and by nitrous acid at low temperatures, into *acetylacetonecarbamide* (2-oxy-4 : 6-dimethyldihydropyrimidine). Ethyl diethylmalonate and methylguanidine condense in the presence of sodium ethoxide at 100—110°, yielding 4 : 6-dioxy-2-methylimino-5 : 5-diethylhexahydropyrimidine, $\text{NMe}:\text{C} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{CEt}_2$; it crystallises in rhombic leaflets, m. p. 233—234°, and is decomposed by hydrochloric acid, yielding 5 : 5-diethylbarbituric acid; the *picrate* has m. p. 190—191°.

The isomeride, 2-imino-4 : 6-dioxy-1-methyl-5 : 5-diethylhexahydropyrimidine, $\text{NH}:\text{C} \begin{array}{c} \text{NMe}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{CEt}_2$, may be prepared by the methylation of 5 : 5-diethylmalonylguanidine; it has m. p. 187°, and is converted by hydrochloric acid into 1-methyl-5 : 5-diethylbarbituric acid.

W. H. G.

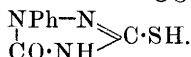
Urazoles. XI. Affinity Constants and Constitution of Several Urazoles. SALOMON F. ACREE and G. H. SHADINGER (*Amer. Chem. J.*, 1908, **39**, 124—145).—In an earlier paper (Acree, *Abstr.*, 1907, i, 796), an account was given of the tautomeric relations of phenylurazole and 3-thio-1-phenylurazole, and it was shown that both the 2 : 3- and 4 : 5-amide groups exist in two tautomeric forms in equilibrium, the enolic form preponderating in the former case and the ketonic form in the latter.

The conductivities at 25° have been determined of solutions of phenylurazole, 1-phenyl-2-methylurazole, 1-phenyl-4-methylurazole, 3-thio-1-phenyl-3-methylurazole, and their sodium derivatives, 3-thio-1-phenylurazole and its sodium and barium derivatives, 3-thio-1-phenyl-4-methylurazole, and 3-thio-1-phenyl-3-ethylurazole. Measurements have also been made of the conductivity of solutions of 3-ethoxy-1-phenylurazole, 3 : 5-diethoxy-1-phenylurazole, and 3-ethoxy-1-phenyl-4-methylurazole in 0.1*N* alcoholic hydrogen chloride.

The results show that the affinity constant of the 2 : 3-amide group of phenylurazole and of 1-phenyl-4-methylurazole is 0.000011, whilst that of 3-thio-1-phenylurazole and 3-thio-1-phenyl-4-methylurazole is 0.017. The affinity constant of the 4 : 5-amide group of the 2-alkyl and 3-alkyloxy-derivatives of phenylurazole is about 0.00000005, whilst that of the corresponding derivatives of 3-thio-1-phenylurazole is considerably greater.

It is evident therefore that those urazoles which seem to have an enolic structure have much larger affinity constants than those which appear to be ketonic compounds. These results support the view that phenylurazole and 3-thio-1-phenylurazole are tautomeric compounds

existing in solution chiefly in the forms $\begin{array}{c} \text{NPh}-\text{N} \\ | \\ \text{CO}\cdot\text{NH} \end{array} > \text{C}\cdot\text{OH}$ and



E. G.

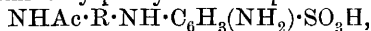
The Safranines. PHILIPPE BARBIER and PAUL SISLEY (*Ann. Chim. Phys.*, 1908, [viii], 13, 96—142).—A detailed account of work already published (compare Barbier and Vignon, *Abstr.*, 1888, 54, 141, 688; Barbier and Sisley, *Abstr.*, 1905, i, 840; 1906, i, 51, 989; 1907, i, 160, 563; this vol., i, 64). M. A. W.

[Preparation of Safraninones containing Aliphatic Groups.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 189078).—Safraninones containing aliphatic groups are prepared by the further oxidation of the indophenols, obtained either by condensing the nitrosophenols with the 4-alkyltolylene-2:4-diamines, or by oxidising a mixture of these bases with the *p*-aminophenols.

Ethotolusafranone hydrochloride (annexed formula) is produced either by condensing nitrosophenol with 4-ethyltolylene-2:4-diamine, or by oxidising a mixture of this base and *p*-aminophenol and then treating the resulting indophenol with more oxidising agent.

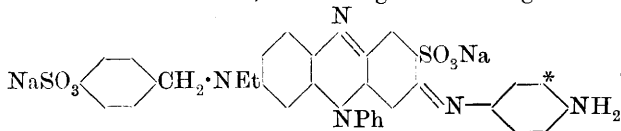
This patent contains a tabulated list of nine of these mixed tolu-safraninones, all of which are constituted similarly to the preceding compound. G. T. M.

Preparation of Sulphonic Acids of the Safranine Series. ACTIENGESSELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 186597).—The acylated *p*-diaminoarylphenylaminesulphonic acids,



when oxidised in the presence of benzylalkylanilinesulphonic acids, furnish indamines, which on further oxidation with primary aromatic bases give rise to safraninesulphonic acids. Wool dyes are produced by eliminating the acyl group Ac from these safranine derivatives.

Acetyl-*p*-diaminodiphenylaminesulphonic and benzylethylanilinesulphonic acids are treated in aqueous sodium hydroxide with sodium dichromate, and the solution poured into cold 30% acetic acid. The indamine is produced immediately, and subsequently aniline and more dichromate are added. The safraninesulphonic acid thus produced is converted into its sodium salt, which is salted out after filtration from chromic hydroxide. When hydrolysed with moderately dilute sulphuric acid, the foregoing colouring matter is converted into a dye giving greener shades of blue on wool, and having the following constitution:



Acetyl-*p*-diamino-*m*-chlorodiphenylamine-*o*'-sulphonic acid, when oxidised successively with benzylethylanilinesulphonic acid and *p*-toluidine, furnishes a safranine which on hydrolysis gives rise to a colouring matter containing a *p*-tolyl group instead of phenyl, and a chlorine atom in the marked position in the foregoing formula. Acetyl-*p*-diaminophenyltolylamine-*o*-sulphonic acid furnishes a safranine of similar constitution, containing a methyl group in the position denoted by the asterisk in the foregoing formula. G. T. M.

Hydrosulphides and Thiohydrosulphides of Dye Bases. LOUIS PELET-JOLIVET and L. GRAND (*Chem. Zentr.*, 1907, ii, 1529; from *Schweiz. Woch. Chem. Pharm.*, 1907, 45, 375—377).—The action of sodium sulphide on the hydrochlorides of methylene-blue and crystal-violet in concentrated aqueous solution leads to the formation of the *hydrosulphides* of the dye bases, $(C_{16}H_{17}N_3S)_2 \cdot H_2S$ and $(C_{25}H_{29}N_3)_2 \cdot H_2S$, which are obtained as coloured precipitates. The following *thiohydrosulphides* have been prepared in the same manner by the action of potassium polysulphide on the hydrochlorides of the dyes named: $(C_{16}H_{17}N_3S)_2 \cdot H_2S \cdot S_7$ (?), from methylene-blue; $(C_{25}H_{29}N_3)_2 \cdot H_2S \cdot S_3$, from crystal-violet; $(C_{22}H_{23}N_3)_2 \cdot H_2S \cdot S_4$, from new-magenta; $(C_{28}H_{23}N_3)_2 \cdot H_2S \cdot S_7$, from malachite-green; $(C_{33}H_{31}N_3Cl)_2 \cdot H_2S \cdot S_5$, from victoria-blue, and $(C_{30}H_{34}O_3N_2)_2 \cdot H_2S \cdot S_5$, from anisoline. G. Y.

Relation of Glycine to Uric Acid. FRANZ SAMUELY (*Chem. Zentr.*, 1907, ii, 1493; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 558—560).—Contrary to Hirschstein's statement (*Chem. Zentr.*, 1907, ii, 1181), uric acid does not yield glycine when treated with a dilute alkali. G. Y.

Constitution of Aniline-Black. FRED. MARSDEN (*J. Soc. Dyers and Col.*, 1908, 24, 9—10. Compare Willstätter and Moore, *Abstr.*, 1907, i, 641).—In order to ascertain the quantity of oxygen absorbed in the formation of aniline-black, known quantities of chromic acid were added to a solution of pure aniline hydrochloride, and the action allowed to proceed in the cold until the odour of aniline disappeared; the aniline and chromic acid remaining unchanged were estimated together with the chromium oxide formed. The result obtained was that between 30 and 35 grams of oxygen were used per gram-mol. of aniline. The aniline-black formed had a composition $(C_{12}H_9N_2O)_x$; such a substance can be considered as formed by the polymerisation of Willstätter and Moore's base, $(C_{24}H_{18}N_4)_x$, and the addition of O_2 . The structure $C_6H_4 \llcorner \begin{smallmatrix} N \cdot C_6H_4 \cdot N(OH) \\ N \cdot C_6H_4 \cdot N(OH) \end{smallmatrix} \gg C_6H_4$ is suggested for it.

W. A. D.

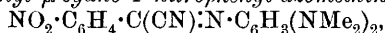
[Azo-colouring Matters from the Aminoanilides of the Higher Fatty Acids.] NATHANAEI SULZBERGER (D.R.-P. 188909).—*p*-Nitrostearinanilide, $C_{17}H_{35} \cdot CO \cdot NH \cdot C_6H_4 \cdot NO_2$, lemon-yellow, felted needles, m. p. 94·5—95·5°, was obtained by adding nitric acid D 1·17 to a solution of stearinanilide in concentrated sulphuric acid at 50—60° and crystallising from alcohol.

p-Aminostearinanilide, $C_{17}H_{35} \cdot CO \cdot NH \cdot C_6H_4 \cdot NH_2$, colourless, felted needles, m. p. 118—119°, obtained by reducing the preceding compound in alcoholic solution with iron and acetic acid, when dissolved in alcohol and treated successively at 0° with hydrogen chloride and nitrous fumes or a nitrite, furnishes a stable, colourless *diazo-chloride*, which condenses with alkaline β -naphthol to form a red *azo*-derivative, m. p. 150°, which can be crystallised from chloroform.

Palmitin- β -naphthalide, oleinanilide, and palmitinanilide, when converted successively into nitro- and amino-derivatives, give rise to similar diazo-salts and azo-derivatives; the latter have a combination of fatty and tinctorial properties, which render them of great technical utility.

G. T. M.

New Derivatives of *m*-Phenylenetetramethyldiamine. FRANZ SACHS and ERNST APPENZELLER (*Ber.*, 1908, 41, 109—113).—Azo-dyes, derivatives of chrysoidine, were prepared by coupling freshly-distilled *m*-phenylenetetramethyldiamine, dissolved in dilute acetic acid, with the diazonium chlorides of aniline, *p*-toluidine, β -naphthylamine, and *m*-nitroaniline. Only the hydrochloride of *m*-nitrobenzene-azo-*m*-phenylenetetramethyldiamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{NMe}_2)_2$, was obtained crystalline in dark violet, matted needles, m. p. 198° . The hydrochloride of *p*-nitroso-*m*-phenylenetetramethyldiamine, prepared by Witt's method (*Abstr.*, 1885, 782; see also Pinnow and Wegener, *Abstr.*, 1898, i, 184), was converted into the free base by cautious addition of sodium hydroxide to the suspension in ice water, and this extracted with ethyl acetate. The purified product forms glistening, greenish-black, prismatic crystals, m. p. 99° , and dissolves with a greenish-yellow coloration. This substance is of interest, as it may be regarded as simultaneously an *o*- and *p*-nitrosoaniline; it can be coupled with methylene and methyl groups to form azomethines. The picrate forms dark violet, glistening crystals, m. p. 169° . 2:4-Bisdimethylaminophenyl- μ -cyano-4'-nitrophenyl-azomethine,



formed by coupling with *p*-nitrophenylacetone nitrile, separates in small, glistening, flat plates or fan-like needles, dark red by transmitted and greenish-bronze by reflected light, m. p. 130° . The 2:4-bisdimethylaminoanil of 2:4-dinitrobenzaldehyde, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{NMe}_2)_2$, forms violet-red needles with a greenish-bronze lustre, m. p. 209° (decomp.).

E. F. A.

Supposed Molecular Transposition in Azo-*o*-carboxylic Acids. MARC TIFFENEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 1201—1205).—It is asserted that Freundler's assumption (*Abstr.*, 1906, i, 544; 1907, i, 158; *Bull. Soc. chim.*, 1907, [iv], 1, 206), that the conversion of benzene-*o*-azobenzoic acid into chloro-3-hydroxy-2-phenyl-

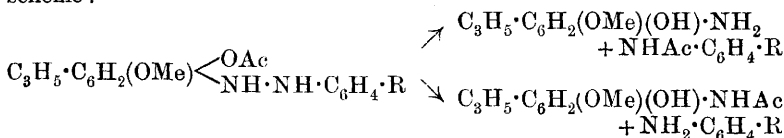
indazole, $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{smallmatrix} \text{NPh}$, is accompanied by the fixation of an atom of chlorine to one of the nitrogen atoms and its subsequent migration into the nucleus, is unnecessary. The transformation of chloroacetylaniline into *p*-chloroacetanilide by the action of heat (Chattaway and Orton, *Trans.*, 1899, 75, 1050), quoted by Freundler as an argument in favour of the possibility of this migration, is not strictly analogous, since in this instance the parent substance, acetanilide, contains the group :NH , in which the hydrogen atom can be readily replaced by chlorine, whereas in benzene-*o*-azobenzoic acid the corresponding group is -N:H- , which has never been known to undergo chlorination by the action of phosphorus pentachloride. It is simpler to suppose that the chlorine atom is directly introduced

into the nucleus by the action of phosphorus pentachloride, since instances are on record in which this occurs (Henry, *Ber.*, 1869, 2, 711; Autenrieth and Mühlingshaus, *Abstr.*, 1907, i, 31; Paganini, *Abstr.*, 1891, 556).
T. A. H.

Constitution of Azo-compounds. Reply to Tiffeneau. PAUL FREUNDLER (*Bull. Soc. chim.*, 1908, [iv], 3, 134—139. Compare *Abstr.*, 1906, i, 544; 1907, i, 158).—Polemical. A reply to Tiffeneau (preceding abstract) on the subject of the transformation of *o*-carboxylic azo-compounds into hydroxyindazolyl derivatives and the validity of representing supposed intermediate compounds in such transformations by constitutional formulæ.
T. A. H.

So-called Mesohydry. KARL AUWERS (*Ber.*, 1908, 41, 403—415).—In connexion with the conception of mesohydry (compare Oddo and Puxeddu, *Abstr.*, 1905, i, 492; 1906, i, 991; Oddo, *ibid.*, 1907, ii, 15), the author has re-examined the derivatives of 5-azoeugenol, and finds that Oddo and Puxeddu's deductions are based on incorrect experimental data. He agrees with these authors in regarding the ethers of the hydroxyazo-compounds as having the azo-structure, and in rejecting the hydrazone formula for the esters, but refutes their arguments against the azo-structure of the latter. Phenolic esters are hydrolysed very easily by phenylhydrazine, and Oddo and Puxeddu's observation that, for example, acetylated benzeneazoeugenol with phenylhydrazine at 110—120° yields aniline and amino-eugenol, does not disprove the fact that the substance is an *O*-ester, but merely shows that hydrolysis has preceded fission. Their second argument, based on the observation that the ethers are hydrolysed by 0.5% sodium hydroxide, whereas the esters are much more stable and consequently cannot have the same structure as the ethers, is quite erroneous; the pure ethers are quite stable, even after being boiled for one hour with 0.5% aqueous or alcoholic sodium hydroxide, whilst under these conditions the acetates are completely hydrolysed.

The author proves that acetylated azoeugenols are *O*-esters by carefully reducing them in alcoholic or ethereal solution by zinc dust and a few drops of acetic acid to hydrazo-compounds, insoluble in alkalis (compare *Abstr.*, 1907, i, 554), which are converted by more vigorous reduction into four fission products, according to the scheme:



The conception of mesohydry, which is thus shown to be unnecessary in the case of the hydroxyazo-compounds, is also criticised adversely in the other directions in which its originators have applied it.

The new compounds described are: *benzenehydrazoeugenyl acetate*, $\text{C}_3\text{H}_5\cdot\text{C}_6\text{H}_2(\text{OMe})(\text{OAc})\cdot\text{NH}\cdot\text{NHPh}$, m. p. 97°, yellowish-white needles; *p*-*toluenehydrazoeugenyl acetate*, m. p. 109—110°, softening at 100°;

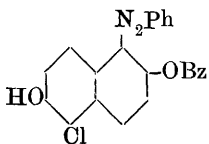
p-chlorobenzenehydrazoegenyl acetate, m. p. 152—154°, white needles ; *p*-bromobenzeneazoegenyl ethyl ether, m. p. 64°, red needles (Oddo and Puxeddu : softens at 68° and m. p. 200°). The m. p. of the preceding hydrazo-compounds, which are readily oxidised, may vary 5° to 10°, according to the rate of heating and to the extent of the previous oxidation.

Oddo and Puxeddu's statement that azoegenols, which contain a methyl group ortho to the azo-complex, do not form ethers is incorrect in so far as *o*-tolueneazoegenol is concerned, the *ethyl ether* of which is a red oil. C. S.

Hydroxyazo-compounds. KARL AUWERS and F. EISENLOHR (*Ber.*, 1908, 41, 415—422).—By condensing benzeneazo- α -naphthol with tetramethyldiaminobenzhydrol, Mühlau and Kegel (*Abstr.*, 1901, i, 56) obtained a substance the acetate of which by reduction yielded acetanilide among other products; hence they concluded that *p*-hydroxyazo-compounds are hydrazones. The authors have repeated the reduction with zinc dust in cold glacial acetic acid, and have failed to detect any trace of acetanilide; aniline, and a substance, probably the acetate of aminonaphthyltetramethyldiaminodiphenylmethane, alone were obtained.

Willstätter and Parnas (*Abstr.*, 1907, i, 1056) have advanced the view that β -benzeneazo- α -naphthol and α -benzeneazo- β -naphthol and their derivatives have different structures, the former being azo-compounds and the latter hydrazones. For this view, they rely solely on the behaviour of the substances on reduction, although several investigators have shown that the reduction of hydroxyazo-compounds is not a safe criterion of structure. The authors have reduced the benzoyl derivatives of the two benzeneazonaphthols with zinc dust and acetic acid; β -benzeneazo- α -naphthyl benzoate yielded aniline, benzanilide, and *N*-benzoyl-2-amino-1-naphthol, whilst α -benzeneazo- β -naphthyl benzoate gave aniline, benzanilide, 1-amino-2-naphthol, and *N*-benzoyl-1-amino-2-naphthol, m. p. 225°; the last-mentioned substance did not depress the m. p., 232—233°, of a pure specimen obtained by Sachs' method (*Abstr.*, 1906, i, 829). There is therefore no difference in the course of the reduction of the benzoyl derivatives, and consequently no necessity to assume different structures for the parent substances.

Willstätter and Parnas (*loc. cit.*) condensed *as*-benzoylphenylhydrazine and 1 : 5-dichloro-2 : 6-naphthaquinone, and obtained a substance which they formulate as an *N*-benzoylated quinone-hydrazone. Its behaviour on reduction, whereby aniline, benzanilide, and two naphthalene derivatives soluble in alkalis are obtained, shows that the annexed formula is preferable. C. S.



Bisazo-dyes from Phenol and Cresols. GUSTAV SCHULTZ and ERNST ICHENHAEUSER (*J. pr. Chem.*, 1908, [ii], 77, 100—124. Compare Meyer and Schäfer, *Abstr.*, 1895, i, 135; Meyer and Maier, *Abstr.*, 1903, i, 870).—As little is known of the simple members of

the series of bisazo-dyes derived from benzidine, the authors have prepared a number of such substances by coupling diazotised benzidine and tolidine with phenol, the three cresols, and the three phenol-sulphonic acids. The resulting bisdiazophenols form dialkyl ethers when heated with alkyl haloids and sodium hydroxide, the reaction taking place more readily with benzyl chloride than with ethyl bromide. Sulphonic acids could not be obtained by sulphonation of the benzyl ethers of diphenylbisazo-*o*- and -*m*-cresols. The colorations given with concentrated sulphuric acid by these bisazo-dyes are described.

Diphenylbisazo-o-cresol, $C_{12}H_8(N_2 \cdot C_6H_3Me \cdot OH)_2$, forms a reddish-brown, crystalline sodium derivative, and on reduction yields 4-amino-*o*-cresol, m. p. 170° . The *diethyl ether*, $C_{30}H_{30}O_2N_4$, was analysed; the *dibenzyl ether*, $C_{40}H_{40}O_2N_4$, crystallises in yellowish-red leaflets, m. p. 243° , and on oxidation with potassium chromate and sulphuric acid yields benzoic acid. The *m-cresol dye* and its sodium derivative are brown powders; reduction leads to the formation of 4-amino-*m*-cresol. The *diethyl ether* crystallises in yellowish-red needles, m. p. above 200° (decomp.); the *dibenzyl ether*, red leaflets, m. p. 183° . The *p-cresol* derivative is orange-yellow, and on reduction yields 2-amino-*p*-cresol.

Ditolylbisazophenol, $C_{26}H_{22}O_2N_4$, forms a reddish-brown sodium derivative. The *ditolylbisazocresols* are obtained as brown powders on acidification of the alkaline solutions; the solubility in dilute alkalis diminishes from the *o*- to the *p*-cresol derivative. The ditolylbisazophenols dye wool in the same manner as the diphenylbisazophenols, but give stronger shades, which, however, are also not fast to soaping.

Sodium benzyloxybenzene-p-sulphonate, $CH_2Ph \cdot O \cdot C_6H_4 \cdot SO_3Na$, prepared by heating *p*-phenolsulphonic acid with benzyl chloride in aqueous or alcoholic solution, crystallises in white leaflets. When coupled with diazobenzene chloride in sodium carbonate solution, *p*-phenolsulphonic acid forms the *phenylhydrazone* of *o*-benzoquinone-sulphonic acid, $NHPh \cdot N : C_6H_3O \cdot SO_3H$, which is obtained in olive-green crystals; the *benzyl ether* forms orange-yellow needles.

The sodium diphenylbisazophenolsulphonates, $C_{24}H_{16}O_8N_4S_2Na_2$, prepared by coupling diazotised benzidine with *o*-, *m*-, and *p*-phenol-sulphonic acid in sodium carbonate solution, and the corresponding compounds, $C_{26}H_{20}O_8N_4S_2Na_2$, prepared from diazotised tolidine, form brown or red powders. The *dibenzyl ethers* form orange-yellow, red, or brown powders. These sodium salts readily dye vegetable fibres, but the dyeings are not fast to soaping. G. Y.

[4-Chloro-5-nitro-2-aminophenol and its Diazo-oxide.]
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186655).—4-Chloro-5-nitro-2-aminophenol, needles, m. p. 225° , obtained together with 4-chloro-6-nitro-2-aminophenol on nitrating 4-chloro-2-aminophenol, is also produced by the nitration of the ethenyl derivative of 4-chloro-2-aminophenol and the subsequent hydrolysis of the nitro-compound.

4-Chloro-5-nitro-1:2-phenylenediazo-oxide, $NO_2 \cdot C_6H_3Cl < \begin{smallmatrix} N \\ | \\ O \end{smallmatrix}^2$, separates

in yellowish-red crystals on diazotising the foregoing aminophenol; it combines in alkaline solution with various naphthol- and dihydroxy-naphthalene-sulphonic acids to furnish a series of hydroxyazo-dyes which yield varying shades of blue on chrome-mordanted wool.

G. T. M.

Preparation of Salts of 1-Diazo- β -naphtholsulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 189179. Compare Abstr., 1906, i, 907).—It has now been found that the free 1-amino- β -naphthol-sulphonic acids may be readily and quantitatively diazotised in aqueous solution with sodium nitrite in the presence of a salt of ammonium or the alkali or alkaline earth metals. A mixture of 1-amino- β -naphthol-4-sulphonic acid with a solution of sodium nitrite and chloride gradually changes to a clear brownish-yellow solution, from which sodium 1-diazo-2-oxynaphthalene-4-sulphonate slowly separates in yellow needles.

G. T. M.

Deaminoedestin. WALTER TRAXL (*Monatsh.*, 1908, 29, 59—68).—Skraup and his co-workers have shown that the deamino-proteins differ from the proteins from which they are formed by the action of nitrous acid in that on hydrolysis they do not yield lysine. This is now found to be the case also with deaminoedestin, which differs from edestin also in other properties. As the average value of several analyses, edestin is found to contain N = 18.92%, and deaminoedestin, N = 19.62%; this increase in the percentage of nitrogen does not result from the formation of a nitroso-derivative and remains unexplained. On hydrolysis, deaminoedestin yields 1.7—2.18% of histidine and 1.5% of arginine, whereas edestin yields about 12% of arginine and 2% of histidine.

G. Y.

Leucine from Casein. FRITZ HECKEL (*Monatsh.*, 1908, 29, 15—21).—The formation of *n*-valeric acid by the action of bromine on casein (Skraup and Witt, Abstr., 1906, i, 916) suggests the presence of *n*-leucine in casein. In agreement with this, it is found that, on oxidation with potassium permanganate, the leucine from the least soluble hydrochloride fraction of the hydrolysis products of casein yields a mixture of acids about one-half of which is *n*-valeric acid. Hence the leucine from casein must contain small amounts of α -amino-*n*-hexoic acid.

G. Y.

Leucine from the Ligamentum Nuchæ of Oxen. MAXIMILIAN SAMEC (*Monatsh.*, 1908, 29, 55—58).—Leucine obtained from the ligamentum nuchæ of oxen (Erlenmeyer and Schäffer, *Zeitsch. Chem. Pharm.*, 59, 315) probably contains *n*-leucine, as on oxidation with permanganate it yields *n*-valeric acid (Heckel, preceding abstract). When treated with hydrogen iodide as described by Kwisda (Abstr., 1892, 38), the leucine yields much inflammable gas, and only small amounts of acids volatile with steam.

G. Y.

Hæmins. J. MERUNOWICZ and JEAN ZALESKI (*Bull. Acad. Sci. Cracow*, 1907, 633—646).—The crystalline hæmin, which Nencki

and Zaleski first obtained by direct extraction of coagulated blood corpuscles with acetone (Abstr., 1900, i, 709), is now shown to be a molecular compound of hæmin with acetone, *acetonehæmin* (most probably $C_{34}H_{32}O_4N_4ClFe, COMe_2$). A simple method for its preparation is described in detail; it cannot be recrystallised as such, but can readily be transformed into Teichmann's crystals by allowing its solution in ammonia to flow into acetic acid saturated with sodium chloride. If a bromide or an iodide is used instead of a chloride in the recrystallisation of Teichmann's crystals, other hæmins are obtained, *bromohæmin*, $C_{34}H_{32}O_4N_4BrFe$, and *iodohæmin*, $C_{34}H_{32}O_4N_4IFe$.

The spectroscopic behaviour and general properties of the three hæmins are very similar. The one containing iodine is somewhat less soluble than the others, and forms unusually large crystals (up to 2 mm.). G. B.

Blood Pigment. VIII. LEON MARCHLEWSKI and J. RETTINGER (*Zeitsch. physiol. Chem.*, 1907, 54, 151—152. Compare Abstr., 1907, i, 738).—The main product of the action of diazobenzene chloride on hæmopyrrole in an ethereal solution is *benzenebisazomethylpropylpyrrole*. From the mother liquor, after the precipitation of this compound, ruby-red crystals of a second substance are obtained on concentration; on further concentration, a third substance in green, badly formed crystals is obtainable. The spectroscopic appearances of these substances are described. W. D. H.

The Fundamental Colouring Matter of Urine. STEPHANE DABROWSKI (*Bull. Acad. Sci. Cracov*, 1907, 777—836).—The use of fixed alkali in the preparation of urochrome was found to be inadmissible, since part of the sulphur contained in this substance is readily eliminated. The method employed finally in the preparation was as follows: to 1500 c.c. of urine a solution of 18 grams of calcium acetate and of 8 grams of barium acetate was added, and then 6.5 c.c. of 21% ammonia. After filtration, the filtrate was neutralised with acetic acid, the urochrome was then precipitated by the addition of cupric acetate, and purified by successive transformation into the barium, sodium, and silver salts. Urochrome is an acid the silver salt of which yields with methyl iodide a methyl ester. Reduced with phosphonium iodide, urochrome does not yield hæmopyrrole, and is therefore not connected with urobilin. It contains, however, a simple pyrrole nucleus, as shown by the pinewood reaction of the distillate obtained by heating urochrome with lime. The absorption spectrum of this distillate closely resembles the spectrum of pyrrole which has undergone spontaneous polymerisation on keeping, and is different from that of urobilin.

Sixty-eight per cent. of the sulphur contained in urochrome is readily eliminated by boiling alkali, and can be estimated as lead sulphide.

Urochrome can be (roughly) estimated in urine by subtracting the amount of purine nitrogen, obtained according to Huppert's modification of Haycraft's ammoniacal silver nitrate method, from the amount

found by Krüger and Wulff's cuprous sulphate method; the difference between the two values represents the nitrogen in urochrome, of which 0.4—0.7 gram are excreted daily by man.

The author does not admit the relationship between urochrome and bilirubin, which exists according to Garrod (*Abstr.*, 1903, ii, 520). Not only does urochrome not yield hæmopyrrole, but it contains sulphur, and has a very different elementary composition from that of urobilin (C 43.09%, H 5.14%, N 11.15%, S 5.09%). G. B.

Physical Modifications of Gelatin in the Presence of Electrolytes and Non-electrolytes. J. LARGUIER DES BANCELS (*Compt. rend.*, 1908, 146, 290—291).—Sadikoff (*Abstr.*, 1904, i, 462; 1906, i, 224) has shown that gelatin dissolves in very concentrated solutions of certain salts. The author has studied the solvent action of 2*M*-solutions of the nitrates and chlorides of sodium, potassium, ammonium, calcium, magnesium, zinc, copper, and manganese on rectangular fragments of gelatin, and finds that the salts of the bivalent metals have a greater action than those of the univalent metals, those of calcium having the greatest activity, and that the nitrates are generally more active than the chlorides.

In the presence of electrolytes, particularly the above salts, gelatin dissolves in mixtures of water with methyl or ethyl alcohol or acetone more readily than in pure water. The presence of a small quantity of water is essential for dissolution, but, apart from this, the gelatin dissolves the more rapidly the larger the quantity of non-electrolyte present.

The gelatin so dissolved can be recovered by eliminating the salts from solution, either by dialysis or by a series of precipitations.

E. H.

Tanning of Gelatin. RICHARD ABEGG and PAUL VON SCHROEDER (*Chem. Zentr.*, 1907, ii, 1346—1347; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 85—87).—As a measure of the extent to which gelatin has been tanned, the authors use the temperature of fusion, which is the temperature at which the gelatin begins to flow in a thin-walled, open glass tube, 2.5 mm. in diameter and 2.5 cm. in length.

A 10% (solid) solution of gelatin, covered with 5% formalin, is kept for twenty-four hours. The surface layer of gelatin, which is strongly tanned, shrivels and darkens at 85° without melting; the following layers have m. p. 48° to 36°. The m. p. of the untanned gelatin is 36°.

Experiments with gelatin plates show that a definite degree of tanning, namely, that corresponding with m. p. 48°, is reached in a time which is nearly inversely proportional to the concentration of the formalin; at very small concentrations, however, the degree of tanning is less than the calculated amount. The process is a unimolecular reaction, the concentration of the gelatin being taken as constant.

The tanning action of 1% formalin is not affected by the presence of 20(vol.%) alcohol. A depression of the m. p. of gelatin to 34° and 32°, without visible tanning, is caused by 10% solutions of potash and chroma alums respectively; ferric alum, however, produces a

hard, brittle gelatin, m. p. 40—38°. Successive treatment in baths of potassium dichromate and sodium thiosulphate, and also solutions of tannin or picric acid, tan gelatin with lowering of the m. p.

The m. p. of untanned gelatin is lowered by neutral salts; the action also occurs with tanned gelatin, for, whereas the m. p. of untanned gelatin is lowered to 33° in a bath of sodium chloride, the m. p. (41°) of a tanned gelatin is depressed to 38°. The addition of sodium carbonate causes a rapid acceleration of the tanning action of formalin or ferric alum with simultaneous elevation of the m. p. of the gelatin.

The internal friction of a dilute solution of gelatin diminishes with time after the addition of formalin; by the addition of potash or chrome alums, it increases to an extent approximately equal to that which the same quantity of water would experience by the addition of these salts.

C. S.

Isolation of Glycine, Albumoses, or Peptones from Dilute Aqueous Solutions. MAX SIEGFRIED (D.R.-P. 188005).—Glycine, albumoses, and peptones may be precipitated with the formation of a complex carbamate by suspending barium or strontium hydroxide in their solutions and passing in carbon dioxide. The precipitate is then warmed with water containing carbon dioxide or ammonium carbonate in order to form calcium carbonate and the free amino-acid.

G. T. M.

Plastein. W. W. SAWJALOFF (*Zeitsch. physiol. Chem.*, 1907, 54, 119—150).—Plastein is the name given to the precipitate which is obtained when solutions of proteoses are subjected to the action of gastric juice. The material is obtained from different kinds of proteose, and the process is regarded as a synthetic one (reversible action of pepsin). By the further digestion of plastein, the usual varieties of proteose and peptone are obtained. The figures given indicate that the reaction is either bimolecular or termolecular; plastein is therefore the result of the union of either 2 or 3 molecules of the proteoses from which it is formed, and its molecular weight is, on the average, twice that of the proteoses. Before precipitation occurs, plastein is present in a soluble form, and is then precipitated by boiling. The plasteins used were prepared from a large range of proteins, and elementary analyses are given. They differ among themselves, and are divided into groups.

W. D. H.

Protagon. WILHELM CRAMER and R. A. WILSON (*Quart. J. Exp. Physiol.*, 1908, 1, 97—110).—Polemical. The individuality of protagon is maintained, and the statements of Gies and his collaborators and of Rosenheim and Miss Tebb criticised.

W. D. H.

A Simple Method of Estimating the Activity of Trypsin. OSCAR GROSS (*Arch. expt. Path. Pharm.*, 1907, 58, 157—166).—The method is based on the fact that caseinogen is precipitated from alkaline solution by the addition of acid, but that the products of its digestion are not precipitated. The moment is noted at which the digesting

solution ceases to give a precipitate on acidification with 1% acetic acid. It is found experimentally that the time required for digestion is inversely proportional to the amount of trypsin employed, so that tryptic digestion does not follow the Schütz-Borissow law of squares, which applies to peptic digestion only. G. B.

Adsorption Affinity of Invertase from Yeast. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1908, 7, 488—492).—The behaviour of invertase from yeast towards kaolin, mastic, arsenious sulphide, ferric hydroxide, and aluminium hydroxide indicates that the enzyme is an electronegative colloid. The precipitate, consisting of ferric hydroxide or aluminium hydroxide, and the adsorbed ferment is as active as an aqueous solution of invertase. A solution containing both albumin and invertase can be freed from the former by means of kaolin. The filtrate from the kaolin and adsorbed albumin contains the invertase. J. J. S.

The Inhibiting Action of Fluorides on Lipase. SAMUEL AMBERG and ARTHUR S. LOEVENHART (*J. Biol. Chem.*, 1908, 4, 149—164).—The inhibiting action of fluoride on lipase decreases on ascending the fatty acid series of esters. The accelerating effect of sodium salts of the fatty acids neutralises the effect of a fluoride. For this purpose, sodium butyrate must be present in a molecular concentration 2100 times as great as that of the fluoride. The action of the sodium salts decreases with increasing molecular weight of the salt, and the protecting action increases with the increasing molecular weight of the ester. The effect of fluorides furnishes a biochemical test for fluorides in food products, and this will doubtless be of value in food inspection. W. D. H.

The Fermentative Change of Glyoxylic Acid in Organs. E. GRANSTRÖM (*Beitr. chem. Physiol. Path.*, 1908, 11, 214—223).—Schloss showed that, of various organs, the liver (minced small) was most effective in causing the disappearance of glyoxylic acid. The property is possessed by extracts of liver made with Ringer's solution, and to a less degree by the precipitate produced by alcohol or acetone in such extracts. Evidence is adduced that the agent is a ferment, and the name *glyoxylase* is given to it. It is relatively resistant towards acids, alkalis, and antiseptics, and its activity is destroyed by heating. It acts in the absence of oxygen; its action is not oxidative, no oxalic acid being formed. The ferment is not identical with aldehydase, or with the uricolytic enzyme. It does not pass through a Chamberland filter. W. D. H.

An Enzyme Phytase which Decomposes Anhydro-oxy-methylenediphosphoric Acid. UMETARO SUZUKI, K. YOSHIMURA, and M. TAKAISHI (*Bull. Coll. Agric. Tokyo*, 1907, 7, 503—512).—When rice bran suspended in water is kept for some days at the ordinary temperature, most of the organic phosphorus dissolves, and phosphoric acid is produced at the expense of the organic phosphorus compounds. The change is shown to be due, not to putrefaction, but to an

enzyme, phytase, which was isolated from rice bran and wheat bran. The enzyme dissolves very readily in cold water, is free from phosphorus, and does not possess either diastatic, peptic, or tryptic activity.

The production of inositol from phytin, which has hitherto only been effected by means of strong mineral acid, is also brought about by phytase. It is therefore probable that phytin has the constitution of inositol-hexaphosphoric acid, $C_6H_8(PO_4H_2)_6$. N. H. J. M.

The Probable Chemical Constitution of Rennet. ALBERTO SCALA (*Chem. Zentr.*, 1907, ii, 1800; from *Staz. sperim. agrar. ital.*, 40, 129—149).—Rennin is regarded as a weak base, consisting of an albumose nucleus and amino-side-chains. Heating destroys its activity, and alters its constitution; formaldehyde has a similar action, which is explained by the replacement of amide-hydrogen by the methylene group. W. D. H.

Pepsin and Rennet. IVAR BANG (*Zeitsch. physiol. Chem.*, 1908, 54, 359—362).—The view is taken that these two substances are not identical, and Gewin's results (this vol., i, 71) are criticised. W. D. H.

Ferments and Antiferments. VI. MARTIN JACOBY (*Biochem. Zeitsch.*, 1908, 8, 40—41. Compare Abstr., 1907, i, 811; ii, 38, 108).—Morgenroth and Willanen (*Virchow's Archiv*, 1907, 190) have questioned the accuracy of the author's observation (Abstr., 1907, ii, 38) that a neutral mixture of rennet and antirennet can be re-activated by the addition of acid. They doubted the activity of the antiferment, and regarded the clotting action after acidification as due to liberation of fresh rennet from (as yet undecomposed) zymogen, or as due to the intensification, by the acid, of the action of traces of rennet which had escaped neutralisation by the antirennet. The reply to these criticisms is that the experiments with antirennet were carried out quantitatively, so that its activity was beyond suspicion; moreover, it was always present in such excess that it would have sufficed to neutralise the rennet several times over. G. B.

Action of Tyrosinase on some Substances Related to Tyrosine. GABRIEL BERTRAND (*Compt. rend.*, 1907, 145, 1352—1355).—In view of extending the study of tyrosinase as a melanogenetic oxydase (compare Abstr., 1896, ii, 571; 1897, ii, 117, 338; Gessard, Abstr., 1900, i, 468; 1902, i, 196; 1903, ii, 165; 1904, i, 539; ii, 833; Lehmann, Abstr., 1902, i, 580; Fürth and Schneider, Abstr., 1902, ii, 36; Cotte, Abstr., 1903, ii, 309; Durham, Abstr., 1905, ii, 101), the author has examined the action of the pure oxydase (Bertrand and Mutermilch, Abstr., 1907, i, 812) on two series of compounds related to tyrosine; the first series includes phenol and its para-substituted derivatives, ethyltyrosine, chloroacetyltyrosine, glycyltyrosine, tyrosine, *p*-hydroxyphenylethylamine, *p*-hydroxyphenylmethylamine, *p*-aminophenol, *p*-hydroxyphenylpropionic acid, *p*-hydroxyphenylacetic acid, *p*-hydroxybenzoic acid, and *p*-cresol. The second series comprises phenylalanine, phenylethylamine, phenylmethylamine, anilinoacetic

acid, phenylpropionic acid, phenylacetic acid, alanine, and glycine. The results show that, whilst each member of the first series of compounds is oxidised by tyrosinase to form intensely coloured derivatives, those of the second series yield no coloration under the same conditions; it follows therefore that only those compounds containing the phenolic hydroxyl group are susceptible to the oxidising action of tyrosinase.

The dipeptide glycyltyrosine is not hydrolysed by tyrosinase, neither is it oxidised by laccase. M. A. W.

The Action of Tyrosinase from *Russula delica* on Tyrosine, Tyrosine-containing Polypeptides, and other Compounds. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Zeitsch. physiol. Chem.*, 1908, 54, 331—353).—The presence of *d*-glutamic and *l*-aspartic acids inhibits the formation of pigment from tyrosine under the influence of tyrosinase. Numerous other amino-acids have no such effect. Various alcohols are also without inhibiting influence. Details are given in regard to the influence of various agencies on the similar action of tyrosinase on polypeptides which contain tyrosine. Tyrosinase produces a red pigment from polypeptides which contain tryptophan, and this is not due to contamination with tyrosine. W. D. H.

Peroxydase Active in Tyrosinase. ALEXIS BACH (*Ber.*, 1908, 41, 216—220. Compare Abstr., 1906, 616, 919).—Tyrosinase consists of an oxygenase for which hydrogen peroxide can be substituted and a peroxydase. Chodat's observation (Abstr., 1907, i, 575, 882) that hydrogen peroxide retards the activity of tyrosinase is due to the use of too concentrated solutions; in suitable dilution, hydrogen peroxide has no influence on the activity of fresh normal tyrosinase. Here it would appear the peroxide produced by the oxygenase is sufficient for the requirements of the corresponding peroxydase. The action of vegetable tyrosinase on tyrosine may be followed quantitatively by decolorising the black oxidation product produced with dilute potassium permanganate and sulphuric acid.

Older and partly exhausted preparations of tyrosinase have their action considerably accelerated on addition of dilute hydrogen peroxide, and a preparation which had entirely lost its activity was rendered very active again in this manner. Seemingly, the oxygenase is very unstable, but it can be completely replaced by the corresponding amount of hydrogen peroxide.

By precipitation with magnesium carbonate and extraction of the dried precipitate with water, the peroxydase may be partly separated from the oxygenase, the magnesium carbonate retaining very much more of the former. A similar partial separation is also effected by methyl alcohol. E. F. A.

Mode of Action of Tyrosinase. ALEXIS BACH (*Ber.*, 1908, 41, 221—225).—Tyrosinase derived from *Russula delica* was allowed to act on tyrosine in dilute sodium carbonate, and the amount of change determined by titration with potassium permanganate and sulphuric

acid (see preceding abstract). The course of change follows the simple law of mass action. The amount changed increases with, although more slowly than, the amount of ferment, and the reaction comes more quickly to a standstill the larger the amount of ferment. With a constant amount of ferment during the middle portion of the reaction, the time taken for a given amount of change is inversely proportional to the amount of tyrosine present. The activity of the ferment is the more rapidly exhausted as the amount of tyrosine present increases.

E. F. A.

Behaviour of Peroxydase towards Light. ALEXIS BACH (*Ber.*, 1908, 41, 225. Compare Abstr., 1907, i, 268).—Under the combined influence of oxygen and of light, there is a slow falling off in the activity of peroxydase as measured by the production of purpurogallin from pyrogallol. Generally speaking, peroxydase appears to be one of the most stable enzymes.

E. F. A.

Amount of Nitrogen in the Oxidising Ferments. ALEXIS BACH (*Ber.*, 1908, 41, 226—227).—Peroxydase from horse-radish, when heated with powdered potassium hydroxide, yields pyrrole and ammonia. In detecting nitrogen in oxidising ferments by the Lassaigne method, it is advisable to use a fair proportion of metallic potassium and not sodium.

E. F. A.

The Enzymic Rôle of Philothion towards Oxygen. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1908, [iv], 3, 159—162. Compare Abstr., 1906, i, 999; 1907, i, 372; 1908, i, 72).—Lambling's statement (*Dict. Chim. de Wurtz*, article "Philothion") that the enzymic nature of philothion is doubtful has led the author to summarise the information he has already brought forward in favour of regarding this substance as an enzyme, and he concludes that its function in the living processes is to hydrogenate oxygen, and that it behaves as an enzyme towards oxygen in this connexion.

T. A. H.

Cleavage of Polypeptides. EMIL ALDERHALDEN and ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1908, 54, 363—389).—In a previous research on the hydrolysis of *d*-alanyl-*d*-alanine by means of yeast-juice (Abstr., 1907, ii, 488), the amount of the dipeptide was kept constant, and the amount of ferment was varied. In the present research, the constant quantity was the amount of ferment, and the variable one the amount of dipeptide. The tabular results and curves given show that the greater the amount of ferment in proportion to dipeptide the more rapidly did hydrolysis take place, especially at the start.

The next experiments relate to the action of pancreatic and intestinal juice on certain tripeptides, namely, *l*-leucyl-glycyl-*d*-alanine and glycyl-*d*-alanyl-glycine. The specific rotatory power of the former is $+20^{\circ}$. By hydrolysis, it is theoretically possible to obtain two dipeptides, namely, *l*-leucyl-glycine and glycyl-*d*-alanine; the rotatory

power of the former is $+85^\circ$, of the latter -50° . So that if leucine is liberated, the rotation will sink, and if *d*-alanine is liberated the rotation will rise. With the second tripeptide, an examination of the rotatory power will also indicate the course of the hydrolysis, for its rotatory power is -64° , and that of the two possible dipeptides -50° and $+50^\circ$. The results show in the case of *l*-leucyl-glycyl-*d*-alanine, the main reaction is the formation of alanine and *l*-leucyl-glycine, and this dipeptide is in small measure resolved into leucine and glycine. In the case of glycyl-*d*-alanyl-glycine, the first cleavage results in the liberation of glycine and *d*-alanyl-glycine.

The next series of experiments relate to the influence of alkalis and acids on the cleavage which pancreatic and intestinal juice produce on glycyl-*l*-tyrosine. Small quantities of alkali retard hydrolysis. The same is true for the action of yeast-juice on *d*-alanyl-*d*-alanine. Even small quantities of acid completely inhibit the hydrolysis. The results with bile acids are inconclusive.

W. D. H.

Sensitising Action of Fluorescent Substances in Yeast and Yeast Press Juice. HERMANN VON TAPPEINER, M. KURZMANN, and FR. LOCHER (*Biochem. Zeitsch.*, 1908, 8, 47—60. Compare Abstr., 1904, i, 131; 1905, ii, 565, 602, 603; 1906, i, 720, 917; ii, 462, 511, 512; 1907, i, 267).—Fluorescent substances can in diffuse daylight inhibit yeast fermentation, and even kill the yeast. Certain fluorescent substances, such as sodium dichloroanthracenedisulphonate, which act strongly on *Paramœcium*, are without action on yeast. On the other hand, all fluorescent substances examined greatly inhibited the fermentative action of yeast-juice (zymase) and of dead yeast preserved by acetone. This destructive action on intra-cellular enzymes is similar to that on extra-cellular ones. It would seem therefore that some fluorescent substances, like sodium dichloroanthracenedisulphonate, referred to above, cannot pass through the cell wall.

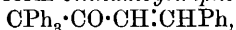
G. B.

Action of Light on Peroxydase; Sensitisation by Fluorescent Substances. KANDO JAMADA and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, 8, 61—83). **Sensitisation of Catalase.** M. ZELLER and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, 8, 84—97).—Peroxydase and catalase are attacked by visible rays in the presence of oxygen, and by ultra-violet rays to an even greater extent, no matter whether oxygen is, or is not, present. Catalase is rendered more susceptible to the light by the presence of hydroxyl ions. All fluorescent substances examined sensitised catalase, but peroxydase was only sensitised by eosin and by tetrabromotetraiodofluorescein. The sensitising action only occurs when the ultra-violet rays are as far as possible absent, and is small compared with the similar action on diastase and invertase. (Compare the references given in the preceding abstract.)

G. B.

Isomeric Organic Magnesium Compounds. JULIUS SCHMIDLIN and HERBERT H. HODGSON (*Ber.*, 1908, 41, 430—437. Compare Abstr., 1907, i, 26, 601).—Cinnamaldehyde reacts in a similar manner

to benzaldehyde with the α - and β -forms of magnesium triphenylmethyl chloride. An ethereal solution of the α -isomeride is prepared in the usual way, and, after the evaporation of the greater part of the ether, the precipitated magnesium compound is re-dissolved by the addition of dry benzene; the addition of cinnamaldehyde leads to the formation of *p*-cinnamoyltriphenylmethane, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$, m. p. 149—151° (corr.), which develops a yellow coloration with concentrated sulphuric acid. The formation of the ketone instead of a secondary alcohol is due probably to atmospheric oxidation. An ethyl ether-benzene solution of β -magnesium triphenylmethyl chloride reacts with cinnamaldehyde to form *cinnamoyltriphenylmethane*,



m. p. 159—160° (corr.), which does not develop a coloration with concentrated sulphuric acid.

Benzyl chloride reacts very feebly with the α -form of magnesium triphenylmethyl chloride, yielding a trace of *as*-tetraphenylethane; with the β -isomeride, however, it readily forms the same hydrocarbon (compare Hanriot and St. Pierre, Abstr., 1889, 882; Gomberg, *ibid.*, 1906, i, 821.)

The α - and β -forms of magnesium triphenylmethyl chloride yield β -benzpinacolin with methyl benzoate, and do not react with acetone, acetaldehyde, or acetyl chloride, although in the case of the β -isomeride minute traces of triphenylmethyl are formed. *m*-Nitrobenzaldehyde does not react with the β -form, and converts the α -isomeride largely into triphenylcarbinol.

p-Tritolylmethyl chloride loses hydrogen chloride at 180—250°, yielding an amorphous powder, m. p. 225—235°, which is possibly ditolylenetolylmethane (tolyldimethylfluorene), $\text{C}_{22}\text{H}_{20}$.

Magnesium p-tritolylmethyl chloride appears to be formed as a yellow precipitate when magnesium and *p*-tritolylmethyl chloride react in ether in the presence of excess of iodine or bromine. It reacts with benzaldehyde to form an amorphous *hydrocarbon*, $\text{C}_{29}\text{H}_{26}$, m. p. 195—200°, but does not yield tritolylacetic acid with carbon dioxide. The acid is formed, however, when carbon dioxide is passed into the ethereal solution in which magnesium and tritolylmethyl chloride are reacting in the presence of a smaller quantity of iodine than that used in the preceding preparation.

C. S.

Organic Chemistry.

Presence of two Paraffin Hydrocarbons in the Unsaponifiable Portion of Chrysalidene Oil. ANGELO MENOZZI and A. MORESCHI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 100—101. Compare Lewkowitsch, *Abstr.*, 1907, i, 521).—The portion of chrysalidene oil which cannot be saponified consists of: (1) bombicesterol (compare this vol., i, 265); (2) a product which dissolves readily in alcohol or ether, and separates as a varnish; (3) a saturated, optically inactive hydrocarbon, $C_{28}H_{58}$, m. p. 62.5° , b. p. $270^\circ/15$ mm. (compare Krafft, *Chem. Zeit.*, 1883, 153); (4) a saturated hydrocarbon, m. p. $41-42^\circ$.
T. H. P.

Action of Nitric Acid on Saturated Hydrocarbons. XIII. Nitration of Saturated Hydrocarbons containing two *iso*Propyl Groups. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1119—1125. Compare *Abstr.*, 1905, i, 762, 763, 764).—By the action of nitric acid on American petroleum, b. p. $55-60^\circ$, β -nitro- β -dimethylbutane, $NO_2 \cdot CMe_2 \cdot CHMe_2$, b. p. $168-169^\circ/750$ mm., is obtained amongst other products; it is either identical or closely analogous to the substance obtained by the nitration of synthetic diisopropyl (β -dimethylbutane), has D_4^{20} 0.9716, D_4^{30} 0.9588, crystallises in a mixture of solid carbon dioxide and ether, and melts below -20° (compare *Abstr.*, 1894, i, 265).

It is reduced by tin and hydrochloric acid, forming the corresponding amine, b. p. $104-105^\circ/751$ mm., D_4^{20} 0.7683, D_4^{27} 0.7514, n_D^{27} 1.40960, and does not solidify at -9° . It readily absorbs carbon dioxide from the atmosphere, forming a solid salt; the hydrochloride of the amine is readily converted into dimethylisopropylcarbinol, $CHMe_2 \cdot CMe_2 \cdot OH$. Simultaneously with the mononitro-compound, β -dinitro- β -dimethylbutane, b. p. 208° , is formed.

Amongst other products obtained by nitrating $\beta\delta$ -dimethylpentane with nitric acid, D 1.11, in sealed tubes are: (1) β -nitro- $\beta\delta$ -dimethylpentane, $NO_2 \cdot CMe_2 \cdot CH_2 \cdot CHMe_2$, b. p. $181-182^\circ/742$ mm., D_4^{20} 0.9559, D_4^{30} 0.9309, n_D^{30} 1.42355, which is reduced by tin and hydrochloric acid forming the corresponding amine, b. p. $121-122^\circ/747$ mm., D_4^{30} 0.7549, n_D^{30} 1.4009; the platinichloride, m. p. 240° (decomp.), is described.

(2) $\beta\delta$ -Dinitro- $\beta\delta$ -dimethylpentane, $NO_2 \cdot CMe_2 \cdot CH_2 \cdot CMe_2 \cdot NO_2$, is crystalline substance, m. p. $81-82^\circ$.
Z. K.

A New Type of Combination of Sulphur with Certain Iodides. VICTOR AUGER (*Compt. rend.*, 1908, 146, 477—479).—The author has prepared a new series of additive or molecular compounds of the type RIn, nS_8 by mixing solutions in carbon disulphide of the two constituents. Iodoform-sulphur, $CHI_3, 3S_8$, forms magnificent yellow prisms, m. p. 93° , stable in air, but coloured red by the action of light. Tetraiodoethylene-sulphur, $Cl_2 : Cl_2, 4S_8$, form large,

yellow plates, m. p. 97—103°. *Arsenious iodide-sulphur*, $\text{AsI}_3 \cdot 3\text{S}_8$, forms long, orange prisms or plates, m. p. 105°. *Antimony iodide-sulphur*, $\text{SbI}_3 \cdot 3\text{S}_8$, forms long, bright yellow prisms, m. p. 117°.

M. A. W.

Reducing Properties of the Organometallic Compounds.

LETELLIER (*Compt. rend.*, 1908, 146, 343—345. Compare Jocitsch, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 443; Sabatier and Mailhe, *Abstr.*, 1905, i, 706; Gattermann and Maffezzoli, *Abstr.*, 1904, i, 172).—When ethyl hydroxypivalate, $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, is treated with magnesium ethyl bromide, besides the production of $\beta\beta$ -dimethyl- γ -ethylpentane- α -diol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CET}_2 \cdot \text{OH}$, m. p. 19°, b. p. 136°/21 mm., predicted by theory, there is formed a smaller quantity of $\beta\beta$ -dimethylpentane- α -diol, $\text{CH}_2\text{Me} \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$, m. p. 59°, b. p. 119°/21 mm., identified by its production when ethyl bromoisobutyrate is condensed with propaldehyde in the presence of zinc (Reformatski) and the ethyl β -hydroxy- $\alpha\alpha$ -dimethylvalerate,



(b. p. 98°/16 mm.), so formed, reduced by sodium (Bouveault and Blanc, *Abstr.*, 1905, i, 11). The mechanism of the formation of the second glycol is represented by $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et} + \text{MgEtBr} \rightarrow \text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CET}(\text{OEt}) \cdot \text{OMgBr} \rightarrow \text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{COEt}$, the ketone formed being reduced by the organometallic compound with evolution of ethylene. Lowering the temperature of the reaction-mixture favours the reduction, the yield of the second glycol being 32% at the ordinary temperature, 35% at 0°, and 60% in a mixture of ice and salt. The first glycol, which forms an *acetate*, b. p. 97—98°/21 mm., and a *urethane*, m. p. 63°, is dehydrated by 20% sulphuric acid, giving $\beta\beta$ -dimethyl- γ -ethyl- Δ^5 -pentenol, $\text{CHMe} \cdot \text{CET} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$, a liquid, b. p. 86°/21 mm., and a small quantity of a liquid *hydrocarbon*, b. p. 119°, probably a nonane. The second glycol, which cannot be dehydrated, forms an *acetate*, b. p. 116°/21 mm.

E. H.

General Method for the Preparation of Fatty or Aromatic Primary Ethers. JULES L. HAMONET (*Bull. Soc. chim.*, 1908, [iv], 3, 254—258).—In view of the publication of Reychler's papers (this vol., i, 158, 159) describing the preparation of complex ethers by the action of chlorodimethyl ether on magnesium alkyl haloids, the author calls attention to the fact that he has already described this reaction (*Abstr.*, 1904, i, 401), and indicated that it is capable of general application.

In the present paper, details are given of the method of working, and it is suggested that on the addition of the halogen methyl ether to the magnesium alkyl haloid an additive compound, which may be represented by the following typical formula: $\text{RR}'\text{BrO} \cdot \text{Mg} \cdot \text{OR}''\text{R}'''\text{Cl}$, is formed in which the two oxygen atoms are quadrivalent, and is therefore analogous in constitution to the compound of ether and magnesium iodide studied by Zelinsky (*Abstr.*, 1903, i, 802) and by Blaise (*Abstr.*, 1905, i, 111).

T. A. H.

Relation of Tetramethylethylene Oxide to Pinacolin. MAURICE DELACRE (*Bull. Soc. chim.*, 1908, [iv], 3, 203—212).—It has been shown previously (Abstr., 1907, i, 581) that this oxide, $O \begin{smallmatrix} \diagup CMe_2 \\ \diagdown CMe_2 \end{smallmatrix}$, may be best prepared from pinacone by Friedel's method, and in the present paper the purification of the oxide is described and its properties are given.

The oxide is not attacked by metallic sodium in presence of potassium hydroxide solution, and this method of freeing it from pinacolin, simultaneously produced, is used for its purification, the crude product obtained on reduction being fractionally distilled, and the fraction boiling at 91.6—91.8° under 743 mm. pressure being collected. It is a colourless liquid, with a piquant agreeable odour, has D 0.8311, is not attacked by its own volume of cold water, but is slowly hydrated in presence of a large excess of cold water, or more rapidly when heated with water in a closed vessel at 150°, or with water containing hydrochloric or sulphuric acid. The hydration is greatly retarded by the presence of an alkali hydroxide. The oxide gives with fuming hydrobromic acid a voluminous precipitate of a substance, which crystallises from light petroleum. The oxide is not reduced by sodium in presence of ether, or by sodium amalgam in alcohol.

From a consideration of its properties, it is held that the direct isomerisation of the oxide to pinacolin in the absence of reagents is not likely to be realised, and it is pointed out that in its resistance to hydrogenation the oxide presents some analogy with *a*-benzopinacolin.

T. A. H.

Chemistry of Lecithin. PAUL MAYER (*Biochem. Zeitsch.*, 1908, 8, 199—202).—A reply to some criticisms of the author's work by I. Bang, in an article on the lipid compounds (*Ergebnisse der Physiologie*, 1907, 6, 131).

S. B. S.

Action of Metallic Magnesium on Certain Aliphatic Acids, and the Detection of Formic Acid. HENRY J. H. FENTON and H. A. SISSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 385. Compare *Trans.*, 1907, 91, 687).—The reduction of acids by means of metallic magnesium only occurs in the lower members of a series, and has been observed in the case of formic, acetic, propionic, butyric, and oxalic acids.

As a specific test for formic acid, the solution to be examined is digested with magnesium ribbon or powder at the ordinary temperature for some minutes, and the resulting product is tested for formaldehyde by any of the usual colour tests. Soluble metallic formates give a similar result, but the reaction is much more delicate with the free acid.

P. H.

Action of Magnesium on Esters of Brominated Fatty Acids. New Synthesis of β -Ketonic Esters. JOSEF ZELTNER (*Ber.*, 1908, 41, 589—594).—The action of magnesium on an ethereal solution of brominated esters of the type $CH_2RBr \cdot CO_2Et$ (where $R = Me$,

Et, or Pr) leads to the formation of the ester $\text{CH}_2\text{R}\cdot\text{CO}_2\text{Et}$ and of the β -ketonic ester, $\text{CH}_2\text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{CO}_2\text{Et}$, the composition of which is determined by hydrolysis with 10% potassium hydroxide, whereby the dialkyl ketone, $\text{CO}(\text{CH}_2\text{R})_2$, is obtained. Ethyl α -bromoisobutyrate reacts in a similar way, yielding ethyl α -isobutyrylisobutyrate. By the action of benzaldehyde on the ethereal solution of the product of interaction of magnesium and ethyl α -bromoisobutyrate, a substance, $\text{C}_{15}\text{H}_{18}\text{O}_3$, is obtained, m. p. $134-135^\circ$, which does not contain a carbonyl or hydroxyl group, yields benzaldehyde and diisopropyl ketone by hydrolysis with potassium hydroxide, and benzoic acid and the same ketone by oxidation with chromic acid; it is probably a δ -lactone, $\text{CO} \begin{smallmatrix} \text{CMe}_2 \\ \text{CMe}_2 \end{smallmatrix} \begin{smallmatrix} \text{---CO} \\ \text{---CHPh} \end{smallmatrix} \text{O}$. C. S.

Electrolytic Reduction of Oleic to Stearic Acid. CHARLES MARIE (*Bull. Soc. chim.*, 1908, [iv], 3, 202--203).—It is stated that Fokin is wrong in assuming (Abstr., 1907, i, 10) that the author has expressed the opinion that in the electrolytic reduction of oleic to stearic acid the nature of the metallic cathode used has no influence on the reaction, since oleic acid was not included among the acids studied by him (Abstr., 1903, i, 605). The author's only contribution to this subject is a note (*Zeitsch. Elektrochem.*, 1905, 11, 649) in which it is merely stated that preliminary experiments on the reduction of oleic acid in alkaline solution gave yields as poor as those recorded by Petersen (Abstr., 1905, i, 678). T. A. H.

Action of Ozone on Compounds containing Triple Linkings. ETTORE MOLINARI (*Ber.*, 1908, 41, 585--589. Compare Abstr., 1907, i, 1039).—In reply to Harries (this vol., i, 75), the author points out that the differences between the results of their work on the action of ozone on stearolic and phenylpropionic acids are due to the fact that Harries uses ozonised oxygen, whilst he uses ozonised air.

He also claims priority in the study of the action of ozone on oils and their constituents. C. S.

Hydroxybehenic Acid. PH. EPIPHANOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 133--138. Compare Fileti, Abstr., 1898, i, 236).— β -Bromobehenic acid, m. p. $32-33^\circ$, was obtained by treating brassic acid with hydrogen bromide in acetic acid solution. With potassium hydroxide, it yields β -hydroxybehenic acid,

$\text{C}_{17}\text{H}_{33}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_{11}\text{H}_{21}\cdot\text{CO}_2\text{H}$, m. p. $89-91^\circ$, solidifying at $74-76^\circ$, and yielding a monoacetyl derivative, $\text{C}_{22}\text{H}_{43}\text{O}_3\text{Ac}$, with acetic anhydride. The sodium, silver, calcium, and iodo-derivatives have also been prepared. An attempt to obtain the β -hydroxy-acid by the action of sulphuric acid on erucic acid was unsuccessful. Z. K.

Synthesis of Dibasic Acids. III. GUSTAVE BLANC (*Bull. Soc. chim.*, 1908, [iv], 3, 286--292).—A continuation of work described in Abstr., 1905, i, 680, 681, giving a résumé of results already published

in Abstr., 1905, i, 682; 1906, i, 399, 523; 1907, i, 763, 1058, and describing in somewhat greater detail the processes used in the preparation of the various dibasic acids and the intermediate products from the decomposition of which they result.

The following points have not been referred to previously: γ -Bromo-*aa*-dimethylbutyric acid, m. p. 48° , is obtained by adding water to the product of the action of phosphorus pentabromide on *aa*-dimethylbutyrolactone. When ethyl δ -bromo- $\beta\beta$ -dimethylvalerate, prepared as already described (Abstr., 1906, i, 399), is heated with potassium cyanide in presence of acetic acid and sodium iodide, $\beta\beta$ -dimethyladipic acid is obtained.

T. A. H.

Synthesis of Dibasic Acids. IV. GUSTAVE BLANC (*Bull. Soc. chim.*, 1908, [iv], 3, 292—301).—A continuation of work already recorded (Abstr., 1905, i, 680, 681, and preceding abstract) and describing the preparation of β -isopropyladipic, $\beta\beta$ -dimethylpimelic, and $\beta\beta\epsilon$ -trimethylpimelic acids by the general process already given (*loc. cit.*).

β -isoPropylvalerolactone, b. p. $138^\circ/14$ mm., obtained by the reduction of β -isopropylglutaric anhydride, for the preparation of which the method of Thorpe, Udall, and Howles (*Trans.*, 1900, 77, 945) is preferred to that of Knoevenagel (Abstr., 1899, i, 116), is a colourless liquid with a lactonic odour, and is but slightly soluble in water or solutions of alkali carbonates; its *hydrazino*-derivative, m. p. 70° , prepared by Blaise and Luttringer's method (Abstr., 1905, i, 329), forms colourless scales. The lactone, on successive treatment with phosphorus pentabromide and alcohol, yields ethyl δ -bromo- β -isopropylvalerate, $\text{CH}_3\text{Br}\cdot\text{CH}_2\cdot\text{CHPr}^\beta\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b. p. $138^\circ/14$ mm., a colourless, mobile liquid of persistent odour. The conversion of this into *r*- β -isopropyladipic acid is accomplished in the same manner as that of ethyl δ -bromo- $\beta\beta$ -dimethylvalerate into dimethyladipic acid (see preceding abstract). *r*- β -isoPropyladipic acid crystallises readily from water containing formic acid, and melts at 85° , in place of 75 — 76° recorded by Wallach for β -isopropyladipic acid obtained by the oxidation of tetrahydrocarvone (Abstr., 1905, i, 451) and phellandrene (Abstr., 1906, i, 194). The remainder of the paper records results already published (Abstr., 1906, i, 399), but gives details of the experimental methods used.

T. A. H.

Preparation of Adipic Acid from cycloHexanol. CARL MANNICH and V. H. HÂNCU (*Ber.*, 1908, 41, 575).—Adipic acid is conveniently prepared in quantity by the oxidation of cyclohexanol in sodium carbonate solution with potassium permanganate at the ordinary temperature for three days, whereby 80 per cent. of the theoretical yield is obtained.

E. F. A.

Digitoxonic Acid. HEINRICH KILIANI (*Ber.*, 1908, 41, 656. Compare Abstr., 1906, i, 66).—Neither digitoxonic acid nor its derivatives could be obtained previously in a crystalline form. A *phenylhydrazide*, $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_2$, crystallising in needles, $[\alpha]_D - 17.1^\circ$, by means of which the acid may be identified, has now been formed by treating the syrupy lactone, prepared by oxidation of digitoxose

with bromine in aqueous solution (*loc. cit.*), with phenylhydrazine in alcoholic solution and adding dry ether after thirty-six hours.

G. Y.

Organic Iron Salts. LEOPOLD ROSENTHALER and A. SIEBECK (*Arch. Pharm.*, 1908, **246**, 51—57. Compare Abstr., 1903, ii, 765).—The following have been prepared and analysed: *basic ferric tartrate*, $2[\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_3] \cdot 3\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$; *basic ferric citrate*, $6(\text{FeC}_6\text{H}_5\text{O}_7) \cdot 7\text{Fe}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$; *basic ferric oxalate*, $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$; *basic ferric malate*, $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 2\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$. *Ferrous malate*, $\text{Fe}(\text{C}_4\text{H}_4\text{O}_5)$, and *normal ferric malate*, $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_5)_3$, could not be obtained pure. All these salts are amorphous precipitates; a separation of the acids cannot be effected by them.

G. B.

Saccharinic Acids. HEINRICH KILIANI (*Ber.*, 1908, **41**, 469—470. Compare this vol., i, 128).—According to Nef's views on the formation of saccharinic acids (this vol., i, 5), lævulose should be one of the best materials from which to prepare *isosaccharinic acid*. This is now shown not to be the case, *isosaccharinic acid* being obtained, together with saccharinic acid, but only in a 1.7% yield on successive treatment of lævulose with calcium oxide and oxalic acid. *isoSaccharinic acid* is obtained in a similar yield from dextrose (probably directly and not from admixed maltose), but in a 15% yield from lactose.

G. Y.

Antimony Thioglycollate. Correction. ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1908, **57**, 359—360).—The statement by the author and Davidsohn (Abstr., 1904, i, 843) that a normal thioglycollate of antimony can be obtained by the action of antimony trichloride on thioglycollic acid is incorrect, the compound described having the formula given later by Klason and Carlson (Abstr., 1906, i, 232; compare Holmberg, this vol., ii, 130).

G. S.

Ketens. VI. Keten. HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1908, **41**, 594—600. Compare Abstr., 1907, i, 424; Wilsmore, Trans., 1907, **91**, 1939).—Pure keten, $\text{CH}_2\text{:CO}$, m. p. -151° , b. p. -56° , has been obtained by treating bromoacetyl bromide in ethyl acetate solution with zinc, rapidly distilling, and subsequently removing the keten from the warm solvent in a current of hydrogen, condensing it by liquid air, and removing traces of ethyl acetate by repeated fractionation at -60° . The purity was determined by estimating the ratio C/H. The keten is colourless in the solid, liquid, or gaseous states, and has an intolerable odour of chlorine and acetic anhydride. In ethereal solution, bromine converts it into bromoacetyl bromide, whilst dry oxygen has no action. Zinc chloride or ferric chloride causes the formation of dark-coloured polymerides; tertiary bases also induce polymerisation, dehydracetic acid being detected among the products. Keten does not form additive compounds with quinone, dibenzylideneacetone, or benzylideneaniline, or keten bases with pyridine or quinoline.

The striking difference between the reactions of keten and those of

disubstituted ketens lends weight to Wilsmore's suggestion that keten may be hydroxyacetylene, $\text{CH}:\text{C}\cdot\text{OH}$. When the pure keten, however, reacts with water, not a trace of an aldehyde can be detected, and an ethereal solution of keten does not react with potassium, sodium, or phenylcarbimide; the author considers therefore that a hydroxyl group is not present, and that keten has the formula $\text{CH}_2\cdot\text{CO}$.
C. S.

Oxidation of Acetone by Potassium Permanganate. H. FOURNIER (*Bull. Soc. chim.*, 1908, [iv], 3, 259—265).—In addition to acetic, oxalic, and carbonic acids, which previous workers have obtained by the action of potassium permanganate on acetone, the author has obtained pyruvic acid, and has investigated the influence of various factors on the yield of this acid.

The acid was isolated and weighed in the form of the phenylhydrazone. The four acids mentioned are always produced when acetone is oxidised in presence of alkali with sufficient permanganate to furnish less than 5 atoms of oxygen per mol. of the ketone and at temperatures between -2° and 25° . Pyruvic acid is formed only in small amount, and the quantity produced is greatly influenced by the amount of the oxidising agent used, the concentration of the alkali and the ketone, the temperature at which the reaction is conducted, and the time taken to effect the oxidation.

The oxidation of acetone by permanganate in neutral solution is slow, and is greatly accelerated by the addition of sodium, calcium, or barium hydroxide, or normal carbonates of the alkalis. T. A. H.

Reactions of β -Chloroethyl- and Vinyl-ketones. M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 280—286).—In continuation of previous work on these ketones (see Abstr., 1907, i, 241, 418; this vol., i, 290), an account is given of the products obtained (1) by their fixation of hydrogen cyanide, halogens, and haloid acids, and (2) by their interaction with organo-magnesium haloids.

β -Bromoethyl ethyl ketone, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{COEt}$, b. p. $72^\circ/16$ mm., obtained by the action of hydrogen bromide on ethyl vinyl ketone, is a liquid, which is at first colourless, but rapidly darkens to almost black; the semicarbazone is colourless and crystalline.

$\alpha\beta$ -Dibromoethyl ethyl ketone, b. p. $97^\circ/13$ mm., similarly obtained by the addition of bromine to ethyl vinyl ketone, is a heavy liquid of sharp odour. Ethyl vinyl ketone, on treatment with a drop of sulphuric acid in presence of ethyl orthoformate, yields the corresponding diethyl-acetal, $\text{CEt}(\text{OEt})_2\cdot\text{CH}\cdot\text{CH}_2$, b. p. $76\text{--}78^\circ/15$ mm., a pleasant-smelling liquid.

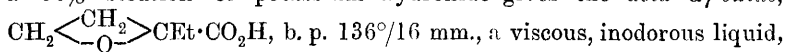
β -Chloroethyl ethyl ketone reacts with magnesium ethyl bromide in ether to form diethyl- β -chloroethylcarbinol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CEt}_2\cdot\text{OH}$, b. p. $90^\circ/13$ mm., a liquid with a slightly camphoraceous odour. Attempts to prepare a phenylurethane and an acetyl derivative resulted in dehydration of the chloro-alcohol. When warmed with a 50% solution of potassium hydroxide, the chloro-alcohol furnished the oxide, $\text{CH}_2\langle\text{CEt}_2\text{O}\rangle\text{CH}_2$, b. p. 126° , a liquid with a penetrating cam-

phoraceous odour. On treatment with diethylamine, the chloro-alcohol yields the corresponding β -diethylamino-derivative,

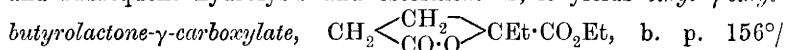


b. p. 93—95°/7 mm., a liquid with a slightly basic odour. No benzoyl derivative of this amino-alcohol could be obtained.

β -Chloroethyl ethyl ketone, on treatment with 1 mol. of potassium cyanide and the equivalent quantity of sulphuric acid and hydrolysis of the resulting nitrile with hydrochloric acid, furnishes *ethyl γ -chloro- α -hydroxy- α -ethylbutyrate*, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CEt}(\text{OH}) \cdot \text{CO}_2\text{Et}$, b. p. 112°/15 mm., an almost inodorous liquid, which on treatment with a 50% solution of potassium hydroxide gives the *acid α -oxide*,



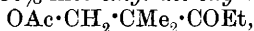
which is much more stable than the corresponding $\alpha\beta$ -acid oxide. Ethyl vinyl ketone, on treatment with 1 mol. of potassium cyanide in presence of $\frac{1}{2}$ mol. of sulphuric acid and hydrolysis of the resulting nitrile with hydrochloric acid and subsequent esterification, yields *ethyl β -propionylpropionate*, $\text{COEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, b. p. 106°/16 mm., a colourless liquid with a feeble odour; the *semicarbazone*, m. p. 106°, crystallises from ethyl acetate on adding light petroleum. The free acid, m. p. 36—37°, forms long tablets from ether and light petroleum, is hygroscopic, and is not coloured red by ferric chloride (compare Zanetti, Abstr., 1892, 351). On treatment with 1 mol. of hydrogen cyanide and subsequent hydrolysis and esterification, it yields *ethyl γ -ethyl-*



16 mm., which may also be obtained directly from ethyl vinyl ketone by the addition of 2 mols. of hydrocyanic acid. The free *lactonic acid*, obtained by hydrolysing the ethyl ester, is a viscous liquid, b. p. 204°/16 mm.

T. A. H.

Syntheses by means of the Mixed Organometallic Derivatives of Zinc. Ketone-alcohols. EDMOND E. BLAISE and I. HERMANN (*Compt. rend.*, 1908, 146, 479—481).—It has been shown previously (Abstr., 1907, i, 750; this vol., i, 78) that β -acetoxy-acid chlorides interact with the mixed organometallic derivatives of zinc to form the corresponding β -acetoxy-ketones, and, in the case when the α -carbon atom is associated with hydrogen, hydrolysis of the acetoxy-ketone does not yield the hydroxy-ketone, but the corresponding unsaturated ketone. In the present paper, it is shown that *aa*-disubstituted β -hydroxy-ketones can be prepared by hydrolysis of the corresponding acetoxy-derivative. Hydroxypivalyl chloride (β -hydroxy-*aa*-dimethylpropionyl chloride), prepared by the action of thionyl chloride on the acid, is converted by the action of zinc ethyl iodide to the extent of 80% into *ethyl acetoxy tert.-butyl ketone*,



m. p. 27°, b. p. 98—99°/14 mm. *Ethyl hydroxytert.-butyl ketone*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{COEt}$, obtained by hydrolysing the acetyl derivative with cold sodium hydroxide solution, is a liquid, b. p. 88°/8 mm., and yields a phenylurethane, oxime, semicarbazone, and *p*-nitrophenylhydrazone.

When ethyl acetoxy*tert.*-butyl ketone is boiled with 10% aqueous potassium hydroxide, it yields formic acid, formaldehyde, and a mixture of ketones, from which ethyl isopropyl ketone has been isolated, and an unsaturated C_7 ketone, which probably has the constitution represented by the formula $CMe_2 \cdot CO \cdot CMe \cdot CH_2$. M. A. W.

Preparation and Properties of Crystallised *d*-Talitol. GABRIEL BERTRAND and P. BRUNEAU (*Compt. rend.*, 1908, 146, 482—484).—Crystallised *d*-talitol can be obtained to the extent of 7.5% from *d*-galactonic acid by means of the following series of reactions: *d*-galactonic acid is partly converted into *d*-talonic acid by heating with pyridine for three hours at 130°, from the mixed calcium salts of the two acids the less soluble galactonate is separated by fractional crystallisation, and the talonic acid is liberated from the mother liquor by means of oxalic acid and converted into the lactone by distillation in a vacuum and subsequent heating for five hours on a water-bath. The lactone is reduced by means of sodium amalgam at 0° to talose, and this on further reduction at 10—20° in a neutral or slightly alkaline medium is converted into talitol, which is isolated in the form of its tribenzylidene derivative (Bertrand and Lanzenberg, *Abstr.*, 1906, i, 728). The *d*-talitol, obtained in the form of a syrup from the tribenzylidene derivative, is crystallised from absolute alcohol; it forms compact, crystalline nodules, m. p. 86°, on the Maquenne metallic block, and has $[\alpha]_D + 3.05^\circ$ in 10% aqueous solution at 18°. The tribenzylidene derivative has m. p. 206° on the Maquenne metallic block [Fischer gives 210° (corr.), *Abstr.*, 1894, i, 395].

M. A. W.

The Properties of Pure Starch. LÉON MAQUENNE (*Compt. rend.*, 1908, 146, 317—318).—The starch deposited, in a granular form resembling natural starch grains, from Fouard's perfect starch solution (this vol., i, 138) is identical with the amylose described by Maquenne and Roux (*Abstr.*, 1905, i, 511, and there termed amylocellulose; a name since changed by them to amylose). Its resemblance to natural starch has led these authors to the conclusion that starch consists of a perfect solution of amylose thickened by amylopectin. The opalescence and precipitation observed by Fouard is the phenomenon called "retrogradation" by Maquenne and Roux, who suggested that it is due either to pseudo-crystallisation or to a polymerisation similar to those undergone by certain sugars, dihydroxyacetone, &c. In view of the variation in the rotatory power of amylose solution with dilution (Fouard), the second of these two theories becomes more probable. Moreover, the phenomenon is reversible, the precipitate dissolving in water under pressure. E. H.

Nature of Iodide of Starch. MAURICE PADOA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 214—215).—A criticism of Katayama's results (compare this vol., i, 9).—It is pointed out that the colorimetric methods of measurement employed by that author give results of doubtful value, since, when such methods are applied to suspensions, the size of the particles may influence both the quality and the quantity of the coloration. Further, conclusions drawn from the

coefficient of distribution of iodine between solutions of iodide of starch and carbon tetrachloride would be valid only if the phase law were applicable, which is not the case; there is no authority for considering a suspension either as a single phase or as composed of two phases, neither can it be admitted that amorphous compounds or substances in the form of minute, suspended particles are capable of forming solutions which are saturated in the sense in which this term is applied to solutions of crystalline substances (compare also Padoa and Savarè, *Abstr.*, 1905, i, 416; Skrabal, *Abstr.*, 1907, ii, 448). T. H. P.

Cellulose and its Derivatives. EUGÈNE GRANDMOUGIN (*Chem. Zeit.*, 1908, 32, 241—242).—A summary of recently published work on the constitution of cellulose and its derivatives. P. H.

Humus Substances Soluble in Water from Scandinavian Fresh Waters. OSSIAN ASCHAN (*J. pr. Chem.*, 1908, [ii], 77, 172—188).—A study of the amount and nature of the dissolved humus substances in the lake and river waters of Finland. These waters are all coloured yellow to brown. The solutions of such humus substances are probably colloidal, and are termed *humussols*, an abbreviation of humus hydrosols. The original must be consulted for the method of isolation of these substances, and for the analytical details. The analytical results quoted by previous authors were obtained with substances dried at high temperatures, and are therefore not to be depended on. The results now given approach the percentage composition of the polysaccharides; small amounts of nitrogen are present in the form of protein substances; sulphur is found mostly in traces. Although the formation of humates, the decomposition of the insoluble humates by alkalis, and the liberation of the humus substances, on addition of an acid to their concentrated alkaline solutions, as a flocculent precipitate soluble in alkalis, indicate that the humus substances are acid in nature, yet their acidity is scarcely greater than that of phenol, and it remains possible that the so-called humates are not salts, but colloidal combinations of varying composition. These views are illustrated by a number of experiments on the formation and decomposition of the ferric humates, the precipitation of the humussols by other metallic salts, and the action of electrolytes on the solutions of the ferric humates. G. Y.

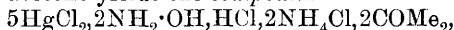
Preparation of Amino-alcohols. J. D. RIEDEL (D.R.-P. 189481. Compare *Abstr.*, 1906, i, 631).—When the halogen hydrins having the general formula $\text{OH}\cdot\text{CRR}'\cdot\text{CH}_2\text{Cl}$ (Br or I) are heated at 125° for about a day with aqueous or alcoholic ammonia, they are converted into a mixture of primary and secondary amines having the general formulæ $\text{NH}_2\cdot\text{CH}_2\cdot\text{CRR}'\cdot\text{OH}$ and $\text{NH}(\text{CH}_2\cdot\text{CRR}'\cdot\text{OH})_2$. The acyl and other derivatives of these bases have valuable therapeutic properties.

Chlorohydrin gives rise to *aminodimethylethylcarbinol*,
 $\text{NH}_2\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$,
 a viscid base, miscible with water, b. p. $75\text{--}80^\circ/30\text{ mm.}$; crystalline,

hygroscopic *hydrochloride*, soluble in acetone; *divaleryl* derivative, b. p. $190^{\circ}/32$ mm., m. p. 50° ; *dibromovaleryl* derivative, needles from light petroleum, m. p. 74° . *Iminobisdimethylethylcarbinol*, a by-product in the foregoing reaction, is very viscid and insoluble in water; its *hydrochloride*, m. p. 144° , crystallises from acetone in nacreous leaflets. Chlorodimethylisoamylcarbinol gives rise to *aminodimethylisoamylcarbinol*, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{C}_5\text{H}_{11}) \cdot \text{OH}$, b. p. $125^{\circ}/68$ mm., and *iminobisdimethylisoamylcarbinol*, a solid base, b. p. $206-207^{\circ}/46$ mm. Phenylchlorodimethylcarbinol, $\text{CH}_2\text{Cl} \cdot \text{CMePh} \cdot \text{OH}$, furnishes *aminophenyldimethylcarbinol*, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CMePh} \cdot \text{OH}$, b. p. $175^{\circ}/40$ mm., and *iminobisaminophenyldimethylcarbinol*, $\text{NH}(\text{CH}_2 \cdot \text{CMePh} \cdot \text{OH})_2$, b. p. $258^{\circ}/40$ mm.; *hydrochloride*, m. p. $228-229^{\circ}$. G. T. M.

Synthesis of Imino- and Nitrilo-Acids. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 140—141. Compare Abstr., 1907, i, 1015, 1016).—The explanation previously given of the mode of formation of iminodicarboxylic acids is amplified further. The reaction between an amino-nitrile or an ester of an amino-acid and a hydroxy-nitrile proceeds in two phases, thus: I. $\text{CN} \cdot \text{R} \cdot \text{CH} \cdot \text{NH}_2 + \text{OH} \cdot \text{CH}(\text{CN}) \cdot \text{R} = \text{NH}(\text{CHR} \cdot \text{CN})_2 \begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix} \rightarrow$ II. $\text{NH}(\text{CHR} \cdot \text{CN})_2 + \text{H}_2\text{O}$. The formation of nitrilopropionitrile by Passavant (Abstr., 1880, ii, 313) is explained similarly; thus $\text{NH}(\text{CHMe} \cdot \text{CN})_2 + \text{CHMe} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix} \rightarrow \text{NH}(\text{CHMe} \cdot \text{CN})_3 \cdot \text{OH} \rightarrow \text{N}(\text{CHMe} \cdot \text{CN})_3 + \text{H}_2\text{O}$. If, on the other hand, there were a heavy radicle in the imino-derivative, the intermediate product would decompose, forming a hydroxy-acid and an imino-nitrile of lower molecular weight. Z. K.

Action of Mercury Diethyl on Mercury Fulminate; Decomposition of the Mixture by Hydrochloric Acid. New Complex, $5\text{HgCl}_2, 2\text{NH}_2 \cdot \text{OH}, \text{HCl}, 2\text{NH}_4\text{Cl}, 2\text{Me}_2\text{CO}$. PAVEL GRIGOROWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1113—1119).—Previous theories regarding the constitution of mercury fulminate are examined, and its reaction with organometallic compounds has been investigated. On mixing perfectly dry mercury diethyl with mercury fulminate, there is no apparent reaction, but, when hydrogen chloride is passed in continuously for three days, the appearance of the mixture changes, and benzene extracts mercury ethyl chloride. The residue extracted with acetone yields the *compound*



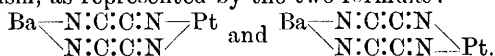
which commences to melt at 50° , and at 100° loses acetone, forming $5\text{HgCl}_2, 2\text{NH}_2 \cdot \text{OH}, \text{HCl}, 2\text{NH}_4\text{Cl}$, m. p. above 300° (decomp.). The acetone compound can also be formed by dissolving mercuric chloride, ammonium chloride, and hydroxylamine hydrochloride in the necessary proportions in acetone, and allowing the excess of the latter to evaporate. Since additive products of mercury diethyl and mercury fulminate are not formed, it is highly improbable that the carbon in

the latter is bivalent, and its formula is most probably $\text{N} \begin{smallmatrix} \text{CH} \\ \text{O} \end{smallmatrix}$, or $\text{H} \cdot \text{C} : \text{N} : \text{O}$. Z. K.

Preparation of Derivatives of Cyanogen Bromide and of Cyanamide. FRITZ BAUM (*Ber.*, 1908, 41, 523—524).—A modification of Scholl's method (*Abstr.*, 1896, i, 585) for the preparation of cyanogen bromide is recommended in those cases where the reagent need not be isolated. A somewhat dilute cold solution of potassium cyanide is dropped slowly into well-cooled bromine covered with water, and the resulting crystalline paste extracted with ether. The ethereal solution is dried over calcium chloride, made up to a definite volume, and the amount of cyanogen bromide calculated from the original quantity of bromine, or estimated by titration with sodium ethoxide.

The ethereal solution of cyanogen bromide reacts with methylamine or aniline to form methylecyanamide or phenylecyanamide, which readily polymerise to termolecular forms, and must therefore be used at once in the preparation of ethyl cyanoanilinoacetate and of cyanoacetylmethylcarbamide (below).
C. S.

Platinocyanides. LEONARD A. LEVY (*Proc. Camb. Phil. Soc.*, 1908, 14, 378—380. Compare *Abstr.*, 1907, i, 689).—When barium platinocyanide crystallises from solutions containing hydroxyl ions, it separates in green, markedly fluorescent crystals, whereas from slightly acid solutions it separates in yellow crystals which fluoresce but slightly. The difference in these two forms is attributed to stereoisomerism, as represented by the two formulæ:



P. H.

Formation of a Double Compound of Mercuric Cyanide and Pyridine. JOHANNES SCHROEDER (*J. pr. Chem.*, 1908, [ii], 77, 269—270).—In continuation of the study of pyridine as a solvent for metallic salts (*Abstr.*, 1905, ii, 306), mercuric cyanide is now found to form a double compound with pyridine, $\text{Hg}(\text{CN})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, which is obtained in colourless crystals. The compound is decomposed by water, as the molecular weight determination in aqueous solution gives results approximately one-third of that corresponding with the double compound.
G. Y.

Organic Salts of Carbamide and Acylcarbamides. FRITZ BAUM (*Ber.*, 1908, 41, 525—532).—Experiments carried out with the object of preparing asymmetrical cyanoacetylmethylcarbamide lead to a study of the interaction of cyanoacetic acid and methylecyanamide. These compounds react very energetically, and, if ether is used as diluent, Traube's symmetrical cyanoacetylmethylcarbamide is obtained in 50% yield (*Abstr.*, 1901, i, 54); the remaining product is soluble in water, and ultimately became crystalline and proved to be *methyl carbamide cyanoacetate*. Cyanamide and cyanoacetic acid yield carbamide cyanoacetate in aqueous solution; on further keeping, heat is developed, and cyanoacetylcarbamide and carbamide can be isolated afterwards. The action of the acid on the cyanamide is therefore, in the first instance, hydration of the cyanamide to carbamide, next

formation of the salt, and then dehydration, yielding substituted carbamides.

This theory of the reaction was proved as follows: (1) it is already known that cyanamide can be hydrated by 50% mineral acid; (2) the formation of salts by melting carbamide and acid together. In this way, it is shown that acetic acid forms no salts with carbamide, methyl-, dimethyl-, or phenyl-carbamides; chloroacetic acid forms salts with methyl- (m. p. 27.5—30°) and dimethyl-carbamides, containing 1 mol. of carbamide and 2 mols. of acid, but not with carbamide itself or phenylcarbamide. Cyanoacetic acid forms salts with all these carbamides. The crude salt containing one of carbamide to one of acid has m. p. 71—74°, that containing 2 mols. of acid forms stout crystals, m. p. 94—95°, and this can also be obtained from cyanamide. With methyl carbamide, 1 : 1, m. p. 41—41.5°, with 2 mols. of acid the product is oily, as is also the case with dimethylcarbamide, both with 1 or 2 mols. of acid.

These salts may be dehydrated by acetic anhydride, which is better than phosphorus pentachloride (Mulder, *Abstr.*, 1879, 618) or phosphoryl chloride (Traube, *loc. cit.*). In this way, the straight-chain *cyanoacetyl*dimethylcarbamide, $C_6H_9O_2N_3$, was prepared, forming monoclinic prisms, m. p. 77.5—78.5° (compare *Farbenfabriken vorm. Friedr. Bayer & Co.*, *Abstr.*, 1906, i, 634; 1907, i, 195). W. R.

Picrolonates. VII. Guanidines. HENRY L. WHEELER and GEORGE S. JAMIESON (*J. Biol. Chem.*, 1908, 4, 111—117).—The picrolonates of the following have been prepared and analysed: cytosine, $C_4H_5ON_3 \cdot C_{10}H_8O_5N_4$, m. p. 270—273°; 2-amino-6-oxypyrimidine (*isocytosine*), $C_4H_5ON_3 \cdot C_{10}H_8O_5N_4$, m. p. 273—275°; 6-aminopyrimidine, $C_4H_5N_3 \cdot C_{10}H_8O_5N_4$, m. p. 261°; 6-oxypyrimidine, $C_4H_4ON_2 \cdot C_{10}H_8O_5N_4$, m. p. 191—193°; 1-methylguanidine, $C_2H_7N_3 \cdot C_{10}H_8O_5N_4$, m. p. 291°; $\beta\beta$ -dimethylguanidine, $C_3H_9N_3 \cdot C_{10}H_8O_5N_4$, m. p. 278°; $\alpha\beta$ -dimethylguanidine, m. p. 262°; β -ethyl- ψ -thiocarbamide, $C_3H_8N_2S \cdot C_{10}H_8O_5N_4$, m. p. 225°. The picrates of the three bases last-named melted at 224°, 178°, and 187° respectively.

The method employed in the synthesis of the substituted guanidines was to leave the methyl iodide additive product of the thiocarbamide at the ordinary temperature with a concentrated aqueous solution of methyl- or dimethyl-amine. G. B.

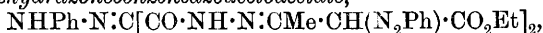
Ethyl Malonylbishydrazoneacetoacetate, a Substance with Three Reactive Methylene Groups. CARL BÜLOW (*Ber.*, 1908, 41, 641—646. Compare *Abstr.*, 1905, i, 660; 1907, i, 301, 986; Curtius, Schöfer, and Schwan, *Abstr.*, 1895, i, 263).—As ethyl malonylbishydrazoneacetoacetate,



contains three reactive methylene and two imino-groups, it must form the starting point for the preparation of a large number of compounds, the formation and reactions of which may be expected to throw light

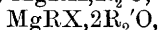
on the nature of such substances in general. An account is now given of the results of the study of the action of diazo-compounds on the bishydrazone ester.

Ethyl malonylbishydrazoneacetoacetate, $C_{15}H_{24}O_6N_4$, prepared by the action of malonyldihydrazide (Bülow and Weidlich, Abstr., 1906, i, 981) on ethyl acetoacetate at 30° , crystallises from a mixture of chloroform and light petroleum in needles, m. p. $96-96.5^\circ$, decomp. $147-150^\circ$, forming a yellow oil, and, when dissolved in water, gradually deposits a white, crystalline derivative, m. p. 147° , decomposing to a substance, m. p. $243-244^\circ$. When treated with diazobenzene chloride in aqueous-alcoholic sodium acetate solution at 10° , ethyl malonylbishydrazoneacetoacetate forms *ethyl phenylhydrazone-mesoxalylbishydrazonebenzeneazoacetoacetate*,



which, when recrystallised rapidly from glacial acetic acid, separates in needles, m. p. 222.5° , is sparingly soluble in alcohol, and on prolonged boiling with acetic acid is converted into two substances, one sparingly, the other readily, soluble in alcohol. G. Y.

Reciprocal Transformations of Magnesium Ammonium and Magnesium Oxonium Compounds. VLADIMIR TSCHELINZEF (*Ber.*, 1908, 41, 646—655. Compare Abstr., 1907, i, 499).—A study of the action of amines on organo-magnesium ethers, and of ethers on organo-magnesium amine complexes. Organo-magnesium compounds form complexes with 1 mol., $MgRX, R_3'O$, and with 2 mols.,

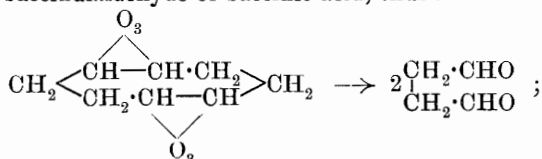


of ethers, but with only 1 mol. of an amine, $MgRX, NR_3'$; these last, although not capable of forming additive compounds with amines, form with ethers the complexes, $MgRX, NR_3', R_3''O$. It is argued that there must exist in the organo-magnesium molecule two unsaturated positions, and that, whilst an ether molecule can be added on to each of these positions, an amine molecule can be added on to only one.

The displacement of an ether by an amine molecule, or conversely of an amine by an ether molecule, is determined more by the nature of the groups in these molecules than by the fact of the one being an oxygen and the other a nitrogen compound. In the action of ethers on ether complexes, or of amines on amine complexes, the compound formed is that having the greater heat of formation; the action may lead to the formation of mixtures. The action of ethers on organo-magnesium ammonium compounds is at first additive, and with aliphatic amines ends at the formation of the amine-ether complex, but with aromatic amines proceeds to the formation of diether complexes. The action of an amine on a monoether complex must be substitutive, but the displaced ether molecule is added on to the second unsaturated position in the organo-magnesium compound, the product of the whole reaction being an amine-ether complex. G. Y.

Constitution of cycloOctadiene from ψ Pelletierine. CARL D. HARRIES (*Ber.*, 1908, 41, 671—678).—Willstätter and Veraguth's cyclooctadiene, obtained by the distillation of *des*-dimethylgranatanine methyl hydroxide (Abstr., 1905, i, 515, 543), was considered by these

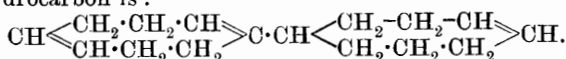
authors to have conjugated double linkings from its readiness in polymerising (Abstr., 1907, i, 303). The conclusion has been drawn that caoutchouc is a polymeride of dimethylcycloocta- $\Delta^{1:5}$ -diene (Abstr., 1905, i, 364), and the great similarity between these substances suggested that the hydrocarbon from ψ -pelletierine had also its double linkings in positions 1 and 5. A study of the action of ozone on the hydrocarbon has proved it to consist of 80% of cycloocta- $\Delta^{1:5}$ -diene, because the diozonide is decomposed by heating with water for two hours into succindialdehyde or succinic acid, thus :



hydrogen peroxide was not obtained, oxygen being liberated.

cycloOcta- $\Delta^{1:5}$ -diene diozonide separates from a carbon tetrachloride solution as a white, amorphous, sparingly soluble mass on treatment for eight hours with ozone diluted with carbon dioxide. After removal of the carbon tetrachloride by distillation in a vacuum, the mother liquor deposits impure cyclooctadiene monoozonide, $\text{C}_8\text{H}_{12}\text{O}_3$, as a syrup.

Dicyclooctadiene (*loc. cit.*, 1905, 515) yields an explosive ozonide, which on treatment with water gives succindialdehyde, and analysis shows it to be a mixture of the diozonide described and a triozonide, $\text{C}_{16}\text{H}_{24}\text{O}_9$; from this result, the deduction is made that the constitution of the hydrocarbon is :



The polycyclooctadiene leads to the formation of a product of composition intermediate between $\text{C}_8\text{H}_{12}\text{O}_3$ and $\text{C}_{16}\text{H}_{24}\text{O}_9$. There is therefore no direct connexion between this and gutta-percha (Abstr., 1906, i, 30).

A series of experiments on the polymerisation of cyclooctadiene were carried out to ascertain whether it was possible to convert it into caoutchouc or gutta-percha like products. Spontaneous polymerisation on slowly warming to 60° , or in the cold, or with boron trifluoride in the hot, lead to Willstätter's polymerides, but boron trifluoride, hydrogen chloride, or phosphoric oxide in the cold lead to the formation of another polymeride, m. p. $115-120^\circ$, in addition to the two previously known, the ozonide of which forms succindialdehyde with water. W. R.

Equilibrium of Hydrogenation. MAURICE PADOA and UGO FABRIS (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 111-115).—The authors have studied the reversibility or otherwise of the hydrogenation of various hydrocarbons in presence of metallic catalysts.

Anthracene, when treated with hydrogen in presence of reduced nickel at $300-330^\circ$, yields tetrahydroanthracene (compare Godchot, Abstr., 1904, i, 987) and a small proportion of a product which smells strongly of naphthalene and no longer contains the anthracene

nucleus. So that, in this case, there is no question of an equilibrium between the anthracene and the products of hydrogenation.

At 200°, naphthalene is hydrogenated to tetrahydronaphthalene, whilst at 300° the latter, in presence of hydrogen and reduced nickel, is converted into naphthalene, which itself undergoes no hydrogenation at this temperature. The reaction is hence, in this case, reversible.

Indene undergoes no hydrogenation at 300°, but is converted into hydrindene at 200°. When heated at 300° in presence of hydrogen and reduced nickel, hydrindene is partly decomposed into indene and hydrogen and partly destroyed.

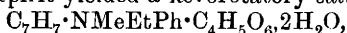
At 300°, acenaphthene undergoes hydrogenation to tetrahydroacenaphthene, and the latter, when heated at 300° in presence of reduced nickel, is partly destroyed and partly converted into acenaphthene. When the vapour of acenaphthene is passed over lead oxide at a dull red heat, dehydroacenaphthene is formed, but this reaction does not take place in presence of reduced nickel at temperatures between 300° and 500°. When dehydroacenaphthene is hydrogenated at 250°, it yields tetrahydroacenaphthene. T. H. P.

Simultaneous Production of 1:6- and 2:7-Dimethylantracenes in the Action of Methylene Dichloride, Chloroform, or Acetylene Tetrabromide on Toluene in the Presence of Aluminium Chloride. JAMES LAVAUX (*Compt. rend.*, 1908, 146, 345—347).—It has been stated previously that in seven out of fifteen cases of the formation of dimethylantracene, the product consists of the mixture of the 1:6 and 2:7 isomerides (this vol., i, 150). In the cases of the action of methylene chloride (Friedel and Crafts, *Abstr.*, 1887, 1102), of chloroform (Elbs and Wittich, *Abstr.*, 1885, 517), and of acetylene tetrabromide (Anschütz and Römig, *Abstr.*, 1885, 768) on toluene in the presence of aluminium chloride, the author offers the following explanation of the sole production of the above two isomerides. In the first place, ditolylmethane, ditolylchloromethane, and ditolyldibromoethane are formed, and it has been shown for the first compound, and deduced by analogy for the others, that the product consists of a mixture almost solely composed of the symmetrical derivatives. Secondly, the latter, reacting with a second molecule of methylene dichloride or chloroform, or losing 2HBr, can only give 1:6-, 1:8-, or 2:7-dimethylantracene derivatives, of which the 1:8 isomeride is formed in relatively small quantities. Lastly, the dihydro- and dichloro-derivatives formed in the first two reactions lose hydrogen and chlorine respectively by reaction with excess of methylene chloride and chloroform, giving the dimethylantracenes themselves. E. H.

Orientation of a Series of Substituted Bromoanilines. JOHN R. HILL (*Proc. Camb. Phil. Soc.*, 1908, 14, 351—353. Compare *Abstr.*, 1907, i, 692).—The bromine atom in each of the five compounds, methylethyl-, methyl-*n*-propyl-, methylisopropyl-, methylisobutyl-, and methylisoamyl-bromoanilines, described previously (*loc. cit.*) was proved to be in the para-position by converting them into their corresponding *methiodides*, melting at 189°, 170°, 167°, 167°, and 176° respectively. These substances when heated in sealed tubes

at 100° with a large excess of methyl iodide all yielded the same *p*-bromophenyltrimethylammonium iodide, m. p. 200°, which was itself synthesised from *p*-bromodimethylaniline and methyl iodide. P. H.

Resolution of Optically Active Ammonium Salts by means of Tartaric Acid. HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1908, 14, 376—377).—Previous attempts by the author to effect the resolution of phenylbenzylmethylethylammonium salts by means of camphor-sulphonic acids (Jones, *Trans.*, 1903, 83, 1419; 1904, 85, 223) having been only partly successful, the acid *d*-tartrate of the ammonium hydroxide was prepared; this substance on recrystallisation from rectified spirit yielded a levorotatory salt,



m. p. 90—93°, $[M]_D - 240^\circ$. Taking the value $[M]_D + 42^\circ$ for the acid tartrate ion, the value for the basic ion becomes $[M]_D - 282^\circ$. The results cannot yet be regarded as final. P. H.

Isomerism of Disulphides. OSCAR HINSBERG (*Ber.*, 1908, 41, 626—634. Compare *Abstr.*, 1906, i, 654).—A third modification of 4:4'-dithioacetanilide, namely, γ -dithioacetanilide, is obtained when an acetic acid solution of the β -modification is exposed to sunlight for twelve days. It appears to be stereoisomeric with the β -compound, from which it is most readily separated by extraction with ethyl alcohol at 0°, in which the β -compound is almost insoluble. It is purified by precipitation with water and crystallisation from a mixture of methyl alcohol and water, when it is obtained in the form of crystalline crusts containing 1H₂O and melting at 120—122°. The same compound may be obtained together with the β -compound by oxidising *p*-acetylaminothiophenol with ferric chloride, and, when reduced, yields acetylaminophenylmercaptan. When hydrolysed with dilute sulphuric acid, it yields a dithioaniline in the form of a yellow powder, different from the ordinary *pp*-dithioaniline (m. p. 76—77°).

A second product, formed on exposure of β -dithioacetanilide to sunlight, is ψ -dithioacetanilide, C₁₂H₁₀N₂S₂Ac₂, which can be purified by crystallisation from alcohol and glacial acetic acid. It forms slender needles, m. p. 162°, containing acetic acid of crystallisation, or m. p. 160° containing alcohol of crystallisation. When reduced with aluminium powder, acetic and hydrochloric acids, it yields a sparingly soluble mercaptan, which dissolves in dilute sodium hydroxide solution. When hydrolysed, the ψ -compound yields a yellow-coloured base, which can be transformed into a colourless, crystalline sulphate.

Benzyl disulphide, when exposed to sunlight in acetic acid solution in the presence of iodine for several days, yields an isomeride, β -benzyl disulphide, m. p. 69—70°, which is more readily soluble in alcohol or glacial acetic acid than the original α -disulphide. When reduced, it yields benzyl mercaptan; when warmed with alcohol and sodium hydroxide solution, it is converted into the original α -compound. A mixture of the α - and β -compounds crystallises with 1CH₃·OH.

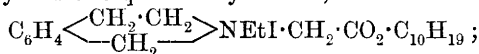
J. J. S.

Asymmetric Nitrogen. XXXI. Stereoisomerism Resulting from the Combination of Asymmetric Nitrogen with Asymmetric Carbon and the Problem of the Asymmetric Synthesis of Ammonium Bases. EDGAR WEDEKIND and O. WEDEKIND (*Ber.*, 1908, 41, 456—463).—Although the problem of the asymmetric synthesis of carbon compounds has been to some extent solved by the work of Marckwald (*Abstr.*, 1904, i, 221, 470) and of McKenzie (*Trans.*, 1905, 87, 1373), an asymmetric synthesis in the simplest manner, the formation of an active form in an active solvent, has not yet been accomplished. An asymmetric synthesis in this manner has now been attempted, but without success, in the nitrogen series. Phenylbenzylmethylallylammonium iodide has been prepared by the action of allyl iodide on benzylmethylaniline in various optically active solvents, such as *d*-limonene, *l*-menthol, and *l*-menthyl chloromethyl ether, and under varying conditions as to concentration and fractional formation of the salt, but an optically active salt has not been obtained in any case. On the other hand, mixtures of optically active salts, which can be separated more or less completely by recrystallisation, are obtained by the action of *l*-menthyl iodoacetate on *N*-ethyltetrahydroisoquinoline and on methylisobutylbenzylamine. More feeble bases enter into reaction with the *l*-menthyl ester only with great difficulty, if at all, whilst stronger bases liberate hydrogen iodide from the iodo-ester and form hydriodides.

l-Menthyl iodoacetate, $\text{CH}_2\text{I} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{18}$, prepared by boiling *l*-menthyl chloroacetate with potassium iodide in alcoholic solution, is obtained as a colourless oil, b. p. $165^\circ/22 \text{ mm.}$, $[\alpha]_D^{20} - 47.29^\circ$, which gradually becomes brown, and reacts with methylethylisobutylamine, forming the *hydriodide*, $\text{NMeEtBu}^i\text{HI}$, m. p. 132° .

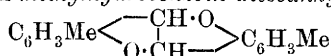
The *additive product* of methylisobutylbenzylamine and *l*-menthyl iodoacetate is obtained as an amorphous mass, which on recrystallisation from a mixture of acetone and ether yields a colourless powder, $\text{C}_{24}\text{H}_{40}\text{O}_2\text{NI}$, decomp. 151.5° , $[\alpha]_D - 28.97^\circ$; the mother liquor from this yields an optically inactive, amorphous *salt* of the same composition, which evolves menthol when heated with potassium hydroxide.

The *additive product* of *l*-menthyl iodoacetate and *N*-ethyltetrahydroisoquinoline, when recrystallised from a mixture of acetone and ethyl acetate, yields two quaternary *iodides*,



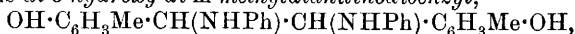
the less soluble iodide crystallises in glistening scales, decomp. 183° , $[\alpha]_D - 44.87^\circ$, and, when gently heated with potassium hydroxide in alcoholic solution, yields menthol and an inactive *betaine*, decomp. 232° . The more soluble iodide forms a crystalline powder, decomp. 155° , $[\alpha]_D - 17.54^\circ$, and, when heated with potassium hydroxide, yields menthol and an optically inactive *betaine*, decomp. 223° . When shaken with moist silver oxide in alcoholic solution, the iodide, decomp. 153° , yields menthol and a *betaine*, $\alpha + 0.21^\circ$ (100 mm. tube), whilst under the same conditions the iodide, decomp. 183° , yields menthol and a *betaine*, $\alpha - 0.19^\circ$ (100 mm. tube); the solutions of these two *betaines* become optically inactive in two days. G. Y.

Reduction Products of Schiff's Bases. OTTO ANSELMINO (*Ber.*, 1908, 41, 621—623. Compare *Abstr.*, 1907, i, 913).—*o*-Hydroxy-*m*-methylbenzylideneaniline, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}\cdot\text{NPh}$, when reduced with sodium and alcohol or with zinc dust and glacial acetic acid at moderate temperatures, yields *o*-hydroxy-*as*-*m*-xylylaniline, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}_2\cdot\text{NPh}$, which crystallises from light petroleum in needles, m. p. 101° . Its *N*-acetyl derivative, $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}$, has m. p. 102° . When heated for some time with zinc dust and acetic acid, the benzylidene compound yields *di*-*o*-hydroxy-*m*-methylhydrobenzoin diisoanhydride,



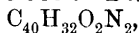
(compare Harries, *Abstr.*, 1892, 168), which crystallises from alcohol in colourless needles, m. p. 172° , but is gradually transformed into an isomeride, m. p. 194° .

When reduced with aluminium amalgam in ethereal solution, the anil yields *di*-*o*-hydroxy-*di*-*m*-methyl dianilinodibenzyl,



which crystallises from light petroleum and ether in compact, colourless prisms, m. p. 169° . The *tetra*-acetyl derivative, $\text{C}_{35}\text{H}_{36}\text{O}_6\text{N}_2$, is sparingly soluble in benzene, and has m. p. 262° .

Dianilinodibenzyl, $\text{NPh}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NPh}$, obtained in the same manner from benzylideneaniline, crystallises from methyl alcohol in plates, m. p. 139° , or in needles, m. p. 164° . *Diacetylanilinodibenzyl*, $\text{C}_{30}\text{H}_{28}\text{O}_2\text{N}_2$, decomposes above 300° . *Dibenzoylanilinodibenzyl*,



sublimes above 300° .

J. J. S.

Preparation of Diphenylamine Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 189939).—*Sodium 2-nitrodiphenylamine-4 : 3' -disulphonate*, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NaSO}_3)\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, red prisms containing water of crystallisation, is obtained by heating sodium *o*-chloronitrobenzene-*p*-sulphonate and sodium metanilate in aqueous sodium carbonate at 140 — 145° . *Sodium 4-nitrodiphenylamine-2 : 3' -disulphonate* is produced in a similar manner from sodium-*p*-chloronitrobenzene-*o*-sulphonate.

G. T. M.

Ammonium Phenoxide. K. BUCH (*Ber.*, 1908, 41, 692—695) — Ammonium phenoxide has not yet been isolated, owing to its easy hydrolysis. The hydrolysis constant has been obtained by mixing known quantities of phenol and ammonia together, and measuring the partial vapour pressure of the ammonia in such solutions by the dynamical method; the gas employed for driving off the ammonia was a mixture of hydrogen and oxygen. Four solutions were thus examined, in three of which there was complete solution, and the fourth contained so much phenol that there existed in the liquid two phases. The moisture in the phenol used was estimated by Koppeschaar's method (this *Journ.*, 1877, i, 746). The hydrolysis constant was found to be 5.1, which agrees with the calculated value obtained from the dissociation constants of phenol and ammonia and the ionisation of water. The constant, however, decreases with increasing concentration, and the

degree of dissociation can be calculated in the usual manner. In the saturated solution, 70% of the salt is dissociated. W. R.

Conditions of Formation of Phenolsulphonic Acids. JULIUS OBERMILLER (*Ber.*, 1908, 41, 696—702. Compare Abstr., 1907, i, 910).—It has been found previously that low temperatures and dilution of the sulphuric acid favoured the production of the ortho-acid. The highest yield of ortho-acid, according to the experiments carried out with 100% sulphuric acid at temperatures varying from 0° to 20°, is 40%; with 1.5 parts of sulphuric acid at 15—20° in one and a-half hours the yield of ortho-acid was 40.7%, and the total yield of both acids 74%, whereas, after leaving overnight, the total yield was 98%, of which 35.4% was ortho-acid. Mercuric oxide has no effect on the reaction.

When the temperature was raised and the sulphuric acid contained sulphur trioxide, the yield of para-acid obtained as the magnesium salt varied from 71% to 85% when the acid employed varied from 70 to 20% SO₃ at 90—100°, disulphonic acid remained in the mother liquor. With monohydrate, an 85% yield of para-acid was obtained at 90—100°, and the mother liquor contained ortho-acid and unchanged phenol.

W. R

Synthesis of Phenols and Phenyl Ethers Containing the *iso*Allyl (Propenyl) Group. AUGUSTE BÉHAL and MARC TIFFENEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 301—310).—The object of this investigation was to effect the syntheses of propenylphenols and propenylphenyl ethers by reactions, such as that of Grignard, which take place at the atmospheric temperature, thus avoiding any risk of intramolecular migration. The following substances were prepared by the Grignard reaction, using the appropriate aldehyde and a magnesium alkyl haloid, usually magnesium ethyl iodide or bromide (compare Klages, Abstr., 1902, i, 609; 1905, i, 344). In some instances, a bimolecular compound (dimeride) is produced simultaneously. *p*-Propenylphenol, HO·C₆H₄·CH:CHMe, b. p. 138—140°/14 mm., m. p. 93°, crystallises in spangles. Anethole (compare Abstr., 1901, i, 272) is formed without any anisylpropanol when excess of the magnesium ethyl iodide is used (compare Klages, Abstr., 1905, i, 344) together with a bimolecular substance, probably identical with Orndorff and Morton's dianethole (Abstr., 1900, i, 289). *p*-Propenylphenetole, b. p. 242°, m. p. 58—59°, yields a *dibromide*, m. p. 55°, and is formed along with a liquid bimolecular substance, b. p. 233°/14 mm., and D_D 1.0366, probably containing a dimeride, derived from cyclobutane, and a noncyclic ethylenic dimeride.

Propenylcatechol [CH:CHMe:OH:OH=1:3:4] cannot be prepared by the action of protocatechualdehyde on magnesium ethyl iodide, this reaction yielding a *phenol*, b. p. 155—160°/16 mm., m. p. 87—88°, which is crystalline and gives a green coloration with ferric chloride, and is probably a physical isomeride of the substance sought, which has m. p. 48—49° (Schimmel's Report, October 1907, 20) and occurs in betel oil. Other substances prepared were *isoeugenol*, *isochavibetol* (compare Pomeranz, Abstr., 1901, i, 699), and propenyl-

veratrole $[\text{CH}:\text{CHMe}:\text{OMe}:\text{OMe}=1:3:4]$, b. p. $260-263^\circ$, $D^{20} 1.0711$, and $D^{20} 1.0551$ (compare Moureu, Abstr., 1897, i, 403).

T. A. H.

Phenolic Ethers Containing the ψ -Allyl Side-chain $\cdot\text{CMe}:\text{CH}_2$.
I. Preparation, Properties, and Nomenclature. II. Anisic and Homoanisic Series. AUGUSTE BÉHAL and MARC TIFFENEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 310—314, 314—321).—An extension of the work described in the preceding abstract. The ethers are prepared by the action of excess of magnesium methyl iodide on cyclic alkyl esters. If insufficient of the Grignard reagent be employed, tertiary alcohols of the type $\text{CRMe}_2\cdot\text{OH}$ are also produced. Many of the results given have been recorded previously (Abstr., 1901, i, 246; 1904, i, 742; 1905, i, 883).

The best nomenclature for the allyl and propenyl ethers is probably that in which the aromatic radicle is regarded as substituted in the olefinic hydrocarbon, so that anethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHMe}$, becomes α -anisyl- Δ^α -propylene, and eugenol, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, α -vanillyl- Δ^β -propylene and so on, but it is probably more convenient to extend the system at present in use and use the prefix *pseudo* to distinguish those ethers containing the *pseudo*-allyl chain and *cyclo* the possible isomerides containing the group $-\text{CH}<\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$, giving, for example, the series estragole, *isoe*stragole (anethole), *pseudo*estragole, and *cyclo*estragole. A third possibility is to use the names of the substituent olefinic radicles, thus: allyl, *iso*allyl, *pseudo*allyl, and *cyclo*allyl.

o- ψ -Propenylanisole, $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}:\text{CH}_2$, may be obtained by methylating *o*- ψ -propenylphenol, b. p. 204° , $D^{20} 1.0528$ (itself prepared by the action of magnesium methyl iodide on methyl salicylate), or directly by the action of magnesium methyl iodide on methyl *o*-methoxybenzoate (Abstr., 1904, i, 742).

m-Methoxyphenyldimethylcarbinol, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{OH}$, the intermediate product obtained by the action of magnesium methyl iodide on methyl *m*-methoxybenzoate, has b. p. $242^\circ/770$ mm. Methyl *p*-methoxybenzoate, treated by the general method, yields in addition to *p*- ψ -propenylanisole (*loc. cit.*) a small quantity of the liquid ether, $\text{O}(\text{CMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, b. p. $260-270^\circ/31$ mm., and a *dimeride*, m. p. 58° , b. p. $210-215^\circ/15$ mm., which is crystalline, and may have the constitution $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}<\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}>\text{CMe}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$. On distillation

at atmospheric pressure, it is partially decomposed into *p*- ψ -propenylanisole and some *isopropylanisole*. *p*- ψ -Propenylanisole, on treatment with iodine and yellow mercuric oxide, yields an iodo-hydrin, which with potassium hydroxide (Abstr., 1905, i, 883) furnishes the corresponding *ethylene oxide* (ψ -estragole oxide),

$\text{O}<\begin{smallmatrix} \text{CH}_2 \\ \text{CMe}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \end{smallmatrix}$, b. p. $130-135^\circ/12$ mm., and this on distillation at atmospheric pressure passes into *p*-methoxyhydratropaldehyde (Bougault, Abstr., 1902, i, 452), the semicarbazone of which exists in

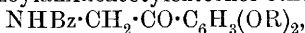
two forms, having m. p. 134° and m. p. $207-208^{\circ}$ (compare Balbiano and Paolini, Abstr., 1906, i, 186). The aldehyde itself on keeping forms a *trimeride*, m. p. $103-104^{\circ}$ or 106° .

p- ψ -Propenylphenetole, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CMe} : \text{CH}_2$, m. p. $27-28^{\circ}$, b. p. $113-114^{\circ}/13$ mm., or $234-235^{\circ}/760$ mm., D^{21}_D 0.969, n^{24}_D 1.540536, similarly obtained from ethyl *p*-ethoxybenzoate, b. p. $274-275^{\circ}$, or $148-149^{\circ}/14$ mm., D^{21}_D 1.076, by the general reaction, crystallises readily from alcohol. The *dimeride*, m. p. 74° , simultaneously formed, is partially depolymerised on heating. *p*-isoPropylphenetole, obtained by reduction of *p*- ψ -propenylphenetole as already described (Abstr., 1905, i, 883), has D^{23}_D 0.9286 and n^{24}_D 1.4974. T. A. H.

Intramolecular Rearrangement Effected by Fusion with Potassium Hydroxide: The Action of Fused Potassium Hydroxide on Quinol and Catechol. JAN J. BLANKSMA (*Chem. Weekblad*, 1908, 5, 93-95. Compare following abstract; Barth and Schreder, Abstr., 1879, 633; Kauffmann, Abstr., 1907, ii, 214 and 519; Hantzsch, Abstr., 1907, ii, 418).—The author has investigated the action of potassium hydroxide on quinol and catechol at temperatures between 130° and 260° . Resorcinol is not formed, indicating that the intramolecular rearrangement resulting from fusion of certain disubstituted derivatives with potassium hydroxide does not take place after substitution by hydroxyl. A. J. W.

Intramolecular Rearrangement Effected by Fusion with Potassium Hydroxide: Behaviour of Chlorophenols and Bromophenols with Potassium Hydroxide, Zinc Chloride, Zinc Bromide, Sulphuric Acid, Potassium Carbonate, and Potassium Acetate. S. TYMSTRA (*Chem. Weekblad*, 1908, 5, 96-101. Compare foregoing abstract).—From the results of experiments on chlorophenols and bromophenols with the reagents named, the author concludes that the intramolecular rearrangement by which resorcinol is formed takes place under the influence of the alkali hydroxide simultaneously with the replacement of halogen by hydroxyl, and that potassium carbonate can effect the transformation into the corresponding dihydroxybenzene, but not the molecular rearrangement. A. J. W.

Preparation of 3-Aminoacetylcatechol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 189483. Compare Abstr., 1907, i, 1049).—The *N*-benzoylaminoacetylcatechol ethers,



obtained by the interaction of hippuryl chloride and catechol ethers, are readily hydrolysed by aqueous mineral acids under pressure to 3-aminoacetylcatechol, which has the powerful hæmostatic properties of the active substances from the suprarenal capsules.

N-Benzoylaminoacetylveratrole, or the corresponding diethyl ether, when hydrolysed in an autoclave with concentrated hydrochloric acid or 30% sulphuric acid at 110° to 190° readily yields the required base. G. T. M.

Preparation of Mixed Alkyl Aromatic Ethers. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 189843).—The nitroso-derivatives of the mono- and di-alkylcarbamides alkylate phenols in the presence of alkalis.

Codeine is obtained by treating morphine with nitrosomethylcarbamide in alcoholic sodium methoxide. β -Ethoxynaphthalene is produced on adding nitrosodiethylcarbamide to a solution of β -naphthol in *N*-sodium hydroxide. Guaiacol is similarly obtained from catechol, sodium hydroxide, and nitrosomethylcarbamide in alcoholic solution, and may be further alkylated to veratrole by a repetition of this process.

The triethyl ether of pyrogallol can be produced by the action of nitrosodiethylcarbamide on pyrogallol dissolved in methyl-alcoholic sodium hydroxide.
G. T. M.

***p*-Iodoguaiacol.** EFISIO MAMELI and GIUSEPPE PINNA (*Chem. Zentr.*, 1907, ii, 2044; from *Arch. Farm. speriment.*, 1907, 6, 193. Compare this vol., i, 18).—A detailed description of the preparation of *p*-iodoguaiacol from *p*-aminoguaiacol by means of the Sandmeyer reaction. The result of experiments with iodoguaiacol on animals and its medicinal properties are given in the original. J. V. E.

Origin and Formation of Cholesterol. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1908, 55, 1—7).—By the oxidation of pure oleic acid in acetic acid solution with potassium permanganate (5% solution in water diluted with four times the volume of glacial acetic acid), a minute quantity of unsaponifiable matter is obtained which gives the characteristic cholesterol reaction of Liebermann. The other products of the reaction are: (1) a mixture of palmitic and oleic acids, and (2) a mixture of acids insoluble in light petroleum. Of the latter acids, one, m. p. 82—85°, of which the potassium salt gives no precipitate with calcium chloride, gave an acid number 460; it appears to be an acid with several carboxylic acid groups. These acids, when submitted to oxidation again, yield small quantities of the substance which gives the cholesterol reactions. S. B. S.

Cholesterol. VI. OTTO DIELS and KARL LINN (*Ber.*, 1908, 41, 544—550).—The observation made by Diels and Abderhalden that cholesterol and cholestenone yield different cholestanols on reduction with sodium and amyl alcohol (Abstr., 1906, i, 272, 425; Neuberg, 1906, i, 356) has led to their reinvestigation in view of the fact that the parent compounds possess the same nucleus (this vol., i, 164). That the two cholestanols are not stereoisomerides is shown by their forming different hydrocarbons on replacing the alcoholic hydroxyl, first by chlorine and then by hydrogen. Windaus' hypothesis that in the production of α -cholestanol from cholesterol and sodium amyloxide (Abstr., 1907, i, 610) the cholesterol merely undergoes an isomeric change, although in agreement with the production of two cholestanes, is not regarded as correct. Sodium amyloxide is actually a reducing agent, as cholestenone gives α -cholestanol after seven hours' heating, a noteworthy result, as reduction with sodium and

amyl alcohol leads to the formation of the β -compound. Further, the inactivity of sodium ethoxide at 140° towards cholesterol is against the Windaus view, and the relationships of the compounds described is an open question.

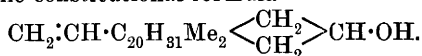
α -Cholestyl chloride, $C_{27}H_{47}Cl$, obtained by the action of phosphorus pentachloride, forms glistening leaflets, m. p. 116° , which on reduction with sodium and amyl alcohol yield *α -cholestane*, $C_{27}H_{48}$, forming long, glistening needles, m. p. 72° , and behaving as a saturated compound towards bromine.

β -Cholestyl chloride, $C_{27}H_{47}Cl$, forms rosettes of stout, white needles, softening at 89° , m. p. 92° , to a cloudy liquid which becomes clear at 100° . *β -Cholestane*, $C_{27}H_{48}$, forms needles, m. p. 80° ; a mixture of the α - and β -compounds gives a m. p. showing a depression of 20° .

Neither of these hydrocarbons gives the cholesterol colour reactions.

W. R.

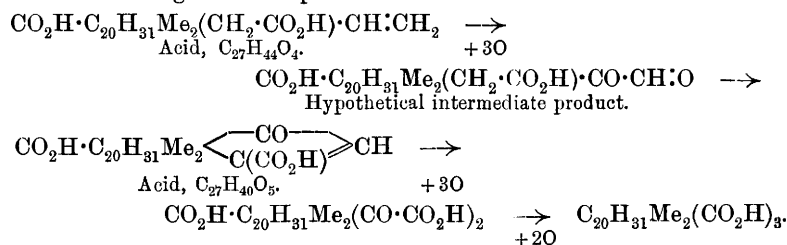
Cholesterol. X. ADOLF WINDAUS (*Ber.*, 1908, 41, 611—621. Compare Abstr., 1907, i, 212, 610).—Previous researches on cholesterol point to the constitutional formula



The present paper contains an account of experiments with the dibasic acid, $C_{27}H_{44}O_4$, obtained by Diels and Abderhalden (Abstr., 1903, i, 819; 1904, i, 880) by the action of potassium hypobromite on cholesterol. With three atoms of oxygen, the acid yields a dibasic acid, $C_{27}H_{40}O_5$, which readily takes up two atoms of hydrogen, yielding a crystalline, dibasic acid, $C_{27}H_{42}O_5$, the fifth oxygen atom in which is present in the form of a carbonyl group. When the acid, $C_{27}H_{40}O_5$, is oxidised with permanganate (3 atoms of oxygen), a tribasic acid, $C_{27}H_{40}O_8$, is obtained, which is also produced when the original acid, $C_{27}H_{44}O_4$, is oxidised with excess of permanganate (6 atoms of oxygen).

The tribasic acid contains at least one, and probably two, carbonyl groups, but no hydroxyl group, and when further oxidised yields a tribasic acid, $C_{25}H_{40}O_6$.

The following scheme represents the reactions:



The *acid*, $C_{27}H_{40}O_5$, is most readily purified by the recrystallisation of its normal sodium salt from dilute alcohol. The acid crystallises from dilute acetic acid in compact prisms, m. p. 216 — 217° . It yields a *monomethyl ester*, $C_{28}H_{42}O_5$, which crystallises from methyl alcohol in long prisms, m. p. 136 — 137° . The reduction *product*, $C_{27}H_{42}O_5$,

obtained with the aid of zinc dust and acetic acid, crystallises from a mixture of chloroform and light petroleum in compact needles, m. p. 158—159°, and is isomeric with the dibasic ketonic acid, obtained by oxidation of cholestandione (Abstr., 1904, i, 49). The *acid methyl ester*, $C_{28}H_{44}O_5$, has m. p. 132°, and the *oxime*, $C_{27}H_{43}O_5N$, m. p. 230—231°.

The *acid*, $C_{27}H_{40}O_8$, is most readily obtained in a crystalline form by solution in glacial acetic acid and the addition of concentrated hydrochloric acid. It forms short, pointed prisms, decomposes at 230—231°, and forms colloidal solutions with water. It yields characteristic, crystalline *potassium hydrogen*, $C_{27}H_{38}O_8K_2$, and *rubidium hydrogen* salts, $C_{27}H_{38}O_8Rb_2$. The salts derived from the alkali-earth metals and the heavy metals are insoluble and amorphous. The *oxime*, $C_{27}H_{41}O_8N$, is amorphous, but yields an acid *potassium salt*, $C_{27}H_{39}O_8NK_2$, which crystallises in prisms.

The *acid*, $C_{25}H_{40}O_6$, crystallises from dilute acetic acid in felted needles containing $1H_2O$. The anhydrous acid is hygroscopic, sinters at 130°, and has m. p. 204—205° (decomp.). The *rubidium dihydrogen salt*, $C_{25}H_{39}O_6Rb_2$, and the corresponding *calcium salt* crystallise well. A crystalline *potassium salt*, $C_{50}H_{77}O_{12}K_3$, has also been prepared.

J. J. S.

The Cholesterol Group. IV. ANGELO MENOZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 91—94. Compare Abstr., 1903, ii, 385).—The properties of the cholesterol of hens' eggs and of its derivatives are identical with those of the cholesterol of bile and of its corresponding compounds.

T. H. P.

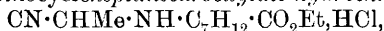
The Cholesterol Group. Bombicesterol, a New Member Existing in the Chrysalis of the Silkworm, Bombyx mori. V. ANGELO MENOZZI and A. MORESCHI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 95—99. Compare preceding abstract).—The authors have isolated from the chrysalis of the silkworm a member of the cholesterol group which differs in its properties from the cholesterol of bile and which they term bombicesterol.

Bombicesterol, $C_{26}H_{43}\cdot OH, H_2O$, crystallises in pointed, elongated, monoclinic or trimetric laminae, m. p. 148°, $[\alpha]_D^{25} - 34^\circ$. The *formate*, $H\cdot CO_2\cdot C_{26}H_{43}$, crystallises from a mixture of alcohol and ether in elongated laminae, m. p. 101°, $[\alpha]_D^{17.5} - 47^\circ$, and the *acetate*, $C_{26}H_{43}OAc$, separates in laminae, m. p. 129°, $[\alpha]_D^{17.5} - 42.7^\circ$; the *benzoate*, $C_{26}H_{43}OBz$, crystallises in slender laminae, m. p. 146°, $[\alpha]_D^{20} - 14.63^\circ$. The *salicylate*, m. p. 173—174°, and the *dibromo-derivative*, m. p. 111°, were also prepared. Treatment of an ethereal solution of bombicesterol with an acetic acid solution of bromine (1 mol.) yields two dibromoacetates differing in solubility; on reduction with zinc dust and acetic acid, the less soluble form yields an acetate, m. p. 114°, which is that of ordinary cholesterol acetate, whilst the more readily soluble form gives an acetate, m. p. 129°.

T. H. P.

Attempt to Synthesise Propionyliminocycloheptanecarboxylic Acid. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 142—150. Compare this vol., i, 251).—The synthesis of this acid was undertaken firstly in order to determine the limit of applicability of

the general method proposed previously (compare Abstr., 1906, i, 425), and secondly, to see whether the imino-group of the acid is hydrolysed by mineral acids. On treating ethyl aminocycloheptanecarboxylate with potassium cyanide and acetaldehyde, the first product of the reaction, $\text{CN}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{C}_7\text{H}_{12}\cdot\text{CO}_2\text{Et}$, decomposes, forming α -aminopropionic acid and iminodipropionic acid, aminocycloheptanecarboxylic acid also being produced. The latter, when similarly treated, produces ethyl cyanoethyliminocycloheptanecarboxylate hydrochloride,



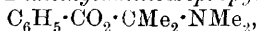
m. p. 141—143° (decomp.), soluble in alcohol and water, insoluble in ether, and decomposing on hydrolysis into an amino- and an hydroxy-acid.

The aqueous solution, after the extraction of the imino-acid, yielded with hydrochloric acid α -aminopropionic acid, an isomeric form of iminodipropionic acid, carbon dioxide and monoxide, and a mixture of volatile alcoholic substances. The mechanism of the reaction is discussed, the explanation given being similar to that proposed previously for other like cases. Z. K.

Preparation of Alkylaminoalkyl Benzoates. FARBERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 190688).—The halogenated alkyl benzoates react with the secondary aliphatic amines to furnish dialkylaminoalkyl benzoates, which are of value as anæsthetics.

Diethylaminoethyl benzoate, $\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, oil, b. p. 132°/5 mm.; the hydrochloride, colourless needles from alcohol-ether, m. p. 124°, is prepared by heating chloroethyl benzoate and diethylamine at 100—120° for twelve hours. The following are similarly obtained: *dimethylaminoethyl benzoate*, $\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$, oil; hydrochloride, lustrous needles, m. p. 148°; *di-n-oamylaminoethyl benzoate*, oil; *hydrogen oxalate*, needles, m. p. 158°; *hydrochloride*, needles, m. p. 107—108°; *diethylaminoethyl benzoate*, oil; *picrate*, yellow needles, m. p. 146°. G. T. M.

Preparation of Dimethylaminoisopropyl Benzoate. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 189482. Compare Abstr., 1906, i, 952).—*Dimethylaminoisopropyl benzoate*,



heavy oil, sparingly soluble in water, is obtained as its hydrochloride, leaflets, m. p. 127—128°, by benzoylating dimethylaminoisopropyl alcohol with benzoic anhydride or benzoyl chloride and extracting the product with hydrochloric acid. G. T. M.

Preparation of Alkylaminoalkyl *p*-Aminobenzoates. EMANUEL MERCK (D.R.-P. 189335).—The chloroethyldialkylamines having the general formula $\text{NRR}'\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ react with the salts of *p*-aminobenzoic acid to furnish the corresponding dialkylaminoalkyl *p*-aminobenzoate, $\text{NRR}'\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$.

Diethylaminoethyl p-aminobenzoate hydrochloride, m. p. 156°, is obtained by heating at 120—130° an intimate mixture of chlorotriethylamine, $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, and sodium *p*-aminobenzoate; the resulting base being neutralised with dilute hydrochloric acid. G. T. M.

Constitution of Anthranil. V. GUSTAV HELLER [and, in part, OTTO NÖTZEL] (*J. pr. Chem.*, 1908, [ii], 77, 145—171. Compare Abstr., 1902, i, 779; 1903, i, 827; 1904, i, 160; 1905, i, 130).—An account of the work of various authors on the constitution of anthranil and a résumé of the evidence for and against the constitutional formulæ $C_6H_4 \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{O}$ and $C_6H_4 \begin{smallmatrix} \text{CO} \\ | \\ \text{NH} \end{smallmatrix}$. The following new experimental evidence in favour of the latter formula is described.

Anthranil is oxidised by potassium dichromate in nitric acid solution at 75°, forming *o*-azoxybenzoic acid (compare Bamberger, Abstr., 1903, i, 634), whereas methylanthrozan, under similar conditions, yields *o*-nitrosoacetophenone, $\text{NO} \cdot C_6H_4 \cdot \text{COMe}$, which crystallises in yellow prisms, m. p. 129° (decomp.), is converted into azoxyacetophenone by the action of dilute alkalis, or into azoxybenzoic acid by oxidation with potassium permanganate, yields a red oil (*o*-acetoazobenzene?) when heated with aniline in 50% acetic acid, and again forms methyl-anthrozan on reduction with zinc dust and acetic acid or sodium hydroxide. The action of benzoyl chloride on anthranil in pyridine solution at -10° leads to the formation of a yellowish-red resin, which contains 2.45% of chlorine, and is probably a mixture of several substances, together with benzoic acid and benzoylanthranil; the resin cannot be converted into benzoylanthranil or benzoylanthranilic acid. Anthranil is not formed when anthroxanic acid is decomposed by prolonged heating at 190°, by heating in a vacuum, or by prolonged boiling in cumene solution. When treated with sodium nitrite in hydrochloric acid solution below -15° , anthranil forms a *nitrosoamine*, $C_7H_4O_2N_2 \cdot H_2O$, which crystallises in needles and rapidly decomposes when dried. Whilst anthranil does not react with hydrogen cyanide, isatin forms an additive compound, $C_9H_6O_2N_2$, which separates from acetone-light petroleum in colourless crystals, and decomposes evolving hydrogen cyanide and yielding isatin when heated or boiled with water.

Methylanthrozan does not react with phenylhydrazine or with benzoyl chloride in pyridine solution. When heated with an excess of benzoyl chloride at 140—150°, it forms small amounts of a substance, crystallising in red needles, m. p. 178°. Whilst anthranil yields isatoic acid when heated with ethyl chlorocarbonate in high-boiling petroleum solution, methylanthrozan, under the same conditions, remains unchanged. Contrary to Bamberger's statement (Abstr., 1904, i, 422), methylanthrozan is almost unattacked when boiled for one hour with 7% aqueous sodium hydroxide. It reacts slowly with methyl sulphate, forming a product, which yields an amorphous *picrate*, and a *platinichloride*, decomp. above 240°. G. Y.

[Properties, Detection and Estimation of] “Saccharin.” GIOVANNI PARMEGGIANI (*Boll. chim. farm.*, 1908, 47, 37—38).—The author's work clears up various disputed points concerning the properties of *o*-benzoicsulphinide.

o-Benzoicsulphinide has m. p. 220°, and dissolves in 400 parts of water at the ordinary temperature and in amyl acetate and ethyl acetate to the extents of 1:50 and 1:20 respectively. It is not

attacked by nascent hydrogen in alkaline solution, by potassium permanganate, by hydrogen peroxide, or by halogens in the cold. Cold nitric acid does not attack it, but, when heated with the acid, it undergoes hydrolysis, the sulpho-group being oxidised to sulphuric acid. The most sensitive precipitant for *o*-benzoicsulphinide is aqueous mercurous nitrate, the precipitate formed with mercuric nitrate being less abundant and soluble in excess of the reagent. Neutral solutions of the sulphinide precipitate solutions of salts of quinine or brucine, but not those of strychnine, morphine, or cocaine. The white, waxy condensation product of *o*-benzoicsulphinide with formaldehyde is unstable at a low heat, whilst the products formed with phenol, resorcinol, phloroglucinol, thymol, and α - and β -naphthols have no characters useful in the detection of the sulphinide.

The extraction of *o*-benzoicsulphinide from foods and its subsequent recognition may be effected as follows: 50 c.c. of the liquid are concentrated to about 25 c.c., acidified, if necessary, with hydrochloric or acetic acid, and extracted once with 30 c.c. of amyl acetate, which dissolves but little colouring matter from wines or liquors. The amyl acetate extract is separated, concentrated to a small volume, and defecated with a few drops of neutral lead acetate solution, the filtered liquid being then freed from lead by means of hydrogen sulphide and shaken with 20 c.c. of ethyl acetate. This extract is separated, evaporated to dryness on the water-bath, and the residue tested by tasting and other methods.

The following method of estimating *o*-benzoicsulphinide gives almost theoretical results. Fifty c.c. of the solution, after concentration and, if necessary, defecation as described above, are shaken several times with a total volume of 50 c.c. of a mixture, in equal volumes, of ether and light petroleum. The combined extracts are evaporated to dryness and the residue titrated with $N/200$ sodium hydroxide solution.

T. H. P.

Preparation of Diphenylated Acid Amides by the Action of Diphenylcarbamide on Acids. JOHANNES HERZOG and V. HÂNCU (*Ber.*, 1908, 41, 636—637).—Diphenylated acid amides are formed when a mixture of acid and diphenylcarbamyl chloride is heated with anhydrous pyridine in a boiling-water bath. Carbon dioxide and hydrogen chloride are evolved, $R\cdot CO\cdot OH + COCl\cdot NPh_2 = R\cdot CO\cdot NPh_2 + HCl + CO_2$, and, after some ten minutes, the product is poured into water and recrystallised from alcohol. Diphenylbenzamide, m. p. 179—180°, and diphenylcinnamide, m. p. 156—157°, have been prepared.

J. J. S.

Resolution of Racemic Amino-acids by Yeast. II. FELIX EHRLICH (and ADOLF WENDEL) (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 626, 198—222; *Biochem. Zeitsch.*, 1908, 8, 438—466).—Further examples of the resolution of amino-acids by yeast, in the presence of sugar, according to the method described (*Abstr.*, 1906, i, 807). The optical antipodes of the naturally occurring amino-acids are thus obtained, but, by applying Walden's inversion, the natural substances are obtainable (*Fischer, Abstr.*, 1907, i, 192).

d-Phenylalanine and *d*-serine have now been obtained from the

synthetic racemic acids with specific rotations agreeing very closely with those given by Fischer; serine is the first amino-hydroxy-acid to be resolved by the yeast method.

α -Aminophenylacetic and α -amino- α -methylbutyric acids have been resolved for the first time. The highest specific rotation observed for *l*- α -aminophenylacetic acid was in water, $[\alpha]_D^{20} - 90.35^\circ$, and in 10% hydrochloric acid, $[\alpha]_D^{20} - 144.83^\circ$. The *l*-acid is more soluble than the *dl*-acid, which fact renders the isolation of the *l*-acid difficult and makes it somewhat uncertain whether the resolution was complete; the rotation is higher than that of any other known amino-acid (except cystine), and very much higher than that of the next homologue, phenylalanine. *l*- α -Aminophenylacetic acid melts at 293° in an open, and at $303\text{--}305^\circ$ in a closed capillary tube (at very similar temperature to the *dl*-acid); the *hydrochloride* forms prisms, m. p. $242\text{--}244^\circ$ and 235° in open and closed tubes respectively; the *phenylcarbimide*, $C_{15}H_{14}O_3N_2$, needles, m. p. 168° , $[\alpha]_D^{20} - 129.27^\circ$ in $N/2$ sodium hydroxide, and the *phenylhydantoin*, $C_{15}H_{12}O_3N_2$ (*l*-diphenylhydantoin), needles, m. p. 191° , laevorotatory, have also been prepared.

The highest specific rotation observed for *l*- α -amino- α -methylbutyric acid ("isovaline") was in water, $[\alpha]_D^{20} - 9.10^\circ$, and in 20% hydrochloric acid, $[\alpha]_D^{20} - 6.11^\circ$.

Attempts to resolve β -aminobutyric acid were wholly unsuccessful. Additional manipulative details regarding the method are given.

G. B.

Action of Nascent Hypiodous Acid (Iodine and Sodium Carbonate) on some Acids having the General Formula $R\cdot CH:CH\cdot CH_2\cdot CO_2H$ (R being C_6H_5 more or less substituted). J. BOUGAULT (*Compt. rend.*, 1908, 146, 411—414).—Substituted isocrotonic acids of the type $R\cdot CH:CH\cdot CH_2\cdot CO_2H$, where R is a phenyl or substituted phenyl group, are converted by the action of iodine and sodium carbonate into substituted acrylic acids of the type $R\cdot CO\cdot CH:CH\cdot CO_2H$; the preparation of benzoylacrylic acid from phenylisocrotonic acid has already been described (this vol., i, 179); the analogous reactions of *p*-methoxy- and methylenedioxy-phenylisocrotonic acids form the subject of the present paper.

Anisylisocrotonic acid can be prepared by Fittig and Politis' method (Abstr., 1890, 770), or more conveniently by the following series of reactions: *anisylidenepyruvic acid*, $OMe\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CO_2H$, m. p. 131° , obtained by condensing pyruvic acid with anisaldehyde, yields *α -hydroxy- γ -anisylisocrotonic acid*, $OMe\cdot C_6H_4\cdot CH:CH\cdot CH(OH)\cdot CO_2H$, m. p. 145° , on partial, and anisylisocrotonic acid on further, reduction.

The iodolactone, $OMe\cdot C_6H_4\cdot \underset{\text{O}}{\underset{|}{CH}}\cdot CHI\cdot CH_2\cdot CO$, m. p. 125° , on treatment

with excess of sodium carbonate is converted into *p*-methoxybenzoyl acrylic acid (anisoylacrylic acid), $OMe\cdot C_6H_4\cdot CO\cdot CH:CH\cdot CO_2H$, m. p. 134° (not 131° as previously stated, this vol., i, 179), which forms pale yellow needles, is decomposed by boiling with dilute alkalis into glyoxylic acid and *p*-methoxyacetophenone, and combines with HBr to form a compound, having m. p. 130° , or with aniline to form an acid, having m. p. 121° .

Piperonylidene-pyruvic acid, m. p. 161° (Scholtz, Abstr., 1895, i, 469, gives $149-150^{\circ}$), on reduction yields α -hydroxy- γ -methylenedioxyphenyl-crotonic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 143° , and, finally, methylenedioxyphenylisocrotonic acid,

$\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$;
 $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\underset{\text{O}}{\underset{|}{\text{CH}}}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}$

the iodolactone, of this acid has m. p.

103° , and on treatment with sodium carbonate yields methylenedioxybenzoylacrylic (piperonylacrylic) acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, which forms sulphur-yellow crystals, darkens and decomposes at 180° , and melts at 200° ; it combines with HBr to form a compound which decomposes before it melts, or, with aniline, to form an acid having m. p. 134° .
 M. A. W.

Liberation of Carbon Monoxide by Heating Acylchlorides.

AUGUSTIN BISTRZYCKI and AUGUST LANDTWING (*Ber.*, 1908, **41**, 686—692. Compare Schmidlin and Hodgson, this vol., i, 170).—Experiments carried out with acids have shown that tertiary acids, like triphenylacetic acid, on dissolution in sulphuric acid, liberate carbon monoxide much more readily than monobasic primary acids (Abstr., 1907, i, 1039), and the research has been extended to the acyl chlorides. It has been found that a mixture of phosphorus pentachloride (1 part) and phosphoryl chloride (5 parts), when heated with the acid (1 part), leads to the formation of the acid chloride in good yield.

Triphenylacetyl chloride (Schmidlin and Hodgson, *loc. cit.*) when heated at $170-180^{\circ}$ is decomposed almost quantitatively into carbon monoxide and chlorotriphenylmethane. Diphenyl-*p*-tolylacetyl chloride, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPh}_2\cdot\text{COCl}$, separates from light petroleum in crystalline aggregates, m. p. $89-90^{\circ}$, and when heated is also decomposed quantitatively above 120° . At 200° , hydrogen chloride is evolved quantitatively, and possibly *p*-tolylfluorene is left behind.

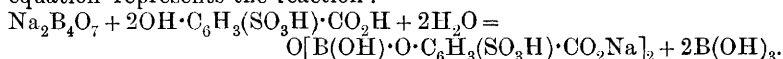
$\beta\beta$ -Di-*p*-tolylpropionyl chloride, $\text{CMe}(\text{C}_6\text{H}_4\text{Me})_2\cdot\text{COCl}$, crystallising in flat prisms from light petroleum, m. p. $54.5-55.5^{\circ}$, is very stable towards water. At 220° , it is slowly decomposed into carbon monoxide, hydrogen chloride, and *as*-di-*p*-tolylethylene (Abstr., 1905, i, 285). Chlorodiphenylacetyl chloride (Bickel, Abstr., 1889, 999) at 280° loses carbon monoxide quantitatively, and somewhat less than half of its chlorine as hydrogen chloride.

The secondary chloride, diphenylacetyl chloride, m. p. $56-57^{\circ}$ (Staudinger, Abstr., 1905, i, 444, gives 55°), loses carbon monoxide less completely and at a higher temperature than with the tertiary chlorides, and primary palmityl chloride gives only traces of an inflammable gas at 275° .

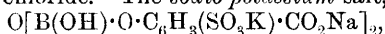
These results are therefore in agreement with those obtained with the acids themselves.

Triphenylacetamide, m. p. 238° (Schmidlin and Hodgson, *loc. cit.*, give $240-241^{\circ}$), at 300° gives a very small quantity of an inflammable gas. Methyl triphenylacetate at 250° gives neither ethylene nor carbon monoxide.
 W. R.

Action of Sulphosalicylic Acid on Sodium Diborate. LÉONCE BARTHE (*Compt. rend.*, 1908, 146, 408—411).—*Sodium oxydiborodisulphosalicylate*. $O[B(OH) \cdot O \cdot C_6H_3(SO_3H) \cdot CO_2Na]_2$, is obtained in the form of magnificent colourless crystals containing $3H_2O$ when an aqueous solution of sodium diborate (1 mol.) is mixed with an alcoholic solution of sulphosalicylic acid (2 mols.); the following equation represents the reaction:



The compound is a tetra-basic acid, it is a more delicate reagent for albumin than sulphosalicylic acid, and its solution gives a violet colour with ferric chloride. The *sodio-potassium* salt,

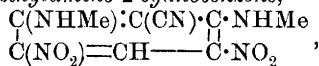


forms brilliant crystalline plates.

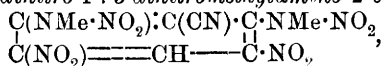
Sulphosalicylic acid reacts with sodium phosphate or arsenate to form crystalline derivatives. M. A. W.

Constitution of Van Geuns' Dinitromethoxybenzonitrile. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 509—511).—The dinitromethoxybenzonitrile prepared by Van Geuns (*Diss.*, Amsterdam, 1903) by acting on 3-nitro-2-cyanoanisole with a mixture of nitric and sulphuric acids is shown to be 3:4-dinitro-2-cyanoanisole; it has m. p. 113° . The corresponding 3:4-dinitro-2-cyanophenetole has m. p. 63° . The 3-nitro-group in these two compounds may be readily replaced by OH, OMe, NH_2 , NHMe, NHPh, &c. The constitution was determined as follows: the nitro-group in position 3 in dinitromethoxybenzonitrile, m. p. 113° , is replaced by an amino-group by heating the substance with alcoholic ammonia, since on removing the amino-group by diazotisation and boiling with alcohol a nitrocyanomethoxybenzene, m. p. 126° , is obtained, not identical with 3-nitro-2-cyanoanisole. The nitro-group in this compound must occupy position 4 or 6, since on nitration it yields 4:6-dinitro-2-cyanoanisole, m. p. 71° . The constitution of this compound was determined by converting it by means of alcoholic ammonia or methylamine into 4:6-dinitro-1-amino-2-cyanobenzene and 4:6-dinitro-1-methylamino-2-cyanobenzene respectively (compare Blanksma, *Abstr.*, 1902, i, 281). That the nitro-group in the nitrocyanomethoxybenzene, m. p. 126° , occupies position 4 and not 6 is shown by its conversion into 5-nitrosalicylic acid by hydrochloric acid under pressure at 150° .

The compound obtained by the nitration of 2-cyano-1:3-dimethoxybenzene or 4-nitro-2-cyano-1:3-dimethoxybenzene (Van Geuns, *loc. cit.*) is 4:6-dinitro-2-cyano-1:3-dimethoxybenzene, since it is converted by hydrochloric acid at 150 — 160° into 4:6-dinitroresorcinol; it has m. p. 81° . Other new compounds which have been prepared have the following melting points: 4-nitro-3-amino-2-cyanoanisole, 180° ; 4-nitro-2-cyanoanisole, m. p. 126° ; 4:6-dinitro-1:3-diamino-2-cyanobenzene, m. p. 293° ; 4:6-dinitro-1:3-dimethylamino-2-cyanobenzene,



m. p. 232°; 4:6-*dinitro*-1:3-*dinitromethylamino*-2-*cyanobenzene*,



m. p. 204°.

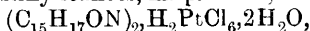
W. H. G.

Benzylethyl-*m*-aminophenol and its Condensation with Esters of 1:3-Ketocarboxylic Acids to Coumarin Derivatives. CARL BÜLOW and THEODOR SPRÖSSER (*Ber.*, 1908, 41, 487—497).—With the object of further investigating basic coumarins, benzylethyl-*m*-aminophenol has been obtained in a pure state (compare Guehm and Scheutz, *Abstr.*, 1901, i, 519) and condensed with ethyl acetoacetate, ethyl methylacetoacetate, and ethyl acetonedicarboxylate (compare Duisberg and von Pechmann, *Abstr.*, 1883, 66; von Pechmann, *Abstr.*, 1897, i, 220). The products obtained with ethyl acetoacetate and ethyl methylacetoacetate are respectively 7-benzylethylamino-4-methylcoumarin and 7-benzylethylamino-3:4-dimethylcoumarin, whilst instead of obtaining ethyl 7-benzylethylaminocoumarin-4-acetate with ethyl acetonedicarboxylate, the carbethoxyl group is eliminated during the reaction resulting in the formation of 7-benzylethylamino-4-methylcoumarin. Very dilute solutions of these basic coumarins exhibit a beautiful blue fluorescence.

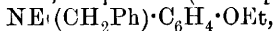
Benzylethyl-*m*-aminophenol, directions for obtaining which in a pure form from the commercial product are given in the original, forms colourless crystals, m. p. 68°, which quickly turn violet on exposure to air and light; the *hydrochloride*, $\text{C}_{15}\text{H}_{17}\text{ON}\cdot\text{HCl}\cdot\text{H}_2\text{O}$, m. p. 91°, crystallises in rosette clusters; the *sodium salt*,



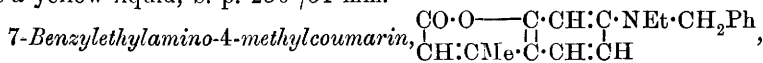
crystallises in white, silky leaflets, m. p. 120°; the *platinichloride*,



forms golden-yellow crystals, m. p. 186° (decomp.); the *ethyl ether*,



is a yellow liquid, b. p. 250°/31 mm.



crystallises in faintly coloured, rhombic leaflets, m. p. 88°.

7-Benzylethylamino-3:4-dimethylcoumarin, $\text{C}_{20}\text{H}_{21}\text{O}_2\text{N}$, forms colourless crystals, m. p. 116·5°.

W. H. G.

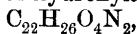
Action of Free Hydroxylamine on Santonin. LUIGI FRANCESCONI and GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1907, [v], 17, i, 64—73, 207—213).—The action of hydroxylamine on santonin in alkaline aqueous solution yields (1) santoninoxime, m. p. 216—219°; (2) *α*-hydroxylaminosantoninoxime, $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}_2$, which separates from water in massive, shining, apparently dimetric crystals, decomposing at 229—230° and melting at a few degrees higher; its aqueous solution is neutral and reduces Fehling's solution, gradually in the cold and immediately on heating, and potassium hydroxide solution and hydrochloric acid dissolve it, yielding liquids which reduce Fehling's solution vigorously.

When effected in methyl-alcoholic solution, the reaction yields the above *α*-compound and an isomeric *β*-hydroxylaminosantoninoxime,

$C_{15}H_{22}O_4N_2$, which crystallises from water or alcohol in elongated, monoclinic prisms, decomposing at $232-233^\circ$. When the original methyl-alcoholic solution is concentrated on the water-bath under diminished pressure, santoninoxime and the above β -compound are formed together with a compound, $C_{15}H_{27}O_6N_3$, which begins to undergo change at 170° , decomposes rapidly at about 230° , and is apparently the hydroxylamine salt of the acid corresponding with the β -compound; it decomposes Fehling's solution, slowly in the cold and rapidly on heating; it has a neutral reaction in aqueous solution, but gradually decomposes with formation of hydroxylamine and β -hydroxylaminosantoninoxime.

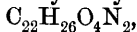
The *benzylidene* derivative of hydroxylaminohydroxylaminosantoninoxime, $C_{22}H_{31}O_6N_3$, crystallises from alcohol or ethyl acetate in short, stout prisms, decomposing at $171-171.5^\circ$, and gives a violet colour with ferric chloride.

The *benzylidene* derivative of hydroxylaminosantoninoxime- β ,



crystallises from methyl or ethyl alcohol, ethyl acetate, or ether in colourless, rectangular plates, which, at 140° , begin to decompose and evolve gas. The *benzoyl* derivative, $C_{29}H_{30}O_6N_2$, crystallises from methyl alcohol in hard, colourless prisms, m. p. 184° (decomp.).

The *benzylidene* derivative of hydroxylaminosantoninoxime- α ,



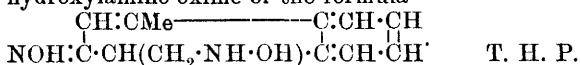
crystallises from aqueous alcohol in tufts of colourless prisms, m. p. 217° (decomp.), and does not reduce Fehling's solution in the cold.

When hydroxylaminosantoninoxime- α is dissolved in cold sodium hydroxide solution and the liquid mixed with a quantity of hydrochloric acid equivalent to the sodium hydroxide, the corresponding *santoninic acid*, $C_{15}H_{24}O_5N_2$, gradually separates; the acid crystallises from water in colourless, rectangular plates, which decompose at 140° , forming hydroxylaminosantoninoxime- α , and its aqueous solution has a strong acid reaction, reduces Fehling's solution, and gives no coloration with ferric chloride.

With dilute hydrochloric acid, hydroxylaminohydroxylaminosantoninoxime gives, in the cold, hydroxylamine and hydroxylaminosantoninoxime- β , whilst in the hot, a mixture of santonin, hydroxylaminosantoninoxime- β , and santoninoxime is precipitated. Hydroxylaminosantoninoxime- β dissolves in cold hydrochloric acid practically unchanged, but on prolonged boiling with the acid it decomposes into santoninoxime and santonin. Hydroxylaminosantoninoxime- α dissolves in hydrochloric acid, giving a solution which readily yields hydroxylamine in the cold, and gradually deposits tufts of white needles, m. p. $200-201^\circ$, which were not further examined. Both the α - and β -hydroxylaminosantoninoximes, dissolved in water, chloroform, or methyl alcohol, undergo oxidation in presence of freshly-precipitated mercuric oxide, the solution becoming first pale yellow and later intensely reddish-yellow. The authors suggest for santonin

the structure
$$\begin{array}{c} \text{CH}=\text{CMe}-\text{C}:\text{CH}\cdot\text{CH} \\ \text{CO}\cdot\text{C}:(\text{CH}_2)\cdot\text{C}:\text{CH}\cdot\text{CH} \end{array}$$
 according to which it should

yield a primary hydroxylamino-oxime of the formula



Dialkylphthalides. I. **5-Amino- and 5-Hydroxy-diethylphthalide.** HUGO BAUER (*Ber.*, 1908, 41, 503—508).—The position of the nitro-group in nitrodiethylphthalide (*Abstr.*, 1904, i, 417) has been determined in the following way. The amino-compound, obtained by reduction, is converted into the hydroxy-derivative, the methyl ether of which yields *m*-hydroxybenzoic acid when fused with potassium hydroxide (compare Gucci, *Abstr.*, 1898, i, 257). The nitro-group is therefore in position 3 or 5 with reference to the carbonyl group. To ascertain which, aminodiethylphthalide is oxidised to the azo-compound, and this reduced to the hydrazo-compound; the last is partly reduced to the amine and partly oxidised to the azo-compound by concentrated mineral acids, a reaction characteristic of hydrazo-compounds which are symmetrically substituted in the para-positions. The nitro-group is therefore in position 5.

5-Aminodiethylphthalide, $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\text{CEt}_2\rangle\text{CO}$, m. p. 165°, crystallises in colourless needles and forms a blue, fluorescent solution in methyl or ethyl alcohol; the *platinichloride* and the *acetyl* derivative, m. p. 121·5—122·5°, are described. *5-Hydroxydiethylphthalide*, m. p. 129·5—130·5°, forms a *benzoyl* derivative, m. p. 101°, and a *methyl ether*, m. p. 79—80°, and by nitration yields *4:6-dinitro-5-hydroxydiethylphthalide*, $\text{OH}\cdot\text{C}_6\text{H}(\text{NO}_2)_2\langle\text{CEt}_2\rangle\text{CO}$, m. p. 169°, which forms intensely yellow solutions in alkali hydroxides or carbonates; the *methyl ether*, obtained by nitrating *5-methoxydiethylphthalide*, has m. p. 131°, and by reduction yields *4:6-diamino-5-methoxydiethylphthalide*, m. p. 205—206°, the *diacetyl* derivative of which has m. p. 131·5—132°.

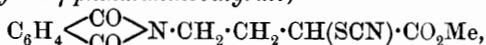
5-Azodiethylphthalide, $\text{O}\langle\text{CEt}_2\rangle\text{C}_6\text{H}_3\cdot\text{N:N}\cdot\text{C}_6\text{H}_3\langle\text{CEt}_2\rangle\text{CO}$, m. p. 174—175°, forms orange-yellow leaflets, and is reduced by alcoholic ammonium sulphide to the *hydrazo*-compound, which crystallises in colourless needles, turns yellow at 190°, and has m. p. 206—208°.

C. S.

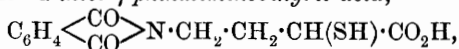
Derivatives of γ -Aminobutyric Acid. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1908, 41, 513—521. Compare *Abstr.*, 1907, i, 625).—The paper merely contains an account of the following substances.

γ -Cyanopropylphthalimide (*Abstr.*, 1890, 360, 1129) is hydrolysed by concentrated sulphuric acid, yielding, according to the conditions employed, *γ -phthaliminobutyramide*, $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{N}\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{NH}_2$, m. p. 165—166°, or *γ -phthaliminobutyric acid*, $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$, m. p. 117—118°, sintering at 115°; the *methyl* ester has m. p. 89—90°, and the *ethyl* ester, m. p. 71—72°. By bromination in the presence of red phosphorus, the acid yields Fischer's α -bromo- γ -phthaliminobutyric acid (*Abstr.*, 1901, 674), the *methyl* ester of which, m. p.

76—77°, reacts with boiling alcoholic potassium thiocyanate to form *methyl α-thiocyano-γ-phthaliminobutyrate*,



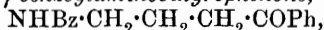
m. p. 88—89°. By hydrolysis with concentrated sulphuric acid, this compound yields *α-thiol-γ-phthaliminobutyric acid*,



m. p. 139—140°. Hydrolysis of this acid by 20% boiling hydrochloric acid, or of methyl *α-thiocyano-γ-phthaliminobutyrate* by acetic and concentrated hydrochloric acids at 140°, leads to the formation of a colourless syrup, which exhibits the reactions of an aminomercaptan and consists probably of the hydrochloride of *γ-amino-α-thiolbutyric acid*, the homologue of *isocystein*. To obtain a crystalline derivative, the syrup is treated with bromine water, whereby *γ-amino-α-sulphobutyric acid*, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{SO}_3\text{H}) \cdot \text{CO}_2\text{H}$, m. p. 263° (decomp.), is obtained.

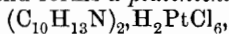
γ-Phthaliminobutyric acid and phosphorus pentachloride yield the acid *chloride*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{N} \cdot [\text{CH}_2]_3 \cdot \text{COCl}$, m. p. 67—69°, which reacts with boiling benzene in the presence of aluminium chloride to form *γ-phthaliminobutyrophenone*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{N} \cdot [\text{CH}_2]_3 \cdot \text{COPh}$, m. p.

132—133°. The ketone is hydrolysed by acetic and concentrated hydrochloric acids at 150—155°, and yields the *hydrochloride*, $\text{C}_{10}\text{H}_{11}\text{N} \cdot \text{HCl}$, which sinters at 200°, and melts at 210° to a turbid red liquid, which becomes clear at 211—212°; the *platinichloride*, $(\text{C}_{10}\text{H}_{11}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, darkens at 200° and has m. p. 220° (decomp.). The free *base*, $\text{C}_{10}\text{H}_{11}\text{N}$, m. p. 44—45°, b. p. 249°/752 mm., has a bitter taste, alkaline reaction, odour of phenyloxazoline, and forms a *picrate*, m. p. 198° (decomp.). The analysis of the base and of its salts shows that in the preceding hydrolysis the expected *γ-aminobutyrophenone* has lost a molecule of water, forming *2-phenylpyrroline*. An analogous formation of *2-methylpyrroline* and of *1:2-dimethylpyrroline* has been observed by Hielscher (Abstr., 1898, i, 338). The pyrroline ring is readily ruptured when *2-phenylpyrroline* is shaken with benzoyl chloride and sodium hydroxide, whereby *γ-benzoylaminobutyrophenone*,



m. p. 125—126°, is produced (compare Markwalder, Abstr., 1907, i, 637). Similarly, phthalic anhydride at 210° converts *2-phenylpyrroline* into *γ-phthaliminobutyrophenone*, mentioned above.

2-Phenylpyrrolidine is reduced by tin and hydrochloric acid to *2-phenylpyrrolidine*, $\begin{array}{c} \text{CH}_2 \cdot \text{CHPh} \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{NH}$, b. p. 241°/771 mm., which absorbs carbon dioxide and forms a *platinichloride*,



m. p. 187—188°, an *aurichloride*, $\text{C}_{10}\text{H}_{13}\text{N} \cdot \text{HAuCl}_4$, m. p. 110°, and a *picrate*, m. p. 148—149°.

C. S.

Tautomerism of Cyclic Monoketones. CARL MANNICH and V. H. HÄNCU (*Ber.*, 1908, 41, 564—575).—Whereas cyclic triketones

and diketones have pronounced tautomeric properties, the only cyclic monoketone hitherto examined from this point of view is *cyclohexanone* (Mannich, Abstr., 1906, i, 432). A number of cyclic monoketones are now found to react in a second tautomeric modification provided they contain a simple ring system. It requires, however, the influence of a very active reagent, such as acetic anhydride, to bring about the formation of derivatives of the enolic isomeride. On hydrolysis of such enolic esters, the corresponding ketones are re-formed, and no evidence could be gained that the enolic isomeride was even for a moment produced.

From *cyclohexanone*, acetic anhydride and sodium acetate, the acetate of *cyclohexenol* is produced; it is a colourless, oily liquid of a fruity odour, and forms adipic acid when oxidised with nitric acid, and not a nitro-derivative. Hydrogen bromide causes the formation of a ketone, $C_{12}H_{18}O$, b. p. 136—138°/10 mm. (*loc. cit.*), and not an additive product. The acetate of 1-methyl- Δ^3 -*cyclohexene*-4-ol is a colourless, oily liquid of a fruity odour, b. p. 191—192°, and gives β -methyladipic acid on oxidation. Hydrogen bromide converts it into a ketone, $C_{14}H_{22}O$, b. p. 157—159°/13 mm., formed by the elimination of water from two molecules of 1-methyl*cyclohexane*-4-one. The *oxime* softens at 155°, m. p. 164°.

The acetate of 1-methyl- $\Delta^{1(or\ 2)}$ -*cyclohexene*-2-ol is a colourless liquid of pleasant odour, b. p. 185—186°. The corresponding derivative of the tautomeric form of 1-methyl*cyclohexane*-3-one has b. p. 195—196°.

The acetate of 1-methyl-4-isopropyl- $\Delta^{2(or\ 3)}$ -*cyclohexene*-3-ol, prepared from *l*-menthone, is an oily, almost colourless liquid of a faint, but not menthone-like, odour, and has $a_D +13.3^\circ$ (200 mm. tube). A dextro-rotatory menthone was obtained on hydrolysis. *l*-Menthone is known to pass over into *d*-menthone when treated with acids, and Beckmann (Abstr., 1889, 721) assumed intermediate formation of enol to explain this, an explanation confirmed by these observations. The corresponding *benzoate acid* is an oily liquid, b. p. 200—202°/30 mm. The acetate of Δ^1 -*cyclopentene*-1-ol is a colourless liquid of characteristic odour, b. p. 156—158°; on oxidation with permanganate in alkaline solution it yields glutaric acid. The acetate of Δ^1 -*cycloheptene*-1-ol, prepared from suberone, is a colourless liquid of refreshing odour, b. p. 194—196°. The action takes place less easily in ketones with five or seven units in the ring than with six. The *propionate* of Δ^1 -*cyclohexene*-1-ol, formed by heating *cyclohexanone* with propionic anhydride, has b. p. 195—197°; the corresponding *butyrate* has b. p. 214—216°; both ethers are colourless, oily liquids of a fruity odour.

No trace of an enolic ether could be obtained from acetone, but mesityl oxide was formed by the interaction of acetone and acetic anhydride. It was not found possible to prepare methyl derivatives of the enolic form of *cyclohexanone*. Pulegone and carvone react in the enolic form, but the change is complicated by secondary reactions, so that the pure ethers could not be isolated. Camphor does not react in the enolic form. Two isomerides of 1:2- and 1:3-methyl*cyclohexanones* and menthone derivatives are possible according to the position of the double linking in the benzene nucleus, and the ethers prepared may represent mixtures of two very similar isomerides. E. F. A.

Chemical Action of Light. XI. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 179—187, *Ber.*, 1908, 41, 1071—1080. Compare Abstr., 1907, i, 587).—Like menthone, *cyclohexanone* and the three isomeric methyl*cyclohexanones* are hydrolysed by the action of light, the ring structure being broken down and a fatty acid, $C_nH_{2n}O_2$, and the corresponding unsaturated aldehyde, $C_nH_{2n-2}O$, being formed.

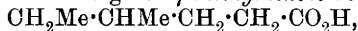
Thus, in aqueous or aqueous-alcoholic solution, *cyclohexanone* yields hexoic acid and the hexylene aldehyde, $CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHO$.

1:2-Methyl*cyclohexanone* hydrolyses to *n*-heptoic acid (α -nanthoic acid) and Δ^6 -heptenaldehyde, $CHMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHO$.

1:3-Methyl*cyclohexanone* yields a heptoic acid, b. p. 215—216°, having the constitution $CHMe_2 \cdot [CH_2]_3 \cdot CO_2H$ or



1:4-Methyl*cyclohexanone* gives γ -methylhexoic acid,



b. p. 217—218°, and an aldehyde, $CH_2 \cdot CH \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CHO$ (?).

The presence of chlorophyll in the solutions retards the hydrolytic action of light in the cases examined, namely, acetone, *cyclohexanone*, and menthone.

T. H. P.

Spontaneous Transformation of Benzophenoneoxime.

MICHAEL KONOWALOFF and K. MÜLLER (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1125—1126. Compare Holleman, Abstr., 1895, i, 475).—Having prepared benzophenoneoxime, m. p. 139—140°, in the ordinary way, it was found to have changed into a yellow liquid after remaining loosely corked for three and a-half years. The liquid consists of water, benzophenone, toluene, nitrotoluene, a small quantity of oxides of nitrogen, and possibly also benzene and its nitro-derivatives. When freshly-prepared benzophenoneoxime is allowed to remain in a loosely-corked flask, it becomes liquid in about fifteen days, and nitrogen oxides are evolved.

Z. K.

Reciprocal Displacement of Hydrocarbon Groups in Friedel and Crafts' Reaction. HENRI DUVAL (*Compt. rend.*, 1908, 146, 341—343).—With the intention of applying to its 2:2'-diamino-derivative the reaction previously described (Abstr., 1907, i, 663), the author has prepared 4:4'-diacetyldiphenylmethane. When diphenylmethane in carbon disulphide solution is treated with acetyl chloride in the presence of aluminium chloride, there are formed acetyldiphenylmethane, 4:4'-diacetyldiphenylmethane, and a considerable quantity of acetophenone. The latter can only have been formed by the displacement of the benzyl by the acetyl group under the influence of the aluminium chloride. Such a reaction has not previously been described under these conditions and at a low temperature. 4:4'-Diacetyldiphenylmethane, $COMe \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot COMe$, has m. p. 93°, b. p. 259—260°/9 mm; it gives an *oxime*, m. p. 210°. Its constitution is established by the production of dinitrodiphenylmethane-4:4'-dicarboxylic acid when it is treated with a mixture of fuming nitric and sulphuric acids, and by the formation of benzophenone-4:4'-dicarboxylic acid when it is oxidised with sodium hypobromite. *Acetyldiphenyl-*

methane, $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$, m. p. 39° , b. p. $197\text{--}198^\circ/9\text{ mm.}$, forms an *oxime*, m. p. $99\cdot5^\circ$. On nitration, it gives *nitroacetyldiphenylmethane*, $\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}$, which forms needles, m. p. $91\cdot5^\circ$, and yields an *oxime*, m. p. 162° . Reduction of the nitro-derivative with alcoholic stannous chloride gives *aminoacetyldiphenylmethane*, m. p. $135\cdot5^\circ$.

E. H.

Direct Hydrogenation of Aromatic Quinones. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 146, 457—458).—The authors have applied the method of direct hydrogenation in the presence of finely-divided nickel to the following aromatic quinones, benzoquinone, toluquinone, *p*-xyloquinone, and thymoquinone, with the result that at about 200° the quinone is converted quantitatively into the corresponding quinol. At temperatures between 220° and 250° , the quinol is reduced with the formation of water and the corresponding hydrocarbon and phenol (compare Sabatier and Senderens, Abstr., 1905, i, 333); at lower temperatures, the quinol is reduced, yielding the corresponding diol of the *cyclohexane* series.

M. A. W.

Hydration of *d*-Pinene. WLADIMIR SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 150—153).—The hydration of *d*-pinene in the presence of sulphuric acid is a catalytic reaction. The *d*-pinene, mixed with an equal volume of alcohol and about 1/10 by volume of dilute acid, is boiled, a *secondary alcohol*, $\text{C}_{10}\text{H}_{16}\cdot\text{H}_2\text{O}$, b. p. $93\text{--}95^\circ/10\text{ mm.}$, being thus obtained, $D_{15}^{25} 0\cdot9216$, $D_4^{18\cdot8} 0\cdot9185$, $n_D^{18\cdot8} 1\cdot4735$, $[\alpha]_D + 44\cdot42^\circ$; when oxidised with chromic acid, it yields a *ketone*, b. p. $200\text{--}205^\circ$, which yields a *semicarbazone*, m. p. $226\text{--}228^\circ$. Possibly the alcohol is identical with the one obtained by Aschan (Abstr., 1907, i, 630) and with the alcohol obtained from *d*-pinene by the action of dilute nitric acid. In addition to the secondary alcohol, a mixture of hydrocarbons was also obtained, b. p. $148\text{--}190^\circ/760\text{ mm.}$ and $\alpha + 15^\circ$ to $+ 31^\circ$ (100 mm.).

It is considered that *d*-pinene, b. p. $155\text{--}157^\circ$ and $\alpha + 27\cdot4^\circ$ (100 mm.), which was the substance hydrated, is a mixture of pinene with pinolene or some other unknown hydrocarbon, or undergoes isomeric change into pinolene.

Z. K.

Sesquiterpene Occurring together with Cadinene in "Oleum Cadinum." NICOLAUS LEPESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 126—133. Compare Wallach, Abstr., 1887, 595).—In the extraction of cadinene from oleum cadinum, but little of this hydrocarbon is obtained, although a great deal of hydrogen chloride is absorbed, and the object of the research was to discover whether this was not due to the presence of some other hydrocarbon. When the oil remaining after the removal of cadinene from oleum cadinum is distilled at low pressure, a new *sesquiterpene*, $\text{C}_{15}\text{H}_{24}$, b. p. $262\text{--}264^\circ/760\text{ mm.}$, is isolated, together with a mixture of oxidation products of this hydrocarbon of higher b. p. The sesquiterpene has $D_{20}^{20} 0\cdot9204$, $D_{20}^{20} 0\cdot9221$, $n_D^{20} 1\cdot5152$, $[\alpha]_D 14\cdot12^\circ$, and differs entirely from cadinene in chemical properties. It absorbs bromine rapidly with evolution of hydrogen bromide, and does not yield crystalline products with the

halogen acid, or give the characteristic colour reactions given by cadinene. With hydrogen iodide at 200° it yields an isomeric *sesquiterpene*, b. p. $250-258^{\circ}/760$ mm., D_4^{20} 0.8946, n_D^{20} 1.4972, either identical or closely related to humulene (Chapman, *Trans.*, 1895, 67, 54). It is possible that the sesquiterpene occurring together with cadinene in oleum cadinum is identical with that occurring in oil of cubebs.

Z. K.

Constituents of Essential Oils. Composition of Ayapana Oil. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 509—512).—Ayapana oil, obtained from *Eupatorium triplinerve*, yields on distillation a main fraction, b. p. $116-119^{\circ}/12$ mm., representing 80% of the total, which by redistillation over sodium yields a liquid, b. p. $118^{\circ}/12$ mm., D^{20} 0.9671, n_D 1.51066. This liquid, in spite of the constancy of the b. p., is not an individual substance, for, after being treated with potassium permanganate in cold acetone solution, the recovered liquid has b. p. $118^{\circ}/12$ mm., D^{20} 0.9913, n_D 1.51339, and $\alpha_D \pm 0^{\circ}$; the other constituent is probably a sesquiterpene. The main portion consists of *thymoquinol dimethyl ether*, $C_{12}H_{18}O_2$, which by treatment with hydriodic acid and red phosphorus at 90° is converted into the *methyl ether* (or a mixture of the isomeric methyl ethers), b. p. $117-130^{\circ}/12$ mm., D^{20} 1.0111, n_D 1.5188, and thymoquinol, $C_{10}H_{14}O_2$, m. p. 143° , the identity of which was proved by oxidation to thymoquinone, m. p. 48° .

C. S.

Essential Oil of Tetranthera polyantha var. citrata. EUGÈNE CHARABOT and G. LALOUE (*Compt. rend.*, 1908, 146, 349—350; *Bull. Soc. chim.*, 1908, [iv], 3, 383—388. Compare Schimmel & Co., *Abstr.*, 1905, i, 538).—The oils from the bark, leaves, and fruits have respectively: $\alpha_D + 20^{\circ}30'$, $-12^{\circ}30'$, and $+12^{\circ}44'$ (100 mm. tube); D^{15} 0.8673, 0.9013, and 0.8872. They respectively contain: citral, 8%, citronellal, 20%, an alcohol (geraniol?), 56.5%, ethers, 2.4%; citral, 6%, cineol, 21.2%, an alcohol (geraniol?), 31.3%; citral, 64%, an alcohol (geraniol?), 19.4%, ethers, 2%.

G. B.

Phosphorus, an Essential Constituent of Chlorophyll. JULIUS STOKLASA, V. BRDLIK, and J. JUST (*Ber. Deut. bot. Ges.*, 1908, 26a, 69—78).—Polemical against Willstätter (*Abstr.*, 1907, i, 71), who found no phosphorus in chlorophyll, or at most traces. The authors have prepared specimens of pure chlorophyll with as much as 3.37% P. The phosphorus content of maple leaves reaches a maximum in July and then falls off, so that only traces are present in October, and at any given time yellow leaves (with little or no chlorophyll) contain much less phosphorus than green leaves of the same plant.

The question is of interest in connexion with the authors' view that chlorophyll is a lecithin-like substance. They have lately shown that choline and glycerophosphoric acids are among its decomposition products.

G. B.

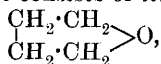
Pigment of Yellow Autumn Leaves. M. TSVETT (*Ber. Deut. bot. Ges.*, 1908, 26a, 94—101).—The yellow leaves do not contain

chlorophyll, but instead a new pigment, which in Kraus' process of separation behaves like carotin, but resembles xanthophyll in that it is wholly adsorbed by calcium carbonate from its solution in light petroleum; it is probably a decomposition product of one of these pigments, or of both. The yellow colouring matter, which is dissolved by boiling the leaves with water, is an artificial product, not concerned in the pigmentation of the living leaf. G. B.

Artificial Melanins, and the Natural Melanin of the Cockchafer. TOMATORO ISHIZAKA (*Arch. exp. Path. Pharm.*, 1908, 58, 198—206).—The melanins were prepared from proteins by the following method. The protein was heated for several hours with hydrochloric acid (10%). The dark-coloured liquid was then neutralised with sodium hydroxide and evaporated on a water-bath. Copper acetate was added, and the melanins thereby precipitated. The washed precipitate was dissolved in ammonia; a small amount remained undissolved. This was treated with potassium hydroxide solution on the water-bath; the filtrate from this was added to the ammoniacal solution and the whole made acid with acetic acid and warmed on the water-bath. The melanin was thereby precipitated, and was purified by re-solution in alkali and re-precipitation by acid. Melanins were prepared from gelatin, feathers, sponge, artolin, and nucleic acid. The amount of melanin formed depends on the quantity of sulphur and iodine in the original protein; the larger the amount of these elements present the greater the yield of melanins.

The melanin from cockchafers was extracted with 20% sodium chloride solution containing a little potassium acetate, slightly acidified with acetic acid; from the solution thus obtained, it was precipitated by copper chloride; the free melanin was obtained from this precipitate by a method similar to that described above for the preparation of the protein melanins from their copper compounds. S. B. S.

Hydrogenation of Furan. A. BOURGUIGNON (*Bull. Soc. chim. Belg.*, 1908, 22, 87—93. Compare Padoa and Ponti, *Abstr.*, 1907, i, 146).—When furan is hydrogenated at 170° by Sabatier and Senderens' method, the principal product consists of *tetrahydrofuran*,



a colourless, mobile liquid, b. p. 64—65°/760 mm., D_4^{25} 0.888 ± 0.002, n_D^{25} 1.40762, having a penetrating odour and a burning, slightly bitter taste, together with a small quantity of *n*-butyl alcohol. Analysis of the gases produced indicates the presence of saturated hydrocarbons, perhaps propane, or a mixture of butane and ethane. Tetrahydrofuran is attacked by bromine, giving a compound in the form of a viscous liquid, b. p. 78°/15 mm., which from a bromine estimation appears to be $\alpha\delta$ -dibromobutane, $\text{C}_2\text{H}_4(\text{CH}_2\text{Br})_2$.

The conclusion is drawn that the furan nucleus is less stable than that of benzene, which is not ruptured on hydrogenation at 170°. E. H.

Constitution of Halogenated Compounds of 3-Hydroxy- γ -pyrone [Pyromeconic Acid]. I. COMPAGNO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 73—81).—The distillation of bromocomenic

acid (compare Peratoner and Castellana, *Abstr.*, 1905, i, 806) yields a bromopyromeconic acid identical with that obtained by the action of bromine on 3-hydroxy- γ -pyrone (compare Brown, *Annalen*, 1845, **92**, 321), the action being represented by the scheme :



T. H. P.

Compounds of Dimethylpyrone and Tribromoacetic Acid.

VLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 64—70. Compare *Abstr.*, 1905, i, 77).—The experiments described confirm the existence of compounds of the type RD_2 (where R = a monobasic acid, and D = dimethylpyrone). Thus, by the action of dimethylpyrone on tribromoacetic acid in chloroform or ethereal solution, three crystalline compounds are formed : $\text{CBr}_3 \cdot \text{CO}_2\text{H} \cdot \text{C}_7\text{H}_8\text{O}_2$; $2\text{CBr}_3 \cdot \text{CO}_2\text{H} \cdot \text{C}_7\text{H}_8\text{O}_2$, and $\text{CBr}_3 \cdot \text{CO}_2\text{H} \cdot 2\text{C}_7\text{H}_8\text{O}_2$, which decompose at 60° without melting. Physically and chemically the compounds are similar in all respects to true salts. The types and structural formulæ of the compounds dimethylpyrone should form with mono- and di-basic acids are discussed.

Z. K.

Atropine. RICHARD WOLFFENSTEIN and LEONARD MAMLOCK (*Ber.*, 1908, **41**, 723—732).—Ladenburg, in 1883, showed that tropine and tropic acid could be condensed to atropine. Attempts now made to condense tropic acid chloride in a similar manner gave rise only to the formation of tropide from two molecules of the chloride. The chloride of β -chlorohydratropic acid condenses readily with tropine, but attempts to replace the chlorine atom in the β -chlorohydratropyltropine so formed by hydroxyl led only to the formation of *apoatropine*. Acetyl-tropic acid condenses to acetyl-atropine, of which the hydrochloride, when left to itself in water, loses the acetyl group, forming atropine.

The *chloride* is obtained from tropic acid by means of thionyl chloride as a yellow oil, which decomposed when distilled. The chloride of β -chlorohydratropic acid is also best prepared by means of thionyl chloride ; it condenses with tropine hydrochloride to form the *hydrochloride* of *chlorohydratropyltropine*, a colourless, crystalline compound, m. p. 167 — 170° , which forms a crystalline *picrate*, m. p. 204° , and an orange-yellow *platinichloride* (decomp. 60°). When treated with sodium carbonate, this hydrochloride yields the free base as an oil, which, when its ethereal solution is heated, gives rise to a colourless, crystalline salt, *apoatropine* hydrochloride. *Bromohydratropyltropine hydrobromide* is a snow-white, crystalline mass, m. p. 180° . When evaporated with a few drops of nitric acid and the residue moistened with alcoholic potassium hydroxide, it gives, like the chloro-compound and atropine itself, a violet coloration. Attempts to obtain the free base resulted in the formation of *apoatropine* hydrobromide. Acetyl-tropic acid was obtained as a yellow, viscid oil, solidifying to a colourless, crystalline mass, m. p. 88 — 90° (Hesse, *Abstr.*, 1901, i, 713, gives

80°). Thionyl chloride converts this into the *chloride*, which condenses with tropine hydrochloride to *acetyl tropine hydrochloride*, a yellow, viscid mass. This is converted readily into atropine on leaving the strongly acid aqueous solution with excess of an alkaline hydroxide.

Physiologically, the chloro- and bromo-hydratropyltropine behave very much as atropine does, showing that the alcoholic hydroxyl in the aromatic acid radicle in tropine is replaceable by halogen without affecting the mydriatic action. E. F. A.

Halogen-substituted Tropine. RICHARD WOLFFENSTEIN and JOHANNES ROLLE (*Ber.*, 1908, 41, 733—740).—Reactions analogous to the conversion of β -chlorohydratropyltropine into apoatropine have been studied in more simple cases, in which the α , β , and γ halogen derivatives of propionic and *n*-butyric acids were substituted for phenylchloropropionic acid (chlorohydratropic acid). The reaction is a general one, but the readiness with which the elimination of the hydrogen halide is effected is markedly influenced by the position of the halogen. The β -position particularly favours the change, whilst the α and γ positions are less favourable.

α -Chloropropionyl chloride has b. p. 107—110°, and forms a *p*-toluidide, m. p. 108°. β -Chloropropionyl chloride has b. p. 144°, and forms a *p*-toluidide, m. p. 121°. α -Chlorobutyryl-*p*-toluidide has m. p. 98°; the β -chlorobutyryl-*p*-toluidide has m. p. 115°, and the γ -chlorobutyryl-*p*-toluidide, m. p. 95°.

These compounds all condense with tropine to form the hydrochlorides of tropine, which were decomposed with alkaline carbonates, forming an oil which was taken up in benzene solution and rapidly passed into the crystalline, unsaturated tropine.

α -Chloropropionyltropine forms an *aurichloride*, crystallising in yellow, glistening plates, m. p. 131°, and a *picrate*, yellow, transparent needles, m. p. 211° (decomp.). Acryltropine forms a crystalline *picrate*, m. p. 198°, and reacts with bromine giving $\alpha\beta$ -dibromopropionyltropine, of which the sparingly soluble *picrate* has m. p. 185°.

β -Chloropropionyltropine forms a *picrate*, m. p. 222°, a *platinichloride*, m. p. 205, an *aurichloride*, m. p. 135°, and yields the above acryltropine with greater ease than the β -compound.

α -Chlorobutyryltropine yields a *picrate*, m. p. 209°, an *aurichloride*, m. p. 125°, and a *platinichloride*, m. p. 212°. Crotonyltropine gives a *picrate*, crystallising in yellow plates, m. p. 190° (decomp.), and an $\alpha\beta$ -dibromobutyryltropine.

β -Chlorobutyryltropine forms a *picrate*, m. p. 216°, an *aurichloride*, m. p. 137° and a *platinichloride*, sparingly soluble needles from alcohol, m. p. 210—212°, and gives the above crotonyltropine.

γ -Chlorobutyryltropine forms a *platinichloride*, m. p. 208°, and yields vinylacetyltropine after remaining for thirty days in benzene solution; the *platinichloride* has m. p. 204°.

The acid chlorides described also condense with other alkamines, such as lupinine, and, in particular, dimethylaminomethyldiethylcarbinol. These alkamine-esters show a similar intramolecular elimination of hydrogen chloride. E. F. A.

Pseudomorphism of Organic Persulphates. RICHARD WOLFFENSTEIN and A. WOLFF (*Ber.*, 1908, 41, 717—723).—The persulphates of the cinchonine alkaloids show a new form of pseudomorphism in that, when heated, an intramolecular rearrangement takes place without any change in the atomic composition or external crystalline form. When acid quinine persulphate is heated slowly in an air-bath for eight days, during which time the temperature is slowly allowed to rise from 80° to 120°, the crystals become at first yellow, then reddish-yellow, and finally ruby-red, whilst retaining their transparent appearance and characteristic crystalline form. There is no appreciable change in weight. The substance, formerly sparingly soluble, now dissolves easily in water, but under no condition could it be obtained again in the same crystalline form from this solution. The oxidising action of the persulphate has disappeared. Whereas crystals of quinine persulphate are doubly refractive and anisotropic, those of the heated salt are only singly refractive and isotropic. The action of light on the persulphate slowly brings about a similar change.

During heating, the sulpho-group reacts to sulphonate the quinine molecule. Sulphur is eliminated, however, by heating the product in aqueous solution at 120° under pressure, and a compound, $C_{20}H_{24}O_3N_2$, m. p. 113—115°, is formed, which differs from quinine in being sparingly soluble in ether.

Acid cinchonine persulphate undergoes a similar pseudomorphism when heated for three to four days at 60—80°; the product is partly sulphonated, but contains also an oxidation product, forming a bright yellow, amorphous *picrate*, free from sulphur, m. p. 210°. Apparently, during heating, part of the alkaloid remains unchanged, part is more or less oxidised, another part sulphonated, whilst the peroxide oxygen disappears.

Sparingly soluble organic persulphates are best prepared by double decomposition of ammonium persulphate with an acid or neutral salt of the alkaloid. The following have been prepared: *acid quinine persulphate*, $C_{20}H_{24}O_2N_2 \cdot H_2S_2O_8$, forms yellowish-white, large, prismatic crystals; the *normal sulphate* gives a mass of small needles. *Acid cinchonine persulphate* crystallises in silky, glistening needles, and the *normal sulphate* in large, prismatic, almost colourless crystals.

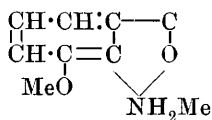
E. F. A.

Alkaloids of the Species of Nigella. OSCAR KELLER (*Arch. Pharm.*, 1908, 246, 1—50. Compare Abstr., 1904, i, 768).—An investigation of the constitution of damascenine and of a new alkaloid, methyl damascenine. The seeds of seven species of *Nigella* contain at most traces of alkaloids, but those of *N. damascena* contain 0.5—0.6%, and of *N. aristata*, 0.1%. In the former of these two species, damascenine only is present, but *N. aristata* contains about equal quantities of damascenine and of a new alkaloid, *methyl damascenine*, $C_{10}H_{13}O_3N$, which is the methyl ester of damasceninic acid. This alkaloid forms an oil, which solidifies at low temperatures; unlike damascenine, it does not fluoresce in ethereal solution. The *hydrochloride*, $C_{10}H_{13}O_3N \cdot HCl \cdot H_2O$, forms glistening plates and needles,

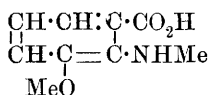
m. p. 121°, and is somewhat less soluble in water than damascenine hydrochloride, which remains in the mother liquor; the *platinichloride*, $(C_{10}H_{13}O_3N)_2 \cdot H_2PtCl_6$, needles, m. p. 190—191°, the *methiodide*, $C_{10}H_{13}O_3N \cdot MeI$, broad needles and plates, m. p. 140°, and the *nitroso*-compound, $C_{10}H_{12}O_3N \cdot NO$, m. p. indistinct (60—72°), have been analysed.

By the determination of the position of the carboxyl group in damasceninic acid (an isomeride of damascenine, formed from it by boiling with alkali), this substance is now proved to be *2-methylamino-3-methoxybenzoic acid*, $OMe \cdot C_6H_3(NHMe) \cdot CO_2H$. The proof of this constitution depends on the following substances, which have been obtained from it by the action of hydriodic acid (besides *o*-aminophenol, previously isolated). By the loss of one methyl group there results *2-methylamino-3-hydroxybenzoic acid*, $OH \cdot C_6H_3(NHMe) \cdot CO_2H$, m. p. about 260°. The *hydrochloride*, $C_8H_9O_3N \cdot HCl \cdot \frac{1}{2}H_2O$, melts at 214—215°, and yields, on reduction with sodium amalgam, methylamine and *m*-hydroxybenzoic acid. From the filtrate of the above acid, methyl-*o*-anisidine, $MeO \cdot C_6H_4 \cdot NHMe$, was obtained by steam distillation, and there remained in solution *2-amino-3-hydroxybenzoic acid*, $HO \cdot C_6H_3(NH_2) \cdot CO_2H$, glistening leaflets, m. p. 164°. The *hydrochloride*, $C_7H_7O_3N \cdot HCl$, forms granular crystals, m. p. 198—200°. This acid was only obtained in minute quantity, and differs from the three other possible isomerides containing the amino- and hydroxy-groups in the ortho-position to each other, all of which are known.

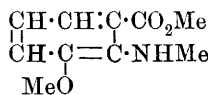
Since damascenine (I) is devoid of acid properties, but is readily converted into the isomeric damasceninic acid (II), a betaine-like constitution is suggested for it. Methyl damascenine has the formula III:



(I.)



(II.)

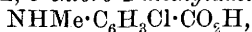


(III.)

Methyl damascenine is readily formed from the silver salt of damasceninic acid and methyl iodide, and yields, on heating with water or dilute alkali, both the original acid and damascenine.

The synthesis of both alkaloids depends therefore on that of damasceninic acid. With this end in view, the introduction of a methoxy-group into methylanthranilic acid was attempted. By nitration, 3-nitro-2-methylaminobenzoic acid, m. p. 146°, and 5-nitro-2-methylaminobenzoic acid are simultaneously formed. The *hydrochlorides*, $NHMe \cdot C_6H_3(CO_2H) \cdot NH_2 \cdot HCl$, of the corresponding aminomethylaminobenzoic acids melt at 205° and 214° respectively. After diazotisation, the direct introduction of a methoxy-group was found to be impossible; neither could a hydroxyl group be introduced, for both acids yielded very stable, red, crystalline substances with feeble acidic, and very feeble basic, properties, m. p. 266° and 268° respectively. These substances both have the composition of a *methylaziminobenzoic acid*, $C_8H_7O_2N_3$, and are presumably internal anhydrides of the

diazonium group with either the carboxyl or the methylamino-group. By Sandmeyer's reaction, 5-chloro-2-methylaminobenzoic acid,



needles, m. p. 173° , was obtained. Of the corresponding 3-chloro-acid, m. p. 143° , mere traces, insufficient for analysis, were obtained.

An attempt to synthesise an isomeride of damasceninic acid led to production (from 3-nitrosalicylic acid) of three substances having the composition $\text{C}_8\text{H}_7\text{O}_5\text{N}$, namely, methyl 3-nitrosalicylate, needles, m. p. 93° , obtained by esterification with hydrogen chloride, and two acids, both crystallising in needles and melting at 110° and 125° respectively. These acids were obtained from the dipotassium salt of 3-nitrosalicylic acid and methyl sulphate, and may hence be regarded as nitromethoxybenzoic acids; their isomerism remains unexplained.

G. B.

Preparation of Narcotine Derivatives. KNOLL & CO. (D.R.-P. 188054 and 188055. Compare Abstr., 1907, i, 235).—Although it was formerly supposed that narcotine was not affected by acetic anhydride, it has now been ascertained that a mixture of this substance and sulphuric acid, which has been heated until it no longer gives the reaction for sulphuric acid, will effect the acetylation of the alkaloid when the reagents are heated together at 80° .

Acetylnarcotine, $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N} \cdot \text{Ac}$, m. p. 159 – 161° , is soluble in alcohol or acids, but does not dissolve in aqueous alkalis. When narcotine is treated in the cold with a mixture of sulphuric acid and acetic anhydride which has not been heated above 30° , it undergoes sulphonation.

Narcotinesulphonic acid, $\text{C}_{22}\text{H}_{22}\text{O}_7\text{N} \cdot \text{SO}_3\text{H}$, is precipitated as a white powder from the sulphonation mixture by the addition of dry ether.

G. T. M.

1-*p*-Hydroxybenzylpiperidine. WILHELM KÖNIGS and KARL BERNHART (*Ber.*, 1908, 41, 499–500).—1-Anisylpiperidine, prepared by acting on piperidine with anisyl chloride, is a colourless oil, b. p. about $283^\circ/712$ mm.; the *picrate* has m. p. about 163° . Boiling concentrated hydrobromic acid converts 1-anisylpiperidine into 1-*p*-hydroxybenzylpiperidine hydrobromide, $\text{C}_{12}\text{H}_{17}\text{ON} \cdot \text{HBr}$, obtained as a colourless, crystalline powder, m. p. about 216° ; the free base crystallises in prisms, m. p. 140° . The hydrobromide is decomposed by bromine water with the formation of tribromophenol and piperidine in quantities represented by the equation: $\text{C}_{12}\text{H}_{17}\text{ON} + \text{H}_2\text{O} + 3\text{Br}_2 = \text{C}_6\text{H}_2\text{Br}_3 \cdot \text{OH} + \text{C}_5\text{H}_{11}\text{N} + \text{H} \cdot \text{CHO} + 3\text{HBr}$, whilst only traces of formaldehyde were detected. The base is not decomposed by dry bromine, but is converted into a *dibromo*-derivative, $\text{C}_{12}\text{H}_{15}\text{ONBr}_2$, crystallising in small, yellow prisms, m. p. about 182° (decomp.); the hydrobromide crystallises in colourless prisms, m. p. about 223° (decomp.).

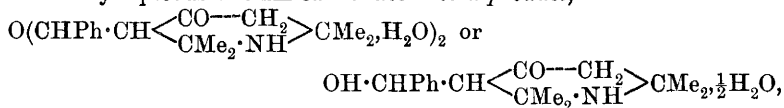
W. H. G.

Condensation of Benzaldehyde with Cyclic Acetone Bases. HERMANN PAULY and O. K. RICHTER (*Ber.*, 1908, 41, 464–469).—A study of the influence of methyl groups on condensation reactions.

Pauly (Abstr., 1899, i, 228) observed that, whilst vinylldiacetonamine reacts normally with mercaptans, forming dimercaptols, the accumulation of methyl groups in triacetonamine influences the course of the reaction in such a manner that the acetone base reacts with only 1 mol. of mercaptan. It is now found that in the condensation of acetone bases with benzaldehyde, the retarding influence of the methyl groups is apparent even in the case of vinylldiacetonamine. In presence of hydrogen chloride in glacial acetic acid solution at the ordinary temperature, vinylldiacetonamine and triacetonamine react with benzaldehyde only after some weeks, forming a monobenzylidene derivative and an aldol-like product respectively. In aqueous alcoholic sodium hydroxide or methoxide solution, vinylldiacetonamine undergoes only partial condensation with benzaldehyde, forming a product, $C_{25}H_{25}O_2N$ (?), crystallising in needles, m. p. 162° , whilst triacetonamine remains unchanged. Hence condensation with benzaldehyde is not an unfailing test for the presence of the group $\cdot CH_2 \cdot CO \cdot CH_2 \cdot$.

Benzylidenevinylldiacetonamine is isolated in the form of its *hydrochloride*, $CHPh \cdot C \begin{smallmatrix} \text{CO} \text{---} CH_2 \\ \text{CHMe} \cdot NH \end{smallmatrix} > CMe_2, HCl, H_2O$, which crystallises in yellowish-white needles, m. p. 204° , and gives a red coloration with sulphuric acid.

The condensation product of benzaldehyde and triacetonamine, $C_{16}H_{22}ONCl, HCl$, crystallises in white needles, m. p. 174° , is decomposed into its generators when gently heated with sodium hydroxide, and is converted by aqueous sodium carbonate into a product,



which crystallises in white needles, m. p. 175° , decomposes slowly at $105\text{--}125^\circ$, and yields benzaldehyde and triacetonamine when boiled with alcohol; the *hydrochloride*, m. p. about 150° . G. Y.

Condensation of Aminohydroxy-acids with Aromatic Aldehydes. I. ERNESTO PUXEDDU (*Gazzetta*, 1908, 38, i, 8—18).—After discussing previous work on this subject, the author describes his attempts to obtain condensation products of 5-aminosalicylic, 5-amino-*m*-cresotic, and 5-amino-*o*-cresotic acids with benzaldehyde, *m*-nitrobenzaldehyde, salicylaldehyde, cinnamaldehyde, and piperonaldehyde. The aldehyde was dissolved in a small quantity of cold alcohol, and was then well mixed for some hours or days with an equal weight of the powdered aminohydroxy-acid. The velocity with which the condensation proceeds varies widely with the nature of the reacting compounds. The condensation products are all of the same type, that formed between salicylaldehyde and 5-aminosalicylic acid having the constitution $OH \cdot C_6H_4 \cdot CH : N \begin{smallmatrix} CH \text{---} CH \\ CH : C(CO_2H) \end{smallmatrix} > C \cdot OH$.

5-Aminosalicylic acid and *m*-nitrobenzaldehyde yield the compound,

$C_{14}H_{10}O_5N_2$, crystallising from alcohol in yellow, prismatic needles, m. p. 245° (decomp.).

5-Aminosalicilylic acid and cinnamaldehyde give the *compound*, $C_{16}H_{13}O_4N$, which crystallises from alcohol in red, prismatic needles, m. p. 130° (decomp.).

5-Aminosalicilylic acid and piperonaldehyde yield the *compound*, $C_{15}H_{11}O_5N$, m. p. 250° (decomp.).

5-Amino-*o*-cresotic acid and *m*-nitrobenzaldehyde give the *compound*, $C_{15}H_{12}O_5N_2$, crystallising from alcohol in minute, faintly-yellow prisms, m. p. 250° (decomp.).

5-Amino-*o*-cresotic acid and salicylaldehyde yield the *compound*, $C_{15}H_{13}O_4N$, which crystallises from alcohol in small, mamillary masses, m. p. 230° (decomp.).

5-Amino-*o*-cresotic acid and cinnamaldehyde give the *compound*, $C_{17}H_{15}O_3N$, crystallising from alcohol in deep, wine-red, acicular prisms, m. p. 175° and onwards (decomp.).

5-Amino-*m*-cresotic acid and salicylaldehyde yield the *compound*, $C_{15}H_{13}O_4N$, which crystallises from alcohol in brownish-green, dichroic prisms, m. p. 223° (decomp.).

5-Amino-*m*-cresotic acid and cinnamaldehyde give the *compound*, $C_{17}H_{15}O_3N$, crystallising from alcohol in prismatic scales, m. p. 174° (decomp.).

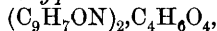
All these compounds are acid in character, dissolving in solutions of alkali hydroxide or carbonate; they give colorations with ferric chloride.

No condensation products were obtained with: 5-aminosalicylic acid and benzaldehyde; 5-amino-*o*-cresotic acid and benzaldehyde; 5-amino-*o*-cresotic acid and piperonaldehyde; 5-amino-*m*-cresotic acid and benzaldehyde; 5-amino-*m*-cresotic acid and *m*-nitrobenzaldehyde; 5-amino-*m*-cresotic acid and piperonaldehyde.

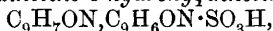
T. H. P.

Preparation of Normal Salts of *o*-Hydroxyquinoline with Polybasic Acids. FRANZ FRITZSCHE & Co. (D.R.-P. 187943).—The normal salts of *o*-hydroxyquinoline with the polybasic acids readily dissociate in solution into acid salts and free *o*-hydroxyquinoline, which is very volatile either alone or in the presence of solvents. On this account, these salts must be prepared directly by precipitation, and not by concentration of their solutions.

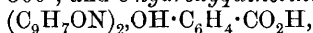
o-Hydroxyquinoline sulphate, $(C_9H_7ON)_2 \cdot H_2SO_4$, a yellow, crystalline powder, m. p. 177.5° , obtained by mixing its components in 96% alcohol, is readily soluble in water and quite insoluble in ether. *o*-Hydroxyquinoline phosphate, $(C_9H_7ON)_3 \cdot H_3PO_4$, yellow, crystalline powder, m. p. 184° , *o*-hydroxyquinoline succinate,



m. p. 138° , *o*-hydroxyquinoline *o*-hydroxyquinolinesulphonate,



satiny needles, m. p. 300° , and *o*-hydroxyquinoline salicylate,



yellow leaflets, m. p. 113° , are similarly prepared. These salts are all readily soluble in water, giving a neutral solution.

G. T. M.

Derivatives of 3-Phenylquinoline. H. HÜBNER (*Ber.*, 1908, 41, 482—487).—A continuation of the investigation on 3-phenylcinchonic acid (*Abstr.*, 1906, i, 383). The hydrazide of 3-phenylcinchonic acid (*loc. cit.*) condenses with benzaldehyde, yielding a *condensation product*, $C_{23}H_{17}ON_3$, m. p. 232° , and with acetone, yielding a *condensation product*, $C_{19}H_{17}ON_3$, m. p. 191° . 3-Phenylquinoline is formed on heating 3-phenylcinchonic acid about 15° above its melting point; it crystallises in large, transparent plates, m. p. 52° ; Friedländer and Gohring state that it is an oil (*Abstr.*, 1883, 1148). The *picrate*, $C_{15}H_{11}N_3C_6H_8O_7N_3$, forms yellow crystals, m. p. 205° ; the *ethiodide* has m. p. 228° ; the *methiodide*, $C_{16}H_{14}NI$, crystallises in small, yellow needles, m. p. 224° , and it is converted by the method of Königs and Meimberg (*Abstr.*, 1895, i, 430) into 3-phenyl-1-methyl-2-quinoline, $C_{16}H_{13}ON$, m. p. 138° .

2-Hydroxy-3-phenylcinchonic acid, $C_6H_4 \begin{smallmatrix} C(CO_2H):CPh \\ N \equiv C-OH \end{smallmatrix}$, prepared by heating isatin with phenylacetic anhydride at 180° , has m. p. 291° ; the *silver* salt, $C_{16}H_{10}O_3Na_2H_2O$, and crystalline *methyl* ester, $C_{17}H_{13}O_3N$, m. p. $258-259^\circ$, were prepared. 2-Hydroxy-3-phenylcinchonoyl chloride, $C_6H_4 \begin{smallmatrix} C(COCl):CPh \\ N \equiv C-OH \end{smallmatrix}$, m. p. 234° , obtained

by heating the acid with thionyl chloride in a sealed tube at 100° , is converted by ammonia into the *amide*, $C_{16}H_{12}O_2N_2$, m. p. $296-298^\circ$, by hydrazine into the *hydrazide*, $C_{16}H_{13}O_2N_3$, m. p. 298° , and by aniline into the *anilide*, $C_{22}H_{16}O_2N_2$, m. p. 313° . 2-Hydroxy-3-phenylcinchonic acid decomposes at $320-330^\circ$ into carbon dioxide and 3-phenylcarbostyryl, which, since it is almost insoluble in alkalis, probably has the formula $C_6H_4 \begin{smallmatrix} CH:CPh \\ NH:CO \end{smallmatrix}$ (compare Bischler and

Lang, *Abstr.*, 1895, i, 250). 2-Chloro-3-phenylcinchonoyl chloride, $C_{16}H_9ONCl_2$,

m. p. 163° , is formed on heating 2-hydroxy-3-phenylcinchonic acid with thionyl chloride under pressure at 180° ; it is converted by ammonia into the *amide*, $C_{16}H_{11}ON_2Cl$, m. p. 302° , and, when boiled with an aqueous solution of sodium hydrogen carbonate, yields 2-chloro-3-phenylcinchonic acid, $C_{16}H_{10}O_2NCl$, m. p. 226° ; the *silver* salt, $C_{16}H_9O_2Na_2G$, was prepared and analysed. W. H. G.

Preparation of Diphenylamine Derivatives. IRMA GOLDBERG (*D.R.-P.* 187870. Compare *Abstr.*, 1906, i, 953).—Diphenylamine derivatives are obtained in good yield when aromatic amines are heated with bromobenzene in the presence of cuprous iodide.

Diphenylamine itself is formed on boiling for fifteen hours a mixture of aniline, cuprous iodide, potassium carbonate, and excess of bromobenzene, and may also be produced from acetanilide, bromobenzene, cuprous iodide, and potassium carbonate when these are heated together in nitrobenzene. The replacement of acetanilide by *p*-nitroaniline in the foregoing condensation leads to the production of *p*-nitrodiphenylamine; the addition of a small amount of iodobenzene to the mixture facilitates the reaction.

o- and *m*-Nitrodiphenylamines can be produced in a similar manner from *o*- and *m*-nitroanilines. Phenylanthranilic acid is obtained by boiling in amyl-alcoholic solution a mixture of anthranilic acid, bromobenzene, potassium carbonate, and cuprous iodide.

It has been stated previously that aromatic amines and bromobenzene do not interact to furnish diphenylamine derivatives, but this want of success is due to the employment of copper powder or cupric chloride as catalyst. In the presence of cuprous iodide, the condensations are readily effected.

G. T. M.

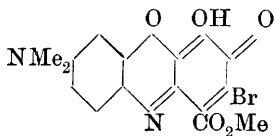
Formation of Dyes in Ultra-violet Light. CARL SCHALL (*J. pr. Chem.*, 1908, [ii], 77, 262—266. Compare Vignon, *Abstr.*, 1888, 1012; 1889, 1099; Gabutti, *Abstr.*, 1902, i, 312).—The behaviour of paper soaked in a molecular, aqueous solution of *p*-phenylenediamine and nitric acid (this vol., ii, 139) results from the formation of the *mononitrate*, $C_6H_4(NH_2)_2.HNO_3$, which crystallises in transparent needles, and becomes greyish-violet when dried or instantaneously green to greenish-blue on exposure to ultra-violet rays. Paper soaked in a solution of the salt and dried, becomes blue when exposed to ultra-violet light. The greenish-blue substance, when shaken with ether and very dilute sodium hydroxide, forms a brownish-red ethereal solution. The nature and mode of formation of the coloured product is discussed.

p-Phenylenediamine dinitrate, $C_6H_4(NH_2)_2.2HNO_3$, forms colourless crystals, and on exposure to ultra-violet light when anhydrous decomposes, becoming yellow and finally dark brown, but, if moist, gives a blue coloration in consequence of hydrolysis to the mononitrate.

G. Y.

Pruneanilide. EUGÈNE GRANDMOUGIN and ERNST BODMER (*Ber.*, 1908, 41, 604—611. Compare *Abstr.*, 1907, i, 355).—Pruneanilide was regarded by Nietzki and Bossi (*Abstr.*, 1893, i, 44) as an additive compound of prune (1 mol.) and aniline (1 mol.), because hydrogen was not evolved in the reaction. Hydrogen is produced, however, as in the equation $C_{16}H_{14}O_5N_2 + NH_2Ph = C_{16}H_{13}O_5N_2.NHPh + H_2$, but is not evolved, being utilised in reducing unchanged prune to the leuco-compound, which does not react with aniline. Only one-half of the prune can therefore be converted into the anilide, but the yield is doubled by passing air through the reacting mixture. Pruneanilide, $C_{22}H_{19}O_5N_3$, forms green prisms which are violet in transmitted light; the reddish-violet solution in concentrated sulphuric acid changes by dilution through blue to red. The constitution has been proved in the following way.

The action of nitroso-dimethylaniline hydrochloride on methyl dibromogallate in methyl-alcoholic solution leads to the formation of bromoprune, which has been obtained impure by Biérix (*Abstr.*, 1897, i, 289) and must, by its method of formation, have the annexed formula. When bromoprune, dissolved in alcohol containing a few drops of hydrochloric acid, is heated with



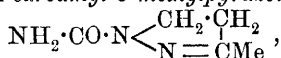
aniline, pruneanilide is obtained by the replacement of the halogen by the anilino-group.

Pruneanilide is hydrolysed by acids, aniline being eliminated and *hydroxyprune*, $C_{16}H_{14}O_6N_2$, formed, in which the presence of two hydroxyl groups is proved by the action of benzenesulphonyl chloride, whereby the *ester*, $C_{28}H_{22}O_{10}N_2S_2$, is obtained, which separates from ethyl acetate in green needles, is sparingly soluble in dilute acids, insoluble in alkalis, and forms solutions with a strong red fluorescence.

Coelestin blue B (Correin RR), the amide corresponding with prune, and aniline also form an *anilide*, $C_{23}H_{22}O_4N_4$, of analogous constitution, the yield of which is increased in a current of air. It separates from glacial acetic acid in green crystals, dissolves in concentrated sulphuric acid with a magenta-red colour, and very slightly in dilute alkalis with a violet-blue colour. C. S.

Action of Nitrogen-containing Reagents on the Carbonyl Group of β -Chloroethyl- and Alkyl Vinyl-ketones. M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 272—280).—When β -chloroethyl ketones are treated with the usual reagents for the detection of a carbonyl group, they condense in the normal manner, but the products are unstable and readily lose 1 mol. of hydrogen chloride to form heterocyclic substances. Similar products are formed by the interaction of these reagents with alkyl vinyl ketones.

The following substances were obtained by boiling aqueous solutions of sodium acetate, holding in suspension the appropriate β -chloroethyl alkyl ketone semicarbazone, the latter being in each case a colourless, unstable, sparingly soluble substance (compare Scholtz and Kipke, *Abstr.*, 1904, i, 508); 1-*carbamyl-3-methylpyrazoline*,



m. p. 167° ; the corresponding *ethyl* compound has m. p. 96° , and yields a *picrate*, m. p. 137° ; the *propyl* derivative, m. p. 108° , forms large crystals from ether.

The oximes of the β -chloroethyl alkyl ketones cannot be isolated, but, on warming the solutions in which they are formed and subsequently extracting with ether, the corresponding 3-alkylisooxazolines,

$N \begin{array}{l} \text{CR} \cdot \text{CH}_2 \\ \text{O} - \text{CH}_2 \end{array}$, are obtained. 3-*Methylisooxazoline*, b. p. $60^\circ/15$ mm.,

and the corresponding *ethyl* and *propyl* compounds, b. p. $69^\circ/11$ mm. and b. p. $77^\circ/8$ mm. respectively, are colourless liquids of unpleasant odour and feebly basic properties; ethyl isooxazoline yields a *platinum derivative*, $2C_5H_9ON, PtCl_4$, m. p. 170° .

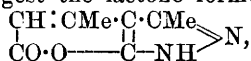
With hydrazine and phenylhydrazine, both the β -chloroethyl alkyl ketones and the corresponding alkyl vinyl ketones yield eventually the same 3-alkylpyrazolines and 1-phenyl-3-alkylpyrazolines respectively. 3-*Methylpyrazoline*, $HN \begin{array}{l} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N} = \text{CMe} \end{array}$, b. p. $56^\circ/15$ mm., gives a *picrate*, m. p. 153° , and a *phenylcarbamide*, m. p. 109° ; 3-*ethylpyrazoline*, b. p. $76^\circ/22$ mm., yields a *picrate*, m. p. 117° , and a *phenyl-*

carbamide, m. p. 76° ; the *propyl* derivative has b. p. $82^{\circ}/15$ mm., and yields a *picrate*, m. p. 150° (approx.), and a *phenylcarbamide*, m. p. 55° .

1-Phenyl-3-methylpyrazoline, $\text{NPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} = \text{CMe} \end{smallmatrix}$, m. p. $76-77^{\circ}$, crystallises from ether. The corresponding *ethyl* and *propyl* compounds are liquids, b. p. $155^{\circ}/9$ mm. and b. p. $162^{\circ}/10$ mm. respectively.

T. A. H.

Lactones of the Pyrazole Series. LUDWIG WOLFF and WILHELM SCHREINER (*Ber.*, 1908, 41, 550—558. Compare *Abstr.*, 1905, i, 839).—The azine of ethyl acetoacetate loses alcohol when heated, forming a compound, m. p. 246° , which is also obtained by melting the condensation product of 3-methylpyrazolone and ethyl acetoacetate. This method of preparation and the conversion by means of sodium hydroxide into an acid containing an additional molecule of water suggest the lactone formula



and further evidence is now adduced in favour of it.

The lactone forms an *acetyl* derivative crystallising in colourless needles, m. p. 184° , and reacts with bromine, forming yellow crystals of the *dibromide*, which are decomposed by moisture, forming the colourless *monobromo*-derivative, m. p. 218° (decomp.). When this is warmed with sodium hydroxide, the lactone ring is broken and the corresponding *brominated acid* formed, m. p. 145° (decomp.).

The *methylated lactone*, $\begin{array}{c} \text{CMe} \cdot \text{CMe} \cdot \text{C} \cdot \text{CMe} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{O} \text{---} \text{C} \text{---} \text{NH} \end{array} \text{N}$, prepared by the condensation of 3-methylpyrazolone with ethyl methylacetoacetate, forms long, colourless needles, m. p. 253° , and is converted by sodium hydroxide into 3-methylpyrazolone-4-isobutylencarboxylic acid, m. p. 162° (decomp.). This acid is converted into the lactone on warming with 5% hydrochloric acid or on boiling with water.

The *dimethylated lactone*, $\begin{array}{c} \text{CMe} \cdot \text{CMe} \cdot \text{C} \cdot \text{CMe} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{O} \text{---} \text{C} \text{---} \text{NMe} \end{array} \text{N}$, prepared by heating ethyl methylacetoacetate with 1 : 3-dimethylpyrazolone, crystallises in long needles, m. p. 181° ; it is sparingly soluble in cold sodium hydroxide, and is decomposed by this on heating. It is isomeric with the lactone of 5-hydroxy-3 : 4-dimethylpyrazole-4-isobutylencarboxylic acid, $\begin{array}{c} \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{O} \text{---} \text{C} \cdot \text{N} \text{---} \text{N} \end{array}$, prepared either by heating the azine of ethyl methylacetoacetate at 200° or by heating 3 : 4-dimethylpyrazolone with ethyl methylacetoacetate, or, finally, by heating dimethylpyrazolone with ethyl acetoacetate, whereby a rearrangement is effected. It crystallises in long, colourless needles, m. p. 181° , and dissolves in warm sodium hydroxide, forming the corresponding *acid*, isolated as *barium* salt, since the acid is very easily reconverted into lactone.

The lactone of 5-hydroxy-3 : 4-dimethylpyrazole-4-isoamylencarboxylic acid, $\begin{array}{c} \text{CEt} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{O} \text{---} \text{C} \cdot \text{N} \text{---} \text{N} \end{array}$, prepared from 3 : 4-dimethylpyrazolone

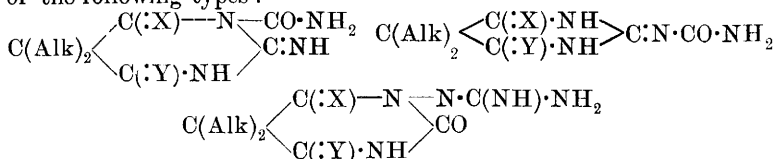
and ethyl ethylacetoacetate, crystallises in long, colourless needles, m. p. 132°. By the hydrolysis of ethyl 3-methylpyrazolone-4-*isopropyl*enecarboxylate with cold sodium hydroxide, a third 3-*methylpyrazoloneisopropyl*enecarboxylic acid is obtained, isomeric with the two previously described (Abstr., 1905, i, 839). The anhydrous acid melts about 90°, but when containing 2H₂O, it shows m. p. 135—140°, decomposing thereby to 3-methyl-4-*isopropyl*enepyrazolone and carbon dioxide.

E. F. A.

Traube's Pyrimidine Synthesis. FRITZ BAUM (*Ber.*, 1908, 41, 532—540. Compare Traube, Abstr., 1901, i, 54; 1904, i, 632; Conrad, 1905, i, 751).—The explanation, that the closing of the ring in the synthesis of a pyrimidine derivative from a cyanoacetic acid is due to the hydrolysis of the nitrile radicle to amide and subsequent withdrawal of the elements of water, is questioned. Cyanoacetyldimethylcarbamide (compare this vol., i, 253) undergoes this change, not only with extraordinary ease in the presence of sodium carbonate or sodium hydrogen carbonate, but also in the presence of disodium hydrogen phosphate, borax, sodium sulphite, or potassium acetate. Cyanoacetyl-methylcarbamide undergoes this change less readily, hydrolysis also occurring, and cyanoacetylcarbamide with these reagents does not yield pyrimidines. However, magnesium oxide converts these open-chain methyl carbamides in hot solution into the corresponding ring compounds, and even in the case of the carbamide compound the presence of the cyclic compound can be demonstrated by the nitroso-reaction. Sodium nitrite also has the property of converting the methylcarbamide. The experiments show that the hydrolysis and the closing of the ring are two independent reactions, and the conclusion is drawn that the unsaturated character of the nitrile group is the prime cause of the ring formation.

W. R.

Preparation of 5:5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 187990. Compare Abstr., 1906, i, 538).—Guanylcabamide reacts in one or other of the forms NH₂·CO·NH:C(NH)·NH₂ and NH₂·CO·N:C(NH)₂, and, when condensed with alkyl dialkylmalonates and alkyl dialkylcyanoacetates, dialkylmalonyl halides or dialkylmalononitriles furnish substances of the following types:

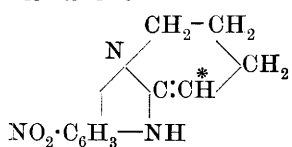


which are readily converted by hydrolytic agents into 5:5-dialkylbarbituric acids.

5:5-Diethylbarbituric acid is obtained by hydrolysing at 100° with 50% sulphuric acid the condensation product from guanylcabamide and ethyl diethylmalonate, ethyl cyanodiethylacetate, or diethylmalononitrile. Oxalic or nitric acid may be also used to effect the hydrolysis.

G. T. M.

Reduction of Dinitrophenylpiperidine. II. LEOPOLD SPIEGEL and H. KAUFFMANN (*Ber.*, 1908, 41, 679—685. Compare Spiegel and Utermann, *Abstr.*, 1906, i, 882).—In the reduction of *o*-*p*-dinitropiperidine by Lellmann and Geller's method (*Abstr.*, 1888, 1107), a base, $C_{11}H_{11}O_2N_3$, is obtained, insoluble in ether and sodium hydroxide, in addition to the *p*-nitro-*o*-aminopiperidine previously described. It forms almost colourless crystals from benzene, m. p. 219—220°; the *hydrochloride* forms large, stepped crystals. On benzylation, the base gives a monobenzoyl derivative, soluble in potassium hydroxide, $C_{18}H_{17}O_4N_3$, and crystallising from benzene in slender needles, m. p. 196°. The chief product is a dibenzoyl derivative, $C_{25}H_{19}O_4N_3$, which crystallises in thick, faintly yellowish-green crystals, m. p. 188°. This substance, when heated at 120—130° for eight hours in a sealed tube with hydrochloric acid (D 1.12), yields benzoic acid and a *ketone*, $C_{18}H_{15}O_3N_3$, which crystallises in slender needles, m. p. 178°; the *oxime*, $C_{18}H_{16}O_3N_4$, crystallises in yellow needles, m. p. 226°. The conclusion is arrived at that the base, *benziminooazopiperidine*, has the annexed constitution, the glyoxaline ring being opened during benzylation, forming 4-nitro-2-benzoylamino-*N*-phenylpiperidone (compare Bamberger, *Abstr.*, 1893, i, 437). The dibenzoyl compound is supposed to be *dibenzoylnitroiminoazopiperidine*, the hydrogen atom marked with the asterisk is, perhaps, active like the methyl in μ -methylbenziminoozoline (Bamberger, *Abstr.*, 1893, i, 433).



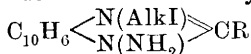
$NO_2 \cdot C_6H_5 - NH$

A better method of preparing dinitrophenylpiperidine from chlorodinitrobenzene, piperidine, and sodium ethoxide is described. The yield is 80%.

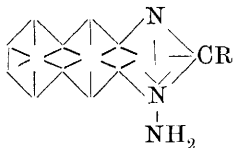
p-Nitro-*o*-aminophenylpiperidine, on oxidation with Caro's acid, leads to the formation of the base. W. R.

***N*-Aminoheterocyclic Compounds. II. 1-Amino-2-*p*-isopropylphenyl-2:3-naphthaglyoxaline.** HARTWIG FRANZEN and R. SCHEUERMANN (*J. pr. Chem.*, 1908, [ii], 77, 193—225. Compare *Abstr.*, 1906, i, 706).—1-Amino-2-*p*-isopropylphenyl-2:3-naphthaglyoxaline, which is prepared from 2:3-naphthylenedihydrazine and *p*-isopropylbenzaldehyde in the same manner as 1-amino-2-phenyl-2:3-naphthaglyoxaline from the dihydrazine and benzaldehyde (*loc. cit.*), is compared, on the one hand, with *as*-*sec*-hydrazines and *N*-aminoheterocyclic compounds, such as piperylhydrazine, which resembles *as*-*sec*-hydrazines, and, on the other, with α -acyl-*prim*-hydrazides. *as*-*sec*-Hydrazines undergo the following typical reactions: (1) oxidation to tetrazones by mercuric oxide; (2) ready conversion into secondary amines by the action of nitrous acid; (3) formation of quaternary azonium derivatives with alkyl iodides; (4) condensation with aromatic and (5) aliphatic aldehydes, and (6) with ketones; (7) condensation with pyruvic acid in cold acid solution; (8) reduction of Fehling's solution when heated; (9) formation of semicarbazides with cyanic acid, and (10) of phenylthiosemicarbazides with phenylthiocarbimide, and (11) formation of acyl

derivatives with acid anhydrides. Of these eleven reactions, α -acyl-*prim.*-hydrazides undergo all except (1), (3), (5), and (7), but the 1-amino-2:3-naphthaglyoxalines undergo only reactions (4), (10), and (11). The formation of derivatives of the type



by the action of alkyl iodides on the 1-amino-2:3-naphthaglyoxalines is explained by assuming a centric structure for the latter, in which the nitrogen atom in position 1 being already quinquevalent cannot form additive compounds.



A list is given of the *N*-aminoheterocyclic compounds which have been described in the literature.

1:3-Di-*p*-isopropylbenzylideneamino-2-*p*-isopropylphenyl-2:3-naphthaglyoxaline, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N(N:CH}\cdot\text{C}_6\text{H}_4\text{Pr}^\beta\text{)} \\ \text{N(N:CH}\cdot\text{C}_6\text{H}_4\text{Pr}^\beta\text{)} \end{array} \text{CH}\cdot\text{C}_6\text{H}_4\text{Pr}^\beta$, prepared by boiling 2:3-naphthylenedihydrazine with *p*-isopropylbenzaldehyde in alcoholic solution, crystallises from xylene in yellow needles, m. p. 220°, and gives a red coloration with concentrated sulphuric acid. When boiled with concentrated hydrochloric acid and glacial acetic acid, it yields benzaldehyde and the *hydrochloride* of 1-amino-2-*p*-isopropylphenyl-2:3-naphthaglyoxaline, $\text{C}_{20}\text{H}_{19}\text{N}_3\cdot\text{HCl}$, which crystallises in yellowish-white needles, m. p. 249° (decomp.). The free base,

$\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{N(NH}_2\text{)} \end{array} \text{C}\cdot\text{C}_6\text{H}_4\text{Pr}^\beta$, crystallises in dirty white leaflets, m. p. 265°. The *sulphate*, $(\text{C}_{20}\text{H}_{19}\text{N}_3)_2\cdot\text{H}_2\text{SO}_4$, yellow needles, sinter at 135°, *nitrate*, needles, m. p. 161° (decomp.), *picrate*,

$\text{C}_{20}\text{H}_{19}\text{N}_3\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, greenish-yellow needles, m. p. 223°, and *platinichloride*, $(\text{C}_{20}\text{H}_{19}\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6$,

decomp. 240°, are described. The *acetyl* derivative, $\text{C}_{20}\text{H}_{17}\text{N}_2\cdot\text{NHAc}$, prepared by boiling the base with acetic anhydride, crystallises in needles, m. p. 248°, and forms a *picrate*, $\text{C}_{28}\text{H}_{24}\text{O}_8\text{N}_6$, crystallising in yellow needles, m. p. 270°. The *phenylthiosemicarbazide*,

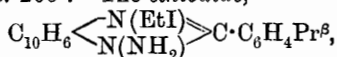


crystallises in prisms or quadratic plates, m. p. 70°. The *benzylidene* derivative, $\text{C}_{20}\text{H}_{17}\text{N}_2\cdot\text{N:CHPh}$, forms yellow prisms, m. p. 151°; the *hydrochloride*, $\text{C}_{20}\text{H}_{17}\text{N}_2\cdot\text{N:CHPh}\cdot\text{HCl}$, yellow needles, m. p. 244° (decomp.); the *sulphate*, $(\text{C}_{27}\text{H}_{23}\text{N}_3)_2\cdot\text{H}_2\text{SO}_4$, yellow needles, sintering at 150°; the *nitrate*, $\text{C}_{27}\text{H}_{23}\text{N}_3\cdot\text{HNO}_3$, yellow needles, m. p. 160° (decomp.); the *picrate*, $\text{C}_{33}\text{H}_{26}\text{O}_7\text{N}_6$, yellow needles, m. p. 228°; the *platinichloride*, $(\text{C}_{27}\text{H}_{23}\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6$, forms a yellowish-red precipitate, decomp. 243°.

The products obtained on treating phenylbenzylbenzylidenehydrazine with hydrochloric and picric acids in hot alcoholic solution yield the unchanged hydrazine on recrystallisation from alcohol.

The *ethiodide*, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N(EtI)} \\ \text{N(N:CHPh)} \end{array} \text{C}\cdot\text{C}_6\text{H}_4\text{Pr}^\beta$, prepared by heating the benzylidene base with ethyl iodide at 100°, forms reddish-yellow crystals, m. p. 179° (decomp.). The *o*-hydroxybenzylidene derivative, $\text{C}_{20}\text{H}_{17}\text{N}_2\cdot\text{N:CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, crystallises in yellow needles, m. p. 223°.

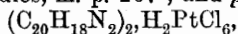
The *p*-isopropylbenzylidene derivative, $C_{20}H_{17}N_2 \cdot N : CH \cdot C_6H_4Pr^{\beta}$, yellow needles, m. p. 260° . The *ethiodide*,



from the amino-base and ethyl iodide at 100° , crystallises in yellow prisms, m. p. 199° .

1-Amino-2-*p*-isopropylphenyl-2:3-naphthaglyoxaline remains unchanged when boiled with acetone or with isovaleraldehyde, or mercuric oxide, or sodium nitrite and hydrochloric acid in alcoholic solution.

The *hydrochloride* of 2-*p*-isopropylphenyl-2:3-naphthaglyoxaline, $C_{20}H_{19}N_2Cl$, is obtained by boiling the 1-amino-compound with hydrochloric acid and amyl nitrite in alcoholic solution, or, together with dibenzylamine, by reduction of the 1-benzylideneamino-compound with zinc dust and glacial acetic acid and treatment of the reaction liquid with hydrochloric acid. It crystallises in yellowish-white needles, m. p. about 288° (decomp.). The free base, $C_{19}H_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} \cdot C_6H_4Pr^{\beta}$, forms white crystals, m. p. 247° . The *nitrate*, $C_{20}H_{18}N_2 \cdot HNO_3$, needles, m. p. 189° (decomp.), *sulphate*, white crystals, not melted at 295° , *picrate*, yellow needles, m. p. 267° , and *platinichloride*,



yellowish-red precipitate, not melted at 292° , are described. G. Y.

Colour Bases of Triphenylmethane Dyes. EMILIO NOELTING and K. PHILIPP (*Ber.*, 1908, 41, 579—585).—The existence of colourless carbinol and of coloured quinonoid forms of the colour bases of mono-, di-, and tri-aminotriphenylmethane dyes has been proved, mainly by Baeyer and Villiger (*Abstr.*, 1904, i, 786). Whilst the constitution of the carbinol bases is beyond doubt, that of the quinonoid forms is established less certainly. Bases which contain unsubstituted or monosubstituted amino-groups appear to lose a molecule of water, yielding imino-bases of the types $CPh_2 \cdot C_6H_4 : NH$, $CPh_2 \cdot C_6H_4 : NPh$, &c. Triphenylmethane bases containing only disubstituted amino-groups have hitherto been known only in the colourless carbinol forms, although Hantzsch and Osswald (*Abstr.*, 1900, i, 256) have shown the possibility of the existence of the coloured isomeric quinoneimonium bases without actually isolating them.

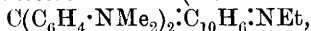
The authors have now succeeded in isolating hexamethyltriaminodiphenylnaphthylcarbinol (Naphtho-Blue), not only as the colourless carbinol, but also in the isomeric coloured quinonoid form; the question is not discussed whether the latter is an imonium or a carbonium hydroxide (compare Gomberg, *Abstr.*, 1907, i, 504), the imonium formula $:C \cdot C_6H_4 \cdot NMe_2 \cdot OH$ being used.

The authors have also isolated in the pure state the colourless and the coloured forms of tetramethylethyltriaminodiphenylnaphthylcarbinol (Victoria Blue R, New Victoria Blue), and have shown definitely that the latter is obtained from the former by the loss of a molecule of water.

Hexamethyltriaminodiphenylnaphthylcarbinol (Naphtho-Blue) is prepared by heating a mixture of Michler's ketone, α -naphthylidimethyl-

amine, and phosphoryl chloride, either alone or, more advantageously, in benzene solution, for ten hours on the water-bath; the base is obtained finally as a reddish-violet, amorphous powder. By repeated crystallisation from absolute ether, it is obtained in colourless crystals, m. p. 153° , whereas from boiling xylene it separates in dark green crystals, m. p. $260-261^{\circ}$; both forms have the composition $C_{29}H_{33}ON_3$. Cold dilute acids are instantly coloured blue in contact with an ethereal or benzene solution of the green crystals, but only after being warmed when a solution of the colourless crystals is used. Naphtho-Blue is reduced to a *leuco-base*, $C_{29}H_{33}N_3$, m. p. 172° , and forms salts which are extremely soluble in water. The dye has the constitutional formula $C(C_6H_4 \cdot NMe_2)_2 \cdot C_{10}H_6 \cdot NMe_2Cl$, since it decomposes smoothly into Michler's ketone and α -naphthyldimethylamine by three days' heating with dilute sulphuric acid.

The *imino-base* of Victoria Blue R (New Victoria Blue),



m. p. 192.5° , is obtained as a reddish-brown precipitate when a hot dilute acetic acid solution of the dye is added to an excess of potassium hydroxide, or by slowly decomposing a hot alcoholic solution with the same alkali; the ethereal solution of the imino-base is intensely orange-yellow. The *carbinol base*, $OH \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot C_{10}H_6 \cdot NH_2$, is obtained by adding a hot solution of the dye to excess of ammonium hydroxide and heating over a naked flame until the originally coloured precipitate becomes grey. It turns red at 150° and has m. p. $159-162^{\circ}$ or $167-170^{\circ}$, according to the rate of heating. The carbinol is converted into the imino-base when its solution in glycerol is heated to incipient ebullition. The *methyl ether*, m. p. 178° , crystallises in colourless needles; the *ethyl ether* has m. p. 153° .

C. S.

Action of Ethyl Oxalacetate on Benzylidene- β -naphthylamine. Syntheses in the Naphthaquinoline Group. LOUIS J. SIMON and CHARLES MAUGUIN (*Ann. Chim. Phys.*, 1908, [viii], 13, 361-395).—Mainly a résumé of work previously published (compare Abstr., 1904, i, 521, 812; Abstr., 1906, i, 887, 888; 1907, i, 725, 963).

In the condensation of ethyl oxalacetate with benzylidene- β -naphthylamine, besides the compound $C_{25}H_{25}O_5N$, there is produced a small quantity of a *substance*, $C_{43}H_{33}O_2N_3$, small needles, m. p. 94° (on Maquenne block), to which the authors assign the constitution

$$\begin{array}{c} CH(CO_2Et) \text{---} CHPh \\ | \\ C(N \cdot C_{10}H_7) \cdot C(N \cdot C_{10}H_7) > N \cdot C_{10}H_7. \end{array}$$

When 2-phenyl- β -naphthaquinoline-3:4-dicarboxylic anhydride in ethereal solution is treated with ammonia, the corresponding *imide*, $C_{19}H_{11}N < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > NH$, m. p. 282° , is formed.

By the action of oxalacetic acid on benzylidene- β -naphthylamine, Döbner's 2-phenylnaphthaquinoline-4-carboxylic acid (Abstr., 1889, 411, 412), but not the di-acid, is formed.

E. H.

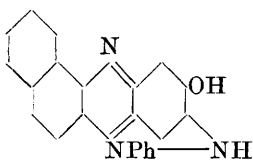
Prasindones. FRIEDRICH KEHRMANN and R. SCHWARZENBACH (*Ber.*, 1908, **41**, 472—481).—With the object of investigating prasindones of a simpler nature than those studied hitherto (Kehrmann and Aebi, *Abstr.*, 1899, **i**, 526), attempts have been made to prepare some simple prasindones by way of the condensation products of 4-amino-5-hydroxy-*o*-benzoquinone (Kehrmann and Prager, *Abstr.*, 1907, **i**, 447) with 2-aminodiphenylamine and 2-anilino-1-aminonaphthalene. The compounds obtained, however, were stable prasindone hydrates, the inner anhydrides of which, that is, the prasindones themselves, could not be prepared. It is therefore evident that the formation of the prasindone-like anhydride is intimately connected with some definite constitution.

4-Amino-5-hydroxy-*o*-benzoquinone condenses with 2-aminodiphenylamine in the presence of hydrochloric acid, yielding small quantities of 2-aminoaposafranone (Fischer and Hepp, *Abstr.*, 1905, **i**, 948), the principal product formed being 3-amino-2-hydroxyphenylphenazonium chloride, annexed formula, obtained as dark brownish-red crystals. The free base,

$C_{18}H_{13}ON_3$, obtained from the chloride on treatment with potassium hydrogen carbonate, crystallises in glistening, reddish-brown leaflets or needles, decomposing above 300° ; the diacetyl derivative, $C_{22}H_{17}O_3N_3$, crystallises in dark green needles with a violet reflex, decomposing at about 290° . The action of sodium nitrite on a solution of the base in sulphuric acid leads to the

elimination of the amino-group, and, on subsequent treatment with sodium nitrate, 2-hydroxyphenylphenazonium nitrate is obtained as a reddish-brown, crystalline powder; the corresponding platinichloride, $(C_{18}H_{13}ON_2)_2PtCl_6$, forms small, glistening, dark brownish-red crystals. The free base could not be isolated; the blue solution obtained by treating the nitrate with sodium carbonate undoubtedly contains the prasindone hydrate.

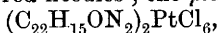
2-Anilino-1-aminonaphthalene condenses with 4-amino-5-hydroxy-*o*-benzoquinone in the presence of hydrochloric acid, yielding the hydrochloride of an aminonaphthaprasindone, $C_{22}H_{16}ON_3Cl$, isomeric with *s*-aminoisorosindone (Fischer and Arntz, *Abstr.*, 1907, **i**, 94); it crystallises in bronzy leaflets, sometimes in green leaflets with a metallic lustre, and dissolves in alcohol, forming a yellowish- to blood-red solution with a brick-red fluorescence. The free base, having the



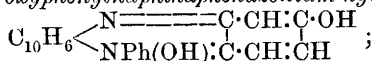
annexed formula, crystallises in dark brown needles with a metallic lustre, and decomposes above 320° . The violet solution of the base in strong sulphuric acid on dilution with ice becomes blue, and finally brownish-red, from which solution the sulphate separates as a reddish-brown, crystalline powder.

The acetyl derivative, $C_{24}H_{17}O_2N_3$, crystallises in bluish-black needles, m. p. 342° . The base, dissolved in sulphuric acid, is converted on treatment with sodium nitrite and sodium chloride into 2-hydroxyphenylnaphthaphenazonium chloride, obtained as a reddish-brown, crystalline powder; the corresponding nitrate, $C_{22}H_{15}O_4N_3$, crystal-

lises in small, yellowish-red needles; the *platinichloride*,

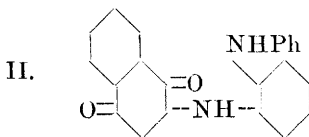
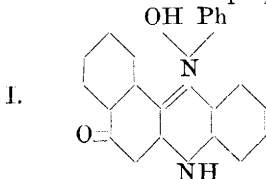


is obtained as a brick-red, crystalline powder. The chloride, on treatment with sodium carbonate, yields the *base*, which from analysis is probably 2-hydroxyphenylnaphthaphenazonium hydroxide,



it crystallises in long, glistening, almost black needles, does not lose water at 180–200°, decomposes above 300°, and forms orange-coloured *salts* with both strong and weak acids. The salts with strong acids are not hydrolysed in aqueous solution. The *platinichloride* of the *acetyl* derivative, $(\text{C}_{24}\text{H}_{17}\text{O}_2\text{N}_2)_2\text{PtCl}_6$, is obtained as a brick-red, crystalline powder.

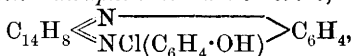
The reddish-brown isomeride derived from the bluish-green prasindone hydrate, to which the formula I was assigned previously (Kehrmann, *Abstr.*, 1896, i, 508), is better represented by formula II, since it shows no basic properties:



W. H. G.

***o*-Amino-*p*-hydroxydiphenylamine.** FRITZ ULLMANN and MATSUO FUKUI (*Ber.*, 1908, 41, 624–626).—A mixture of *o*-phenylenediamine and phenol behaves in much the same manner as a mixture of *p*-phenylenediamine and phenol (D.R.-P. 15915) when oxidised with manganese dioxide. A compound of an indophenol character is deposited in the form of crystals with a coppery lustre, and, when these are reduced with sodium sulphide, 2-amino-4'-hydroxydiphenylamine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is formed. It crystallises from dilute alcohol in large, colourless, flat needles, m. p. 149.5°. Its solution in hydrochloric acid is readily oxidised by ferric chloride, and its solution in sodium hydroxide by atmospheric oxygen.

Hydroxyphenylphenanthraquinone phenazonium chloride,



obtained by condensing acetic acid solutions of the aminohydroxydiphenylamine and phenanthraquinone with a little hydrochloric acid, crystallises from dilute acetic acid in dark brown, glistening needles. The *nitrate*, $\text{C}_{26}\text{H}_{17}\text{O}_4\text{N}_3$, is less soluble, and forms small, red crystals.

4'-Hydroxy-2-phenylaziminobenzene, $\text{C}_{12}\text{H}_9\text{ON}_3$, obtained by the action of nitrous acid on the aminohydroxydiphenylamine, forms colourless crystals, m. p. 170°.

J. J. S.

Formation of Indazole Derivatives from ortho-Methylated Anilines. PAUL JACOBSON and L. HUBER (*Ber.*, 1908, 41, 660–671).—When boiled in acid solution, diazotised *o*-toluidines, containing

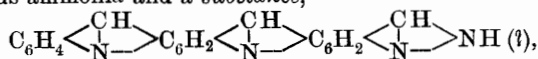
substituting nitro-groups or bromine atoms in the benzene nucleus, undergo ring condensation, forming indazoles (Noelting, Abstr., 1904, i, 690). In the absence of negative substituting groups, the indazole formation takes place to only a very small extent whether in acid, neutral (Noelting, *loc. cit.*), or alkaline (Bamberger, Abstr., 1899, i, 543) solution. The present authors have now found that indazoles are obtained from *o*-toluidines in good yields, which do not contain negative substituting groups, by converting the base into the *N*-nitroso-acyl-*o*-toluidine, $C_6H_4Me \cdot N(NO) \cdot COR$, and gently heating this in benzene, when the indazole, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ N \end{smallmatrix} N$ or $C_6H_4 \begin{smallmatrix} CH \\ | \\ N \end{smallmatrix} N$, and the acid, $R \cdot CO_2H$, are formed. The indazoles are obtained in yields equal to 20—25% of the acylnitrosoamines.

Benzoyl-o-tolylnitrosoamine, $C_6H_4Me \cdot NBz \cdot NO$, prepared by the action of nitrous acid on benzo-*o*-toluidide suspended in glacial acetic acid, forms a yellow, crystalline mass, m. p. 62—63° (decomp.), detonates when heated on platinum, decomposes gradually at the ordinary temperature, yields a sublimate of yellow needles, and couples with α -naphthol in alkaline, or with α -naphthylamine in acetic acid, solution. When heated with alcohol, or more slowly at the ordinary temperature, it yields benzo-*o*-toluidide, but in anhydrous chloroform or benzene solution it develops heat and forms benzoic acid and indazole. This forms a stable, white, amorphous *silver*, $C_7H_5N_2Ag$, and a crystalline *mercuric*, $(C_7H_5N_2)_2Hg$, derivative.

Acetyl-v-m-xylidylnitrosoamine, $C_6H_3Me_2 \cdot NAc \cdot NO$, crystallises in yellow plates, m. p. 62—63°, and couples slowly with alcoholic α -naphthol, forming a red *dye*, but not with α -naphthylamine. When boiled with benzene, it forms acetic acid and 7-methylindazole, $C_8H_8N_2$, which separates from light petroleum in crystals, m. p. 138°, or from water in long, colourless needles, yields a white sublimate, has an odour resembling iodoform, volatilises in a current of steam, and forms a yellow, crystalline *nitroso*-derivative.

5-Methylindazole was obtained in the same manner from *as-m*-xylidine.

Since phenylenediazosulphide, $C_6H_4 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ N \end{smallmatrix} N$, on prolonged heating yields diphenylene disulphide, $C_6H_4 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ S \end{smallmatrix} C_6H_4$, if indazole has the constitution $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ N \end{smallmatrix} N$, it might be expected when heated to yield nitrogen and 9:10-dihydroanthracene, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} C_6H_4$. It is found, however, that, when heated with copper powder at 270—290°, indazole yields ammonia and a *substance*,



which crystallises from aniline in yellow prisms, m. p. 318—319° (corr.), is soluble in concentrated hydrochloric or sulphuric acid, and is not attacked by acetic anhydride or methyl iodide or sulphate, but on

treatment with nitric acid, D 1.48, yields a *trinitro*-derivative,
 $C_{21}H_9N_4(NO_2)_3$,
 crystallising in scarlet prisms, commencing to sinter at 320°.

When heated with copper powder at 280°, 7-methylindazole yields a yellow condensation *product*, which could not be purified, whilst 5-methylindazole gave only resins.

Indazole remains unchanged when boiled, or heated under pressure at 200°, with glacial acetic acid and zinc oxide (compare Plancher, Abstr., 1902, i, 640; Plancher and Caravaggi, Abstr., 1905, i, 298; Plancher and Ciusa, Abstr., 1907, i, 80). G. Y.

Influence of Hydroxyl Ions on Azo-coupling. GUSTAV HELLER (*J. pr. Chem.*, 1908, [ii], 77, 189—192).—It was found previously (Abstr., 1907, i, 800) that the action of diazobenzene chloride on anthranil in sodium carbonate solution leads to the formation of trisbenzeneazophenol. The further investigation of the reaction has shown that in the absence of anthranil only bisbenzeneazophenol and small amounts of benzeneazophenol are formed, and that trisazo-compounds are not formed by the action of diazotised *p*- or *o*-toluidine on anthranil. On the other hand, trisbenzeneazophenol is formed by the action of diazobenzene chloride on phenol in presence of a free alkali, or by the action of diazobenzene chloride on methylanthroxan or other bases, such as quinoline, but not on pyridine or diethylamine. Hence it is concluded that the trisazo-compound is formed from diazobenzene chloride in consequence of the conversion of a part of this into phenol, and the coupling of the phenol with unchanged diazo-chloride under the influence of hydroxyl ions. The reaction is found, moreover, to depend on the concentration of the hydroxyl ions; when this increases above a certain limit, the formation of the trisazo-compound ceases and there ensues another reaction, which is still to be investigated. G. Y.

Replacement of the Sulphonic by the Cyano- and Carboxyl Groups in Azo-compounds. MARTIN LANGE (D.R.-P. 189935 and 191838).—The azo-derivatives of β -naphthol-3:6-disulphonic acid when heated with an aqueous solution of cyanide exchange the sulphonic group in position 3 for a cyano-group.

Sodium m-xylene-4'-azo-3-cyano- β -naphthol-6-sulphonate,
 $C_6H_3Me_2 \cdot N_2 \cdot C_{10}H_5(OH)(CN) \cdot SO_3Na$ or

$C_6H_3Me_2 \cdot N_2H : C_{10}H_5O(CN) \cdot SO_3Na$,
 separates in sparingly soluble, glistening crystals on heating sodium *m*-xylene-4'-azo- β -naphthol-3:6-disulphonate with aqueous sodium cyanide at 60—90°.

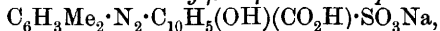
Sodium p-nitrobenzeneazo-3-cyano- β -naphthol-6-sulphonate,
 $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(OH)(CN) \cdot SO_3Na$ or

$NO_2 \cdot C_6H_4 \cdot N_2H : C_{10}H_5O(CN) \cdot SO_3Na$,
 prepared in a similar manner from sodium *p*-nitrobenzeneazo- β -naphthol-3:6-disulphonate, separates in well-defined needles with a metallic lustre. These new azo-derivatives dye wool in darker shades than the original azo-disulphonates.

The foregoing cyanoazo-derivatives when boiled with aqueous

sodium hydroxide undergo hydrolysis and become converted into the corresponding carboxyl compounds. The production of the carboxyl derivatives can be effected in one operation by boiling the azo-derivatives of β -naphthol-3:6-disulphonic acid with aqueous sodium cyanide and hydroxide.

Sodium m-xylene-4'-azo-3-carboxy- β -naphthol-6-sulphonate,



and six other azo-derivatives of sodium 3-carboxy- β -naphthol-6-sulphonate are described in the patent.

G. T. M.

Electrolytic Preparation of Hydrazo-compounds. FRIEDRICH DARMSTÄDTER (D.R.-P. 189312).—The conditions necessary for the electrolytic reduction of nitrobenzene to hydrazobenzene are efficient agitation, considerable excess of current, and suitable concentration of alkali hydroxide or salt. Nitrobenzene (100 grams) is suspended in 1 litre of 3% sodium hydroxide contained in the cathode cell; the anode liquid is 5% to 10% aqueous sodium hydroxide. The electrodes are preferably of iron or nickel, and 150% to 200% of the calculated current is sent through the cell with a current density of two to three amperes per square dm. of cathode. The cathode solution is thoroughly agitated. In this way, the nitrobenzene is almost entirely reduced to hydrazobenzene, and the latter is separated from a small proportion of azoxybenzene by the action of hydrochloric acid, which transforms the hydrazo-derivative into soluble benzidine hydrochloride.

The reduction of *o*-nitrotoluene or *o*-nitroanisole when effected in the foregoing manner leads to the production of tolidine or dianisidine.

G. T. M.

Protein Nomenclature. (Report of a Joint Committee of the Amer. Physiol. Soc. and the Amer. Soc. of Biol. Chemists. Signed by R. H. CHITTENDEN, O. FOLIN, W. J. GIES, W. KOCH, T. B. OSBORNE, P. A. LEVENE, J. A. MANDEL, A. P. MATHEWS, and L. B. MENDEL. *Proc. Amer. physiol. Soc.*, 1907—8, xxvii.—xxx.; *Amer. J. Physiol.*, 21).—The term Protein as a class name is accepted. The following are the main points of difference between this report and that of the English Committee which considered the subject (see *Proc.*, 1907, 23, 55).

The term albuminoid is retained for the collagen keratin group. The class of phospho-proteins (caseinogen, vitellin) is transferred to the subdivision of conjugated proteins. The following five additional groups are inserted at various places: (1) Glutelins, vegetable proteins soluble in dilute alkali. (2) The alcohol-soluble proteins of vegetable origin. (3) Coagulated proteins, the result of the action of heat or alcohol. (4) Lecitho-proteins. (5) Proteans, insoluble products which result from the incipient action of water, very dilute acids, or enzymes.

W. D. H

Union of the Serum Proteins with Alkali. LAWRENCE J. HENDERSON (*Amer. J. Physiol.*, 1908, 21, 169—172).—Some experiments are recorded on the assumption that the serum proteins behave

with alkalis like simple substances. They indicate the magnitude of the union in very faintly alkaline solutions. The matter is treated in a preliminary manner, the object of the work being to elucidate carbon dioxide transport in the blood; Zuntz believes that the passing off of this gas involves a transfer of sodium from carbon dioxide to protein.

W. D. H.

Leucine Fraction from Protein Hydrolysis. FELIX EHRLICH and ADOLF WENDEL (*Biochem. Zeitsch.*, 1908, 8, 399—437).—Determinations of the optical rotation in hydrochloric acid of leucine, obtained by the hydrolysis of proteins, have yielded numbers varying between $[\alpha]_D + 16.9^\circ$ and $[\alpha]_D + 18.9^\circ$, whereas Fischer's synthetic active leucine has $[\alpha]_D + 15.6^\circ$. This is due to the fact that the leucine from protein hydrolysis has not yet been obtained pure. It has been shown already that the leucine fraction contains an *isoleucine*, from which it can be separated by taking advantage of the fact that the copper salt of *isoleucine* is soluble in methyl alcohol, whereas that of leucine is insoluble. By the simple extraction with methyl alcohol, the separation is not, however, complete, an insoluble residue is left containing large quantities of leucine and small quantities of *isoleucine*. On decomposing this residue with hydrogen sulphide, re-converting into the copper salts, and re-extracting with methyl alcohol, a further separation is effected, and by repetition of this process a pure leucine can be obtained finally from several proteins with a rotatory power agreeing with that of the synthetic substance.

In all cases of protein hydrolysis, the methyl-alcoholic extract contained, besides *isoleucine*, valine. The separation of these two substances presents very great difficulties, owing to the similar solubilities both of the free acids and their copper salts. By treating the acids with baryta water under pressure, the valine was completely racemised, whereas the *d-isoleucine* was about half converted into *d-allo-isoleucine*, that is, a stereoisomeric substance which is not the optical antipode of the original body. The *d-l-valine* yielded a copper salt which was much less soluble than that of the optically active substance both in methyl and ethyl alcohols. By extracting the copper salts of the racemised acids with alcohols, the valine can be nearly completely separated from the leucines. On subjecting to yeast fermentation, the free acids, obtained by the employment of this method of separation, nearly pure *l-valine*, and *d-allo-leucine* can be obtained both from casein and yeast. The *l-valine* obtained from yeast gave $[\alpha]_D^{20} - 27.62^\circ$ (in hydrochloric acid); *l-valine* prepared by E. Fischer gave $[\alpha]_D^{20} - 28.40^\circ$. The *d-allo-isoleucine* from the same source gave $[\alpha]_D^{20} - 35.7^\circ$, also in 20% hydrochloric acid.

S. B. S.

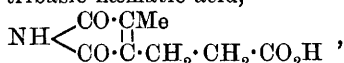
Elementary Composition of Different Caseinogens. FRANZ TANGL and J. CSÓKÁS (*Pflüger's Archiv*, 1908, 121, 534—549).—Analyses of the caseinogen prepared by Hammarsten's method from the milk of the cow, buffalo, sheep, goat, horse, and ass are given; they show slight differences, which are considered to prove that

caseinogen is a different substance in different milks, and to confirm what has been found by the precipitin reaction. The closer the biological relationships between the different animals on the list the closer is the correspondence in ultimate analysis of the caseinogens.

W. D. H.

Hæmatin; Salts, Esters, and Aniline Derivatives of the Hæmatic Acids, and Condensation Products of the Esters. WILLIAM KÜSTER (with F. LACOUR and A. NICOLE) (*Zeitsch. physiol. Chem.*, 1908, 54, 501—547. Compare Abstr., 1905, i, 622; 1906, i, 337).—The main object of the investigation was to obtain condensation products of the esters of hæmatic acid which might show a certain resemblance to hæmatin itself.

From the imide of tribasic hæmatic acid,



a *potassium* salt, $\text{C}_8\text{H}_8\text{O}_4\text{NK}$, needles, decomposing at 212° , a basic *lead* salt, and a *silver* salt, $\text{C}_8\text{H}_7\text{O}_4\text{NAg}_2$, have been prepared.

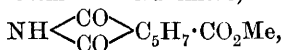
The esterification of the monobasic hæmatic acid, $\text{C}_8\text{H}_8\text{O}_5$, with dilute alcoholic hydrochloric acid produces a mixture of esters; the chief constituent (70%) of this mixture, soluble in sodium carbonate, is *methyl dihydrogen hæmatate*, $\text{CO}_2\text{H} \cdot \text{CMe} : \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, b. p. $173\text{—}176^\circ/11$ mm., from which a crystalline *calcium* salt, $\text{C}_9\text{H}_{10}\text{O}_6\text{Ca}$, an amorphous *silver* salt, $\text{C}_9\text{H}_{10}\text{O}_6\text{Ag}_2$, and an amorphous *ammonium* salt, $\text{C}_9\text{H}_{18}\text{O}_6\text{N}_2$, were obtained. Besides the acid methyl ester, there are formed simultaneously smaller quantities of *methyl anhydrohæmatate*, $\text{O} \begin{array}{c} \diagup \text{CO} \\ \text{C} \\ \diagdown \text{CO} \end{array} \text{C}_5\text{H}_7 \cdot \text{CO}_2\text{Me}$, and normal trimethyl

hæmatate. The last two substances are separated by passing dry ammonia gas into the ethereal solution, when the anhydride ester combines with two molecules of ammonia, and is precipitated as the amorphous substance, $\text{C}_9\text{H}_{16}\text{O}_5\text{N}_2$, which is regarded as the *ammonium* salt of *monomethylhæmatate amide*, and which is converted by acidification of its aqueous solution into the acid methyl ester already described. *Trimethyl hæmatate*, $\text{C}_{11}\text{H}_{16}\text{O}_6$, b. p. $300\text{—}301^\circ/760$ mm. and $165\text{—}167^\circ/10$ mm., is formed in small quantity (12%) by the esterification with alcohol and hydrochloric acid, and is not precipitated by ammonia from its ethereal solution; it is formed quantitatively from silver hæmatate and methyl iodide.

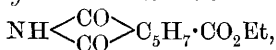
The corresponding ethyl esters were prepared in a similar manner, although not so readily. *Ethyl dihydrogen hæmatate*, $\text{C}_{10}\text{H}_{14}\text{O}_6$, b. p. $165^\circ/10$ mm., was freed from unchanged acid by fractional distillation; its composition corresponded with that of an anhydride, $\text{C}_{20}\text{H}_{28}\text{O}_{11}$, but molecular weight determinations indicate that it is an equimolecular mixture (of constant boiling point) of the ester $\text{C}_{10}\text{H}_{14}\text{O}_6$ and the anhydride ester, $\text{C}_{10}\text{H}_{12}\text{O}_5$. The *salts*, $\text{C}_{10}\text{H}_{12}\text{O}_6\text{Ca}$, $\text{C}_{10}\text{H}_{12}\text{O}_6\text{Pb}$, and $\text{C}_{10}\text{H}_{12}\text{O}_6\text{Ag}_2$, were analysed. By combination with ammonia, a substance, $\text{C}_{20}\text{H}_{38}\text{O}_{11}\text{N}_4$, is formed. As in the case of the corresponding methyl derivative, the *ethyl* ester of anhydrohæmatic acid, $\text{C}_{10}\text{H}_{12}\text{O}_5$, could only be isolated as the ammonia additive product,

$C_{10}H_{18}O_5N_2$, which passes by the evaporation of its aqueous solution into *diammonium ethyl hæmatate*, $CO_2Et \cdot C_5H_7 \cdot (CO_2NH_4)_2$. The triethyl ester of hæmatic acid (unlike the trimethyl ester) cannot be prepared by hydrochloric acid; there is formed instead *hydrogen diethyl hæmatate*, $CO_2H \cdot C_5H_7 \cdot (CO_2Et)_2$, b. p. 179—180°/15 mm. *Triethyl hæmatate*, $C_{14}H_{22}O_6$, b. p. 191°/19 mm., is, however, obtainable from the silver salt and ethyl bromide.

The *methyl* ester of hæmatic acid imide,

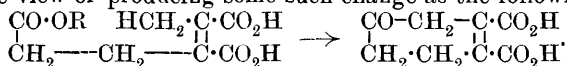


b. p. 170—172°/10 mm., separates from water in needles, m. p. 64°, and is prepared by treating the silver salt, $C_5H_7O_4NaAg_2$, with methyl iodide and distilling the product under diminished pressure, or, more conveniently, by heating the ammonia additive product of methyl dihydrogen hæmatate, $C_5H_{12}O_6$, or of the anhydride ester, $C_9H_{10}O_5$; one molecule of ammonia is then eliminated (the corresponding additive product of the free acids loses both molecules of ammonia when heated). The *ethyl* ester of hæmatic acid imide,



b. p. 195°/10 mm., is a viscid oil, and can be prepared according to both the methods employed for the methyl ester.

The intramolecular condensation of the esters was next attempted with the view of producing some such change as the following :



By heating the ester $C_{20}H_{26}O_{11}$ (or $C_{10}H_{14}O_6$) with sodium ethoxide, a small quantity of a *substance*, $C_{18}H_{20}O_{10}$, m. p. 146—147°, was obtained, which yielded with dry ammonia a *substance*, $C_{18}H_{26}O_{10}N_2$. No further elimination of alcohol could be achieved. By using a larger proportion of sodium ethoxide, a *substance*, b. p. 175—178°/14 mm., was obtained, to which the formula $C_{48}H_{40}O_{26}$ is assigned; this is regarded as being formed by the elimination of three molecules of alcohol and one of water from three molecules of the ester $C_{20}H_{26}O_{11}$; no molecular weight determination is given. By the action of sodium methoxide on the methyl ester, $C_9H_{12}O_6$, a minute quantity of a *substance*, m. p. 189°, was obtained, which probably represents the desired cyclic condensation product, $C_8H_8O_5$, represented above.

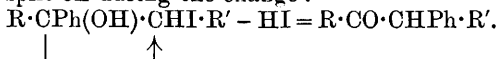
By addition of aniline to the ethereal solution of the acid, $C_8H_8O_5$, the *aniline* salt of *hæmatic anilide*, $C_{20}H_{22}O_5N_2$, m. p. 86—87°, is obtained, which, on boiling with water, is transformed into a *substance*, $C_{14}H_{15}O_5N$, m. p. 110°, probably *hæmatic anilide*, and more readily to *anilhaematic acid*, $C_{14}H_{13}O_4N$, m. p. 120°.

The *ammonium* salt of *monomethylhæmatic anilide*, $C_{15}H_{20}O_5N_2$, m. p. 132—133°, and *methyl anilhaematate*, $C_{15}H_{15}O_4N$, m. p. 47—48°, were prepared in a similar manner from monomethylhæmatate.

G. B.

Organic Chemistry.

Structural Changes in Organic Chemistry. MARC TIFFENEAU (*Chem. Zentr.*, 1908, i, 112—113; from *Rev. gén. Sci. pur. appl.*, 1907, 18, 583—594).—A theoretical paper dealing with the changes in the "carbon skeleton" through the wandering of a carbon radicle. Such structural transformations are divided into two groups, as taking place in a stable or in an unstable molecule. In the first group are placed those changes which involve the formation of a more stable molecule; for instance, the change of a carbylamine into a primary amine. The second group is considered to be due to the setting free of valencies caused by the interaction of one or more elements in the molecule; the freed valencies only being satisfied through a molecular rearrangement. This last group is subdivided into two classes: (a) carbon wandering, owing to the setting free of two valencies on the same element; an example being the change of diphenylchloroethylene into tolane and the Beckmann intramolecular change. (b) Carbon wandering, due to the setting free of two valencies on two neighbouring or distant elements; for instance, the pinacolin transformation and the Auwers transformation. The author points out that the wandering of an aryl radicle only takes place when the compound contains an OH group attached to the same carbon atom as the wandering group, which is not split off during the change:



J. V. E.

Applications of Grignard's Reaction. ALEXANDER MCKENZIE (*Brit. Assoc. Report*, 1907, 77, 273—298).—A detailed account of the reactions to which Grignard's reagent is applicable, and of the theoretical considerations underlying these reactions. T. H. P.

Boiling Point of *iso*Butane. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1908, 30, 142—143).—*iso*Butane, prepared by the reduction of *isobutyl* iodide with zinc and dilute alcohol, has b. p. $-11.5^{\circ}/760$ mm. The hydrocarbon (b. p. 0°) obtained by Mabery from American petroleum (*Abstr.*, 1897, i, 389) and regarded by him as *isobutane* was not this substance, but probably *n*-butane. E. G.

Relative Volatility of Certain Groups of Mixed Carbon Compounds. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 842—855. Compare *Abstr.*, 1907, i, 1102).—The boiling points of series of disubstituted ethane compounds represented by the general formulæ $\text{CH}_2\text{R} \cdot \text{CH}_2\text{R}$, $\text{CH}_2\text{R} \cdot \text{CH}_2\text{R}'$ and $\text{CH}_2\text{R}' \cdot \text{CH}_2\text{R}'$ are compared.

In certain cases the boiling point of the mixed compound is the arithmetic mean of the boiling points of the corresponding simple compounds. This is the case when R and R' represent chlorine and

bromine, fatty acid radicles of similar structure, isomeric fatty acid radicles, methoxy- and ethoxy-groups, or bromine and the ethoxy-group.

The boiling point of the mixed compound is higher than the mean of the boiling points of the simple compounds when R and R' represent the hydroxyl and amino-group, or chlorine and the acetyl group.

Finally, the boiling point of the mixed compound is lower than the mean of the boiling points of the simple compounds when R and R' represent bromine and hydroxyl, hydroxyl and ethoxyl, or ethoxyl and the amino-group.

The differences between the three groups of comparable compounds are attributed to the circumstance that certain substituting groups do not appreciably alter the degree of association in the liquid state, whilst other groups exert a marked effect, the extent of the influence varying considerably from one substituting group to another.

H. M. D.

Chloroform and Acetone. DAVID B. DOTT (*J. Soc. Chem. Ind.*, 1908, 27, 6, 271).—The formation of chloroform from ethyl alcohol is shown to be best indicated by $3C_2H_5O + 8Ca(OCl)_2 = 2CHCl_3 + 3CaCO_3 + CO_2 + 8H_2O + 5CaCl_2$, and the equation generally given for the formation of chloroform from acetone, $2CO(CH_3)_2 + 3CaOCl_2 = 2CHCl_3 + (CH_3 \cdot CO)_2Ca + 2Ca(OH)_2$, agrees well with results found. The observation of Finnemore and Wade (*Trans.*, 1904, 85, 938), that a small proportion of ethyl chloride is formed in preparing chloroform from ethyl alcohol, is confirmed. When purifying acetone, it is advisable to avoid treatment with mineral acids or other methods likely to cause formation of condensation products, such as mesityl oxide, phorone, or mesitylene, which, although shown by about 7% distilling above 58°, do not affect the iodoform or other methods of estimation. A rise of temperature, 11.7°, is observed when two molecular proportions of chloroform are mixed with one molecular proportion of acetone, and the resulting mixture distils for the most part above the b. p. of either constituent.

J. V. E.

Oxidation of Ethyl, Propyl, *iso*Butyl, and Amyl Alcohol by a Contact Process. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 203—215. Compare this vol., i, 77).—A stream of dry air is saturated with the vapour of the given alcohol, and then passed through a heated tube containing freshly-reduced copper gauze. As in the case of methyl alcohol, $c^2 \cdot c_1/v^2$ is a constant, and for ethyl alcohol = 0.0003—0.00024; for *isobutyl* alcohol = 0.0004—0.00045; for amyl alcohol = 0.0005—0.00048; for propyl alcohol = 0.00107. The products of oxidation are carbon mon- and di-oxides, both saturated and unsaturated hydrocarbons, aldehydes (chiefly), and very small quantities of acids and ketones. In the case of propyl alcohol, when the conditions are such that the copper is heated without the application of external energy, an almost exactly theoretical quantity of air is needed for the oxidation, but with ethyl, *isobutyl*, and amyl alcohols an excess of air must be employed. When, however, in all these cases the concentration of the alcohol is near the theoretical, there is no spontaneous rise in the temperature of the copper; this

being due to the fact that side by side with the exothermic reaction of oxidation there is also an endothermic reaction of decomposition (very slight in the case of propyl alcohol) of the alcohol into water and unsaturated hydrocarbons, and, in order to maintain the exothermic character of the reaction, it is necessary to have an excess of air, which oxidises the carbon monoxide with development of heat. Detailed tables of the products obtained for each of the alcohols are given.

Z. K.

Action of Organo-magnesium Haloids on Ethylideneacetone. A. GRY (*Bull. Soc. chim.*, 1908, [iv], 3, 377—381).—This work was undertaken with the view of synthesising and investigating tertiary alcohols containing an ethylenic linking. The results have been in part anticipated by those of Kohler (*Abstr.*, 1907, i, 1050), but the latter author by using excess of the Grignard reagent obtained as the principal products the corresponding saturated ketones, whereas when the quantities of ethylideneacetone and organo-magnesium haloid used are equimolecular the principal product is the corresponding tertiary olefinic alcohol. These alcohols undergo dehydration when treated with the ordinary acetylating reagents, and the hydrocarbons described below were obtained in this way. These are colourless, resemble light petroleum in odour, and give precipitates with aqueous solutions of mercuric chloride.

Dimethylisobutylcarbinol, $\text{CHMe}:\text{CH}:\text{CMe}_2\cdot\text{OH}$, b. p. 79—80°/145 mm., D_0^{20} 0.8154, D_4^{20} 0.8347, n_D^{20} 1.4302, obtained by the action of magnesium methyl iodide on ethylideneacetone, is a colourless, mobile liquid (compare Pawlowsky, *Abstr.*, 1872, 1093), and on dehydration yields a hydrocarbon which may be identical with Ipatieff's trimethylallene, $\text{CHMe}:\text{C}:\text{CMe}_2$. δ -Methyl- Δ^{β} -hexene- δ -ol (methylisobutylcarbinol), $\text{CHMe}:\text{CH}:\text{CMeEt}\cdot\text{OH}$, b. p. 72—73°/60 mm., D_0^{20} 0.8471, D_4^{20} 0.8360, n_D^{20} 1.4268, is a colourless liquid with a pleasant, fruity odour. On dehydration, it yields a diethylenic hydrocarbon, b. p. 107—109°, which may have the formula $\text{CHMe}:\text{C}:\text{CMe}\cdot\text{C}_2\text{H}_5$. $\delta\zeta$ -Dimethyl- Δ^{β} -heptene- δ -ol (methylisobutylisobutylcarbinol), $\text{CHMe}:\text{CH}:\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CHMe}_2$, b. p. 68—69°/17 mm., D_0^{20} 0.8105, D_4^{20} 0.8281, n_D^{20} 1.4285, similarly obtained, is a pleasant-smelling liquid. $\delta\eta$ -Dimethyl- Δ^{β} -octene- δ -ol (methylisobutylisobutylcarbinol), $\text{CHMe}:\text{CH}:\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$, b. p. 87—88°/18 mm. (decomp.), D_0^{20} 0.8442, D_4^{20} 0.8330, n_D^{20} 1.4368, is a liquid of insipidly sweet odour.

T. A. H.

Action of Alkalis on Alkylene Glycol-chlorohydrin Ethers. JOSEF HOUBEN (*Ber.*, 1908, 41, 1027—1029. Compare Houben and Führer, this vol., i, 73).—Polemical. A reply to the criticisms of Hoering (this vol., i, 119).

W. H. G.

Density, Refractive Index, Surface Tension, and Viscosity of Various Mixtures of Glycerol and Water at 18°. PABLO MARTÍNEZ-STRONG (*Anal. Fis. Quim.*, 1908, 6, 75—77).—The following table shows the results of the measurements:

Composition.	Relative density.	Refractive index.	Surface tension, number of drops.	Viscosity.	
				No. of seconds.	μ .
Water	1·0000	1·3277	102	105	1·0000
10 per cent. glycerol	1·0295	1·3390	106	134	1·3137
20 " "	1·0681	1·3528	110	170	1·7197
30 " "	1·0860	1·3650	114	245	2·534
40 " "	1·1094	1·3787	119	345	3·6451
50 " "	1·1340	1·3891	124	476	5·4108
60 " "	1·1602	1·4020	130	640	7·0716
70 " "	1·1860	1·4129	136	1258	14·2094
80 " "	1·2142	1·4386	147	4165	48·1632
90 " "	1·2330	1·4529	158	6900	81·0256
Glycerol	1·2599	1·4650	172	64800	777·5382

The surface tension was determined by means of a Duclaux pipette, which, when filled with water at 15°, delivered 100 drops. The viscosity was measured by an Ostwald viscosimeter. μ is the coefficient of viscosity. W. A. D.

Derivatives of Epichlorohydrin. EMANUALE PATERNÒ and MASANIELLO CINGOLANI (*Gazzetta*, 1908, 38, i, 243—247; *Atti R. Accad. Lincei*, 1908, [v], 17, i, 237—241).—The authors have investigated the properties and derivatives of epichlorohydrin cyanate (compare Thomsen, *Abstr.*, 1879, 217), which can be obtained by the action of either cyanic acid or potassium cyanate on epichlorohydrin. When potassium cyanate is employed, it is probable that an additive compound is formed, which is hydrolysed immediately, yielding potassium hydroxide; the latter then acts on some of the epichlorohydrin, giving potassium chloride and glycerol, so that half of the epichlorohydrin is destroyed. The maximum yield of epichlorohydrin cyanate obtained is about 37% of the theoretical amount.

With fuming nitric acid, epichlorohydrin cyanate yields a *nitro*-derivative, $C_4H_5O_4N_2Cl$, which crystallises from water in shining needles, m. p. 70°, and is a nitroamine, as it gives a hydrazine on reduction. The hydrazine could not be isolated, but it gives a *benzylidene* derivative, $CON \cdot C_3H_5ClO \cdot N : CHPh$, which crystallises from alcohol in yellow plates, m. p. 191°. Epichlorohydrin cyanate yields an oily *nitroso*-derivative, whilst it gives *isopropylamine* when reduced with sodium in alcoholic solution.

From these results, it is concluded that epichlorohydrin cyanate

possesses the structure
$$\begin{array}{c} CH_2Cl \cdot CH \cdot NH \\ | \\ CH_2 - O \end{array} > CO.$$

T. H. P.

Organic Polysulphides. BROR HOLMBERG (*Annalen*, 1908, 359, 81—99).—Whilst the organic hydrosulphides, sulphides, and disulphides have been investigated repeatedly, little is known as to the methods of formation or the properties of the organic polysulphides. The author, therefore, has made these the object of a systematic study, and now describes the results obtained, including a method for the preparation of organic trisulphides hitherto formed only with great difficulty.

Whilst alkali sulphides unite with sulphur, forming polysulphides, alkali mercaptides are oxidised by sulphur or alkali polysulphides in aqueous solution at the ordinary temperature. Thus potassium ethyl-mercaptide, when shaken with sulphur in aqueous solution, yields ethyl disulphide and only small amounts of polysulphides, a result obtained also by treating the mercaptide with potassium disulphide. Potassium phenyl sulphide, on the other hand, although oxidised in the same manner by sulphur, forming phenyl disulphide, is not attacked by potassium di- or tri-sulphide, and is oxidised only slowly by potassium tetrasulphide.

Previous authors (Müller, *J. pr. Chem.*, 1871, [ii], 4, 40; Klason, *ibid.*, 1877, [ii], 15, 216; Böttger, *Abstr.*, 1884, 1282) have found that ethyl sulphide, disulphide, and tetrasulphide form higher polysulphides when heated with sulphur at 150—180°. It is now shown that ethyl disulphide unites with sulphur in absolute alcoholic solution if saturated with anhydrous ammonia at the ordinary temperature. Ethyl dithioglycollate under the same conditions forms a brownish-red solution, from which the unchanged ester and sulphur are recovered on evaporation. When shaken with aqueous potassium hydroxide, potassium sulphide, and sulphur, ethyl bromide forms an oil consisting chiefly of ethyl disulphide together with ethyl sulphide and polysulphides (Spring and Demarteau, *Abstr.*, 1889, 1110). It is concluded that such reactions, the mechanism of which is discussed, do not throw any light on the constitution of the polysulphides.

Mercaptans react with sulphur dichloride, prepared by passing chlorine into an ethereal solution of disulphur dichloride, forming mixtures of several products, chiefly di- and tetra-sulphides. This is in agreement with Aten's observation (*Abstr.*, 1906, ii, 157) that sulphur dichloride is partly dissociated even at low temperatures.

The action of thionyl chloride on mercaptans in cooled ethereal solution takes place almost quantitatively according to the equation: $4R\cdot SH + SOCl_2 = R_2S_2 + R_2S_3 + H_2O + 2HCl$. The di- and tri-sulphides are separated by fractional distillation. Ethyl trisulphide, S_3Et_2 , is a yellow, strongly refracting oil, b. p. 84—85°/15 mm., and has the characteristic odour of the organic sulphides.

A short résumé is given of other methods of forming polysulphides described by previous authors.

Trithiodiacetic acid, $S_3(CH_2\cdot CO_2H)_2$, formed together with the disulphide from thioacetic acid, crystallises from water in white leaflets, m. p. 123·5—124°, and has the electrical conductivity $K = 0\cdot104$; the *lead* and *silver* salts are described.

The *tetrasulphide* of acetic acid, $S_4(CH_2\cdot CO_2H)_2$, prepared by the action of disulphur dichloride on thiolacetic acid in ethereal solution, crystallises in prismatic needles, m. p. 112·5—113°, is partly decomposed with separation of sulphur on titration with alkalis, and yields the disulphide when boiled with water. The *silver* and *lead* salts are described. Reduction of the tetrasulphide with zinc and sulphuric acid leads to the formation of hydrogen sulphide and thiolacetic acid; on oxidation with bromine in aqueous solution, the tetrasulphide yields sulphuric and sulphoacetic acids. The *ethyl* ester is obtained as an oil.

G. Y.

Action of Magnesium on Ethyl Bromoacetate. ROBERT STOLLÉ (*Ber.*, 1908, 41, 954—955).—The reaction between ethyl bromoacetate and magnesium in ethereal solution leads to the formation of ethyl acetoacetate and of ethyl γ -bromoacetoacetate (compare Zeltner, this vol., i, 243). C. S.

Vapour Density of Propionic Acid. A. FAUCON (*Compt. rend.*, 1908, 146, 691—694. Compare this vol., ii, 257).—Like the lower homologues of the fatty acids, propionic acid has an abnormal vapour density at its boiling point, the values obtained, using Dumas' method, being 3.75 and 3.80 at 148°, 3.58 and 3.60 at 152°, 3.39 at 160°, 2.98 at 162°, 2.96 at 170°, 2.77 at 180°, 2.70 at 190°, and 2.57 at 210°, the theoretical value calculated from $D = M/28.95$ being 2.55. The vapour density of the acid at its boiling point (140°), obtained by extrapolation, is 4.0; it follows, therefore, that the molecular complexity at that temperature is 4/2.55 or 1.56.

Knowing the value of the vapour density of propionic acid at its boiling point, the author has calculated its heat of vapourisation by two methods, using Clapeyron's formula $L = T/425.(u' - u).dp/dT$ and Raoult's formula $L = 1.988.T_2/(M.d/d.f).df/dT$; the values obtained are 90.9 Cal. and 91.2 Cal. respectively, and these are in close agreement with the experimental value 90.43 Cal. (*loc. cit.*).

The factor $(u' - u)$ in Clapeyron's formula represents the difference between the volumes occupied by one gram of the saturated vapour and one gram of the liquid acid; in order to calculate the value of u , the specific gravity and coefficient of expansion of the liquid acid at 130° were determined, and found to be 0.8567 and 0.00153 respectively. M. A. W.

***l*- and *d*-Hexoic Acids.** CARL NEUBERG and B. REWALD (*Biochem. Zeitsch.*, 1908, 9, 405—413).—Neuberg and Rosenberg have shown that the hexoic acids, obtained from the putrefaction products of egg-white, contain about 50% of an optically active acid, which is, by reason of its origin, presumably β -methylvaleric acid. The racemic form of the acid has been synthesised by van Romburgh. This substance was prepared by a modification of van Romburgh's method, and separated into its antipodes by means of the brucine salt. The *l*-form was obtained pure, and gave $[\alpha]_D^{17} - 8.98^\circ$. S. B. S.

Preparation of the Alkyl Esters of the Higher Iodated Fatty Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 188434).—*Ethyl iodobehenate*, thin prisms, m. p. 290°, obtained by boiling together iodobehenic acid, alcohol, and concentrated sulphuric acid, crystallises from light petroleum.

Ethyl iodostearate, prepared in a similar manner, is a pale yellow oil of faintly fruity odour. G. T. M.

Preparation of Diacyl Glycerides of the Higher Fatty Acids. FERDINAND ULZER, J. BATIK, and RUDOLF SOMMER (D.R.-P. 189839).—The diglycerides of the higher fatty acids (C_{16} — C_{22}) are readily prepared by heating a mixture of the acid with excess of

glycerol at 170° under 10 mm. pressure. After four to six hours, the diglyceride is separated from the glycerol by extraction with light petroleum.
G. T. M.

Catalytic Reactions of Oxidation and Reduction of Unsaturated Organic Compounds. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 276—321. Compare Abstr., 1907, i, 820).—The oxidation of such substances as linseed oil is probably a process of molecular autoxidation accompanied by the decomposition of the products of the reaction into more volatile compounds, as well as by more complex reactions.

The absorption of oxygen by unsaturated compounds can be accomplished without any formation of decomposition products if metallic oxides are employed as catalysts, the explanation of their action being similar to that given previously, but the formation of unstable intermediate oxygen compounds must also be assumed.

The results obtained in the absorption of oxygen by thin layers of drying oil and by passing oxygen into solutions of various unsaturated oils are similar in character.

The reaction takes place in two stages, for which the equations $x = k_1 t$ and $k_2 = 1/t \log a/(a - x)$ are proposed; Ostwald's formulæ for autocatalysis do not yield satisfactory results, but Nernst's theory connecting the influence of diffusion and the chemical action itself should be taken into account here; thus, in accordance with this theory, the first (linear) stage is prolonged as the quantity of catalyst is diminished; again, the results of Geate's experiments with ultra-violet light agree far better with the equation $dx/dt = 1/t \log a/(a - x)$ than with $dx/dt = (k_1 + k_2 x)(a - x)$, which shows that no autocatalyst can be present.

Experiments with linseed oil, cod liver oil, almond oil, some fatty acids, and mulberry oil are described; in the case of the latter it is possible that autocatalysis does occur.

Moisture retards the absorption of oxygen by drying oils, but to a less extent than is usually assumed. Light considerably hastens the process, even in the presence of strong catalysts. Rise of temperature hastens the process. The absorption tends to become proportional to the pressure of the oxygen; for pressures of 15—20 atmos., at the same time, the colour changes, but on removal of the high pressure the substance regains the original colour.

A simple and convenient apparatus is described for carrying out reduction experiments. The process of reduction is a unimolecular reaction and is not autocatalytic, the shape of the reduction curve depending on the diffusion of the gaseous particles, the condition of the surface of the catalyst, and the possibility of the decreasing effect of the latter owing to fatigue or poisoning. Unsaturated compounds containing a closed-chain do not react under the conditions of the experiments, although this inertness can probably be overcome under certain conditions of temperature even without the application of high pressures. Unsaturated compounds with low b. p. change but slightly. The stereo-isomeric forms of a substance react identically. The number of electro-negative groups, the occurrence of double link-

ings in close proximity to these groups, and the size of the molecule all influence the rate and limits of the catalytic reduction of the substance. The catalytic properties of solid molecular platinum are almost identical with those of colloidal solutions of platinum.

The rate of the reaction with 2% platinum is already sufficiently great to furnish a method for detecting various impurities by the estimation of the quantity of hydrogen absorbed. Palladium acts as a far weaker catalyst than platinum. Z. K.

The Carrying Down of Soluble Oxalates by Oxalates of the Rare Earths. GREGORY P. BAXTER and HERBERT WILKENS DAUDT (*J. Amer. Chem. Soc.*, 1908, 30, 563—572).—An investigation on the effect of conditions on the quantity of alkali oxalates carried down by the oxalates of neodymium, lanthanum, samarium, and yttrium. In general, it is found that: (1) the oxalates of the rare earths show a marked, but varying, tendency to carry down the oxalates of alkalis and ammonium, which increases with an increase in temperature and in the concentration of the molecular alkali oxalate at the moment of precipitation; (2) potassium and ammonium oxalates are occluded to a much greater extent than sodium oxalate. Precipitation with the latter gives, in most cases, precipitates only slightly contaminated with this salt; (3) by conducting the precipitation in the presence of a quantity of a strong acid, considerably more than equivalent to the alkali oxalate, the occlusion is in many cases wholly prevented; in the case of yttrium, the diminution is, however, slight; (4) in order to obtain a precipitate of a rare earth oxalate as pure as possible by means of an alkali or ammonium oxalate, precipitation should be conducted in cold dilute solution in the presence of a quantity of strong acid, considerably more than equivalent to the oxalate added.

The following table gives the molecular ratio of occluded oxalate to rare earth oxalate when precipitated from neutral and acid solutions:

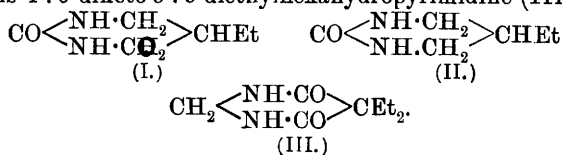
	$\text{Na}_2\text{C}_2\text{O}_4$		$\text{K}_2\text{C}_2\text{O}_4$		$(\text{NH}_4)_2\text{C}_2\text{O}_4$	
	Acid.	Neutral.	Acid.	Neutral.	Acid.	Neutral.
$\text{Nd}_2(\text{C}_2\text{O}_4)_3$	0·02	0·02	0·01	0·79	0·01	0·71
$\text{La}_2(\text{C}_2\text{O}_4)_3$	0·04	0·02	0·00	0·09	0·01	0·27
$\text{Sm}_2(\text{C}_2\text{O}_4)_3$	0·00	0·30	0·00	0·94	0·00	0·32
$\text{Y}_2(\text{C}_2\text{O}_4)_3$	0·04	0·04	0·69	0·73	0·65	0·82

W. H. G.

New Drugs. IV. [Derivatives of Malonic Acid.] ALFRED EINHORN [and, in part, HEINRICH VON DIESBACH, RICHARD FEIBELMANN, and CARL LADISCH] (*Annalen*, 1908, 359, 145—187. Compare Abstr., 1901, i, 439, 493; 1903, i, 257).—A study of the influence of substituting groups on the reactions of derivatives of malonic acid.

Various authors have observed that diethylmalonic acid and its derivatives undergo abnormal reactions. Thus, whilst the action of ammonia on methyl dimethylmalonate and methylethylmalonate leads to the formation of the corresponding amides, methyl diethylmalonate does not form an amide under the same conditions (Fischer and Dilthey, Abstr., 1902, i, 269; Meyer, Abstr., 1906, i, 137). Tafel and

Thompson (this vol., i, 58) found that, on electrolytic reduction, barbituric acid yields hydrouracil and trimethylenecarbamide, whilst 5-ethylbarbituric acid is reduced similarly to 5-ethylhydrouracil (I) and 4-ethyltrimethylenecarbamide (II), but that 5:5-diethylbarbituric acid forms 4:6-diketo-5:5-diethylhexahydropyrimidine (III):



Again, the action of phosphoryl chloride and carbamide on diethylmalonic acid leads to the formation of diethylacetylcarbamide (Fischer and Diltthey, Abstr., 1905, i, 35), whereas barbituric acid and 5:5-dimethylbarbituric acid are formed by the action of these reagents on malonic and dimethylmalonic acids respectively. It is evident, therefore, that the abnormal reactions result from the presence of the two ethyl groups.

In agreement with Fischer and Diltthey's view (*loc. cit.*), that the first stage in the action of phosphoryl chloride and carbamide on diethylmalonic acid leads to the formation of diethylmalonuric acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO}_2\text{H}$, it is now found that this acid is formed by the action of carbamide on diethylmalonyl chloride in cold pyridine solution and subsequent addition of dilute hydrochloric acid, but that, if the reaction mixture is heated on the water-bath and the pyridine removed by distillation in a current of steam before the acidification, the product obtained is 5:5-diethylbarbituric acid. It is assumed that in these reactions an intermediate *additive* compound of diethylmalonuric acid and pyridine, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{CO} \cdot \text{NC}_5\text{H}_5\text{Cl}$, is formed.

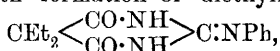
The action of carbonyl chloride on diethylmalonic acid and carbamide in pyridine solution, on the other hand, leads to the formation of diethylacetylcarbamide (compare Einhorn and Hollandt, Abstr., 1898, i, 577). The first stage of this reaction probably leads to the formation of the monochloride, $\text{CO}_2\text{H} \cdot \text{CEt}_2 \cdot \text{COCl}$, which must decompose at low temperatures, forming hydrogen chloride and the anhydride of diethylmalonic acid, since it is found that the action of aqueous pyridine on diethylmalonyl chloride leads to the formation of this anhydride (Abstr., 1906, i, 398).

As it has been generally considered that anhydrides of the malonic acid series are incapable of existence, it was of special interest to study the action of aqueous pyridine on other malonyl chlorides. It is found that such anhydrides are obtained only from disubstituted malonyl chlorides, and that the stability increases with the size of the substituting groups. Thus dimethylmalonyl chloride yields a duodeci-molecular anhydride, which is more easily hydrolysed than the diethyl-anhydride, but ethylmalonyl and malonyl chlorides yield substances which are probably mixtures, cannot be purified, and do not yield pure decomposition products.

The influence of the two ethyl groups on the reactions of malonic acid derivatives has been studied also in the action of sodium amalgam

on the thiobarbituric acids. Whereas thiobarbituric and 5-ethylbarbituric acids react with sodium amalgam and water only with great difficulty, and yield oily decomposition products, 5:5-diethylthiobarbituric acid is rapidly converted in the cold into, chiefly, diethylmalonamide, formic acid, and hydrogen sulphide, 4:6-diketo-5:5-diethylhexahydropyrimidine (Tafel and Thompson, *loc. cit.*) and bisdiethylmalonyltetra-aminoethane (2-bisdeoxyveronyl), which has the annexed constitution, being formed as by-products. In explanation

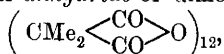
of these reactions, the transient formation of the bivalent group, $\text{CEt}_2 \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} \text{C:}$, is assumed. In agreement with this, it is found that the sulphur atom of diethylthiobarbituric acid is readily displaced by the action of aniline and phenylhydrazine with formation of diethylmalonylphenylguanidine,



and diethylmalonylphenylaminoguanidine, $\text{CEt}_2 \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} \text{C:N}\cdot\text{NHPh}$, whilst the thio-acid is converted into diethylbarbituric acid when boiled with mineral or organic acids.

Molecular weight determinations with the higher polymeride of diethylmalonic acid (Abstr., 1906, i, 398) in benzene and in ethylene dibromide agree with the formula $(\text{C}_7\text{H}_{10}\text{O}_3)_{12}$, but in nitrobenzene with the formula $(\text{C}_7\text{H}_{10}\text{O}_3)_8$. This anhydride is hydrolysed slowly by aqueous potassium hydroxide at the ordinary temperature; when heated with a limited amount of sodium ethoxide in alcoholic solution, it yields ethyl diethylacetate and diethylmalonate and *ethyl hydrogen diethylmalonate*, which is obtained as an oil, decomposes at 150° , forming carbon dioxide and diethylacetic acid, is soluble in alkalis, and on evaporation with aqueous sodium carbonate yields sodium diethylmalonate (compare Brown and Walker, Abstr., 1893, i, 394). Tables are given showing the amounts of diethylmalonamide, diethylmalonic acid, and diethylmalonamic acid formed by the action of ammonia, and of diethylacetyldiethylamide, diethylmalondithiethylamic acid, and diethylmalonic acid formed by the action of diethylamine, on the anhydride under varying conditions as to solvent, molecular proportions, and temperature.

The duodeci-molecular *anhydride* of dimethylmalonic acid,



is obtained as a white, amorphous powder, m. p. $145\text{--}148^\circ$ (decomp.), cannot be converted into a quadrimolecular modification, is readily hydrolysed by moisture, forming dimethylmalonic acid, and when heated with aqueous ammonia yields dimethylmalonamide and dimethylmalonic acid.

The action of aqueous pyridine on ethylmalonyl chloride leads to the formation of a yellow oil, which mostly contains ethylmalonic acid and chlorine, and sometimes pyridine. The product obtained similarly from malonyl chloride is a yellowish-brown powder, m. p. $190\text{--}195^\circ$ (decomp.).

5-Ethylthiobarbituric acid, $\text{CHEt} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CS}$, prepared by heating ethyl sodioethylmalonate with thiocarbamide in alcoholic solution, crystallises in yellow needles, m. p. 192°.

5 : 5-Dimethylthiobarbituric acid, $\text{C}_6\text{H}_8\text{O}_2\text{N}_2\text{S}$, prepared from thiocarbamide and ethyl sodiodimethylmalonate, crystallises in yellow needles, m. p. 216°, and on treatment with sodium amalgam and water is converted partly into dimethylmalonamide.

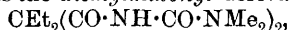
Bisdiethylmalonyltetra-aminoethane, $\text{C}_{16}\text{H}_{26}\text{O}_4\text{N}_4 \cdot 2\text{H}_2\text{O}$, crystallises in white prisms, loses $2\text{H}_2\text{O}$ at 110°, m. p. 340°, is soluble in aqueous sodium carbonate, being reprecipitated on acidification, and is stable towards oxidising agents.

4 : 6-Diketo-5 : 5-diethylhexahydropyrimidine, m. p. 293° (292° : Tafel and Thompson, *loc. cit.*), has feeble basic properties, is stable towards oxidising agents, and does not condense with benzaldehyde in presence of zinc chloride; the mercurichloride, $\text{C}_8\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{HgCl}_2$, long needles, m. p. 215—218°.

5 : 5-Dipropylthiobarbituric acid, $\text{C}_{10}\text{H}_{16}\text{O}_2\text{N}_2\text{S}$, prepared by heating dipropylmalonyl chloride with thiocarbamide or by condensation of ethyl dipropylmalonate with thiocarbamide in presence of sodium ethoxide, crystallises in yellow needles, m. p. 154°, and on treatment with sodium amalgam and water at the ordinary temperature yields dipropylmalonamide and a small amount of a substance which is probably bisdipropylmalonyltetra-aminoethane.

Diethylmalonylphenylguanidine (2-phenyliminodiethylbarbituric acid), $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3$, prepared by heating diethylthiobarbituric acid with aniline at 120—130°, crystallises from alcohol in white needles, m. p. 253°, and is readily soluble in dilute alkalis. Diethylmalonylphenylamino-guanidine (2-phenylhydrazinodiethylbarbituric acid), $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_4$, formed from diethylthiobarbituric acid and phenylhydrazine at 120—130°, crystallises in yellow needles, m. p. 215°, and yields a blue sodium salt, which forms a red solution in much water. These two malonyl-guanidines are decomposed by boiling mineral acids, forming diethylbarbituric acid and the bases from which they are prepared.

When heated at 100—130° with *as*-dimethylcarbamide, diethylmalonyl chloride forms the diethylmalonyl derivative,



which separates from hot water in rhombic crystals, m. p. 158°, and is soluble in aqueous alkalis. The diethylmalonyl derivatives of *as*-diethylcarbamide, $\text{C}_{17}\text{H}_{32}\text{O}_4\text{N}_4$, white needles, m. p. 125°, and *as*-phenylmethylcarbamide, $\text{C}_{23}\text{H}_{28}\text{O}_4\text{N}_4$, white needles, m. p. 172°, are formed in the same manner. These diethylmalonylcarbamides are hydrolysed, forming diethylbarbituric acid, when heated with a mixture of concentrated and fuming sulphuric acids.

Diethyl- and dipropyl-barbituric acids are formed when the corresponding malonamides are heated with phenyl carbonate at 200—215°.

The diethylmalonate of glycollamide, $\text{CEt}_2(\text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, formed by heating sodium diethylmalonate and chloroacetamide with a small amount of sodium iodide at 110—120°, separates from water in white crystals, m. p. 126°.

Diethylaminoethyl diethylmalonate, $\text{CEt}_2(\text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NEt}_2)_2$,

prepared by the action of diethylmalonyl chloride on cooled diethylaminoethyl alcohol, is obtained as a yellow oil which decomposes partly on distillation; the *citrate*, $C_{19}H_{38}O_4N_2 \cdot 2C_6H_8O_7$, was analysed.

Diethylmalonylhydrazide, $CEt_2 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ | \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$, prepared from hydrazine hydrate and diethylmalonyl chloride in aqueous solution, crystallises in prisms, m. p. 256° .

The *diethylmalonyl* derivative of anthranilamide, $CEt_2(CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH_2)_2$, prepared by the action of diethylmalonyl chloride on anthranilamide in cooled pyridine solution, crystallises in microscopic prisms, m. p. 215° . G. Y.

Refractometric Evidence for the Constitution of Carbon Suboxide. ARTHUR MICHAEL (*Ber.*, 1908, 41, 925—928).—The conclusion drawn by Diels and Blumberg (this vol., ii, 103) from the determinations of the molecular refraction and dispersion, that the author's representation of it as β -hydroxypropionic lactone (*Abstr.*, 1906, ii, 442) is incorrect, is controverted. The calculated values given for this formula are not accepted, as Moureu (*Abstr.*, 1906, ii, 1) has shown that Brühl's numbers for the acetylenic linking in hexylpropionic acid are too low, 2.22 and 0.19 instead of 3.60 and 0.455, and therefore this optical method cannot decide between the two formulæ at present. W. R.

Action of Zinc or Magnesium on Mixtures of Esters of Oxalic and of α -Brominated Fatty Acids. New Syntheses of *as*-Dialkylmalic and Dialkylloxalacetic Esters. BERTHOLD RASSOW and R. BAUER (*Ber.*, 1908, 41, 963—965).—The reaction between ethyl oxalate and ethyl bromoisobutyrate in the presence of zinc at 60 — 65° leads to the formation of ethyl *as*-dimethylmalonate, whilst the same two substances in ethereal solution react with magnesium to form ultimately ethyl dimethylloxalacetate, the *semi-carbazone* of which, $C_{11}H_{19}O_5N_3$, has m. p. 96° .

Ethyl oxalate and ethyl bromodiethylacetate react in a similar manner under the latter conditions, yielding the *substance*, $C_{12}H_{20}O_5$, b. p. 135 — $136^\circ/12$ mm. C. S.

Behaviour of Cholic Acid towards Ozone. KURT LANGHELD (*Ber.*, 1908, 41, 1023—1025. Compare this vol., ii, 211).—Cholic acid resembles cholesterol, to which it is generally assumed to be chemically related, in its stability towards oxidising agents, which if sufficiently powerful to attack the molecule break it down to simple acids. Hence, although cholic acid has formed the subject of many investigations, its constitution has been elucidated only so far that it is known to be a monocarboxylic acid containing two primary and one secondary carbinol groupings. With the object of throwing further light on the constitution of cholic acid, the author has now studied its behaviour towards ozone.

When treated with 10% ozone in presence of chloroform, cholic acid

combines with 4 atoms of oxygen, forming a solid *ozonide*, $C_{24}H_{40}O_9$, which when boiled with water is partly decomposed, yielding hydrogen peroxide and a reducing *substance*. The ozonide decomposes at $120-130^\circ$ in a vacuum, forming aldehydes which have an aromatic odour, can be distilled, and react with phenylhydrazine and semicarbazide. This behaviour of cholic acid towards ozone is analogous to that which has been observed with unsaturated acids and with hydroaromatic substances (Harries, *Abstr.*, 1906, i, 225).

Cholesterol, when treated in the same manner with ozone, forms an *ozonide*, which contains two or more O_3 -groups and decomposes on distillation in a vacuum. G. Y.

Formation of Acetaldehyde in Alcoholic Fermentation.

J. AUGUSTE TRILLAT (*Compt. rend.*, 1908, 146, 645—647. Compare *Abstr.*, 1903, ii, 231; 1907, ii, 492).—Contrary to the observations of Roeser (*Ann. Inst. Pasteur*, 1893, 41), the author finds that in alcoholic fermentation the production of aldehyde is only a concomitant phenomenon and does not occur in the absence of oxygen. Comparative experiments were made in which nutrient liquids containing lactose were sown with yeasts obtained from cheese, in the first case allowing free access of air, and in the second case expelling all the oxygen both from the nutrient liquid and the space above it by a current of hydrogen or carbon dioxide. The aldehyde was estimated colorimetrically by means of rosaniline hydrogen sulphite, the precaution being taken in the second series of experiments to distil off the alcohol in the absence of air. The results show that no aldehyde is produced in an atmosphere of hydrogen or carbon dioxide, that introduction of a small amount of air caused the production of 2—10 mg. of aldehyde per litre, and that 50 mg. per litre are produced with free access of air. E. H.

Formation of Acetaldehyde in Alcoholic Fermentation.

E. KAYSER and A. DEMOLON (*Compt. rend.*, 1908, 146, 783—784).—Trillat's conclusion (preceding abstract) relative to the origin of acetaldehyde in alcoholic fermentation had already been arrived at by the authors (*Abstr.*, 1907, ii, 714). Production of acetaldehyde is intimately connected with the presence of a living aerobic yeast on the surface. Addition of antiseptics capable of killing the yeast considerably reduces the proportion of aldehyde, and aseptic addition of yeast afterwards killed by heat has no action on the aldehyde production. The magnitude of the differences observed leads the authors to conclude that living yeast is an essential agent of the phenomenon. E. H.

Molecular Dispersion of Succindialdehyde. CARL D. HARRIES (*Ber.*, 1908, 41, 909—910. Compare this vol., i, 133).—A correction. The dispersion was calculated for the F—C lines and not for the G'—C as Brühl's figures require. A redetermination of these constants shows the molecular dispersion to be 0.52, a result in close agreement with that calculated for the dialdehyde, namely, 0.55. W. R.

Formation of Aldehydes or Ketones during Acetic Fermentation. K. FARNSTEINER (*Zeitsch. Nahr. Genussm.*, 1908, 15, 321—326).—An investigation showed that all liquids which have undergone more or less complete acetic fermentation contain a neutral, volatile substance which reduces Fehling's solution (compare Abstr., 1901, i, 625). The substance is similar to acetol in its physical properties and in its behaviour to Fehling's solution and sulphurous acid; when treated with phenylhydrazine, however, it yields an osazone, m. p. 243°, and also an oily product. W. P. S.

Formation of Thio-aldehydes. LUDWIG VANINO (*J. pr. Chem.*, 1908, [ii], 77, 367—368. Compare Abstr., 1902, i, 744; Schmidt, *ibid.*, 1906, i, 711; 1907, i, 282).—Trithioformaldehyde is readily formed when sodium thiosulphate crystals are fused, mixed with an equal weight of 40% formaldehyde solution, and this mixture poured into half its weight of 38% hydrochloric acid. The crystalline thioaldehyde is deposited almost immediately, and is removed, washed with water, and recrystallised from benzene. Other aldehydes react in a similar manner. J. J. S.

Keten. NORMAN T. M. WILSMORE and ALFRED W. STEWART (*Ber.*, 1908, 41, 1025—1027. Compare Abstr., 1907, i, 478; Wilsmore, *Trans.*, 1907, 91, 1938).—Polemical. A claim for priority over Staudinger and Klever (this vol., i, 246). W. H. G.

Ketens.* VII. Classification. HERMANN STAUDINGER and H. W. KLEVER (*Ber.*, 1908, 41, 906—909. Compare this vol., i, 246).—Dilute ethereal solutions of methyl- and ethyl-keten are obtained when zinc reacts with ethereal solutions of α -bromopropionyl bromide and α -bromobutyl bromide and the products are distilled. The yields are poor and the solutions react with aniline, forming the anilides of propionic and butyric acids. Carbon suboxide (Diels, Abstr., 1906, ii, 227) is also a keten, and may be obtained by the action of zinc on *dibromomalonyl bromide*, which is an oil, b. p. 91—92°/13 mm. The ketens are divided into the following groups: 1. Keten, its monoalkyl derivatives, and carbon suboxide. They are colourless and not capable of autoxidation. They are polymerised by pyridine or quinoline, and do not form additive compounds with substances containing the C:N or C:O groups.

2. Dialkylated ketens. These are coloured, and readily undergo autoxidation. They yield keten bases with pyridine and quinoline, and form additive compounds with benzylideneaniline (C:N group) and quinone (C:O group).

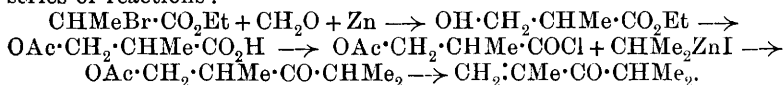
Both groups readily combine with water, alcohols, or amines, and also with bromine or chlorine.

The first groups are termed *aldo-ketens* and the second, *keto-ketens*.

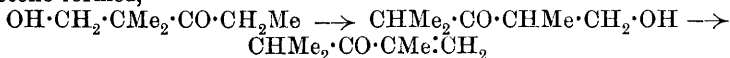
J. J. S.

β -Hydroxy- $\alpha\alpha$ -dialkyl Ketones. Migration under the Influence of Alkalis. EDMOND E. BLAISE and I. HERMAN (*Compt. rend.*, 1908, 146, 700—702).—The unsaturated C₇ ketone, obtained as

one of the products of the action of potassium hydroxide solution on ethyl hydroxy*tert.*-butyl ketone (this vol., i, 248), is *isopropyl methylvinyl ketone*, $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CMe} \cdot \text{CH}_2$, for it is identical with the synthetical product obtained from ethyl α -bromopropionate by the method described by Blaise and Maire (Abstr., 1907, i, 749), and involving the following series of reactions:



*iso*Propylmethylvinyl ketone has b. p. $55\text{--}56^\circ/60$ mm., the *semi-carbazone* has m. p. $90\text{--}5^\circ$, and the *p*-nitrophenylhydrazone has m. p. 89° , and its formation from ethyl hydroxy*tert.*-butyl ketone is probably the result of an intramolecular change, involving the migration of the carbinol group $-\text{CH}_2 \cdot \text{OH}$ and subsequent dehydration of the hydroxy-ketone formed,



(compare Blaise and Courtot, Abstr., 1905, i, 853).

The author discusses and rejects two other possible explanations of the course of the reaction.

In addition to *isopropyl methylvinyl ketone*, a hydroxy-ketone is obtained in small quantity by the action of potassium hydroxide solution on ethyl hydroxy*tert.*-butyl ketone; it is an isomeride of the original ketone, has b. p. $62\text{--}63^\circ/15$ mm., yields a phenylurethane derivative and a *p*-nitrophenylhydrazone, and is converted into *isopropyl methylvinyl ketone* by the dehydrating action of 50% sulphuric acid; it probably has the constitution represented by the formula $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{OH}$.

M. A. W.

Behaviour of Dextrose, Lævulose, and Galactose towards Dilute Sodium Hydroxide. JAKOB MEISENHEIMER (*Ber.*, 1908, 41, 1009—1019).—Buchner, Meisenheimer, and Schade (Abstr., 1907, i, 17) found that the action of hydrogen peroxide on lævulose in alkaline solution leads to the formation of formic and glycollic acids, and a hydroxy-acid having the composition of erythritic acid. The identity of the last is now doubtful, as the supposed *i*-erythritylphenylhydrazide obtained from it has since been found to be acetylphenylhydrazide (compare Lespieau, Abstr., 1907, i, 173; Nef, this vol., i, 5), and it may have been a mixture of polyhydroxy-acids having the composition of erythritic acid. The present author has now studied the behaviour of hexoses towards dilute sodium hydroxide in absence of an oxidising agent, as this also is of interest in connexion with the problem of alcoholic fermentation.

Dextrose and lævulose behave similarly, yielding, after some months in dilute sodium hydroxide at the ordinary temperature, 50—60% of *i*-lactic acid, 30—50% of a mixture of polyhydroxy-acids, 0.5—2% of formic acid, and a small amount of a brown, amorphous substance, whilst about 1% of the hexose forms carbon dioxide and alcohol. Under the same conditions, galactose yields less than 20% of lactic acid, but about 70% of the mixture of polyhydroxy-acids, together with traces of formic acid. The mixture of polyhydroxy-acids forms a

calcium salt, which, on analysis, gives results corresponding with an acid, $(\text{CH}_2\text{O})_{5.5}$; hence the polyhydroxy-acids are not all saccharinic acids, $\text{C}_6\text{H}_{10}\text{O}_5$, as assumed by Nef (*loc. cit.*). On prolonged extraction with ether, the mixture of acids yields small amounts of dihydroxybutyric acid. The presence of sodium sulphite or of potassium cyanide does not prevent the coloration of sugar solutions by alkalis (compare Schade, *Abstr.*, 1906, i, 931); the decomposition of the sugar is only slightly, if at all, retarded by the sulphite. G. Y.

A Crystallised Lævulose Tetra-acetate. D. H. BRAUNS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 563—566).—Lævulose reacts with an excess of acetyl bromide at -15° , and the yellow product, after removal of the acetyl bromide under low pressure, dissolution in alcohol, and evaporation in a desiccator, yields colourless crystals.

Laevulose penta-acetate has m. p. $131-132^\circ$, D^{15}_D 1.388, and has a bitter taste. In chloroform solution, it has $[\alpha]^{20}_D - 91.38^\circ$. Crystals monoclinic; $a : b : c = 1.3463 : 1 : 1.5733$, $\beta = 52^\circ 12'$. C. H. D.

Condensation of Formaldehyde and Lactose. PAUL ROSENBERG (D.R.-P. 189036).—*Formaldehyde-lactose*, $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 5\text{CH}_2\text{O} \cdot \text{H}_2\text{O}$, is obtained by heating lactose with 40% formaldehyde solution at 65° in a vacuum, and finally evaporating the solution to dryness. The product is soluble in water, alcohol, or acetone. On warming its alcoholic solution at $60-70^\circ$, the compound decomposes, regenerating lactose. G. T. M.

Formulæ of Polysaccharides. HEINRICH KILIANI (*Chem. Zeit.*, 1908, 32, 366).—The formula for starch or cellulose should not be $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, the correct general formula for a polysaccharide being $(\text{C}_6\text{H}_{10}\text{O}_5)_n \cdot \text{H}_2\text{O}$ or $\text{C}_{6n}\text{H}_{10n} + 2\text{O}_{5n} + 1$. This is proved by the author's previously published analyses of the three anhydrous trisaccharides, raffinose, melezitose, and mannasaccharide, all of which pointed to the formula $\text{C}_{18}\text{H}_{32}\text{O}_{16}$. Similarly, the analysis of inulin led to the formula $\text{C}_{36}\text{H}_{62}\text{O}_{31}$. Although Brown and Morris (*Trans.*, 1889, 55, 463), from molecular weight determinations, are in favour of doubling the formula for inulin, it is at least doubtful whether the ordinary methods of determination yield trustworthy results in the case of substances of such high molecular weight. P. H.

Composition of Starch Grains. Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1908, 146, 540—542).—The separation of starch into amylopectin and amylose (Maquenne and Roux) can be effected by placing the grains in very dilute sodium carbonate until their envelope of amylopectin is burst; by subsequent neutralisation, the envelope contracts again and can be separated, the amylose remaining in solution. G. B.

Composition of Starch Grains. LÉON MAQUENNE (*Compt. rend.*, 1908, 146, 542—545).—Amylose (compare preceding abstract) gives a pure blue colour with iodine, and amylopectin a violet colour; these substances are probably related, and intermediate substances may

exist. Starch paste which has not been superheated is not a true colloid, but contains amylose in a state of true solution together with particles of the grain envelope (amylopectin), which are to some extent organised and are much larger than ordinary colloid particles. Amylopectin can also be separated from amylose by boiling with salt solutions. G. B.

The Influence of the Alternating Current on the Rate of Hydrolysis of Starch by Diastase and Mineral Acids. A. LEBEDEFF (*Biochem. Zeitsch.*, 1908, 9, 392—402).—Alternating currents of weak strength (0.013—0.015 ampere) increase the rate of formation of sugar by diastase; stronger currents act in a similar way at first, but afterwards the enzyme loses its activity. Weak currents also increase the rate of starch hydrolysis by acids. Various hypotheses are suggested to account for these facts; the author is inclined to regard the change in the surface tension of the colloidal particles as the most likely cause. S. B. S.

Cellulose and its Derivatives. CARL G. SCHWALBE (*Chem. Zeit.*, 1908, 32, 287—288).—Polemical. A reply to Grandmougin (this vol., i, 250). P. H.

Preparation of Formyl Esters of Cellulose. J. P. BEMBERG (D.R.-P. 189836 and 189837).—Formic acid in the presence of sulphuric acid reacts with cellulose, yielding a formate. Cotton wool (15 parts) is added to 100 parts of 98% formic acid containing 3—10 parts of concentrated sulphuric acid. After several hours, a colourless, syrupy solution of *cellulose formate* is obtained, which is precipitated by water as a white mass. Instead of cellulose, hydrocellulose, cellulose hydrate, and mercerised cellulose may be employed. Formic acid alone does not condense in this way, but the sulphuric acid may be replaced by 2% to 4% of hydrogen chloride. G. T. M.

Acetylation. DOUGLAS J. LAW (*Chem. Zeit.*, 1908, 32, 365—366).—The author has investigated the action of the new acetylating agent recommended by Cross, Bevan, and Briggs, which is obtained by adding 100 grams of acetic anhydride to a solution of 50 grams of zinc chloride in 100 grams of glacial acetic acid. With cellulose, it gives a triacetate, but with starch it does not react at all; it converts sucrose into the octa-acetyl derivative and dextrose into a tetra-acetyl compound, indefinite crystals, m. p. 98°. Added in slight excess to benzaldehyde, a violent reaction takes place; after some time, the fluorescent solution is poured into cold water, when crystals of a *diacetate*, $C_6H_5 \cdot CH(OAc)_2$, are obtained; this substance crystallises from alcohol, and has m. p. 43° and b. p. 225—230°. When furfuraldehyde dissolved in glacial acetic acid is treated with an excess of the reagent and the mixture is cooled in a freezing mixture, a dark solution is obtained. On pouring into water, after half an hour, an oil separates out which gradually crystallises; this substance, which is also a *diacetyl* derivative, $C_4OH_3 \cdot CH(OAc)_2$, crystallises from alcohol, and has m. p. 45° and b. p. 220°. If the reagent

is allowed to react with furfuraldehyde at the ordinary temperature, a black substance is obtained which is not attacked by acids or alkalis. P. H.

Constitution of ψ -Ammonium Bases. II. JOHANNES GADAMER (*Arch. Pharm.*, 1908, 246, 89—90).—An introduction to the paper dealt with in the next abstract; this paper brings experimental evidence to support Gadamer's view as to the three tautomeric forms of ψ -ammonium bases (*Abstr.*, 1905, i, 368). G. B.

Chloral Alcoholates. Connexion with the Constitution of ψ -Ammonium Bases. F. KUNTZE (*Arch. Pharm.*, 1908, 246, 91—111. Compare preceding abstract).—The conversion of a chloral alcoholate into that of another alcohol by evaporation of its solution in an excess of this second alcohol is due to mass action and to the dissociation of the alcoholate, as supposed by Gadamer. This is proved by the polarimetric investigation of the equilibrium in chloroform solution between *l*-amyl alcohol, chloral *l*-amyl alcoholate, and an inactive alcohol with its chloral compound, at a temperature of 20°. The equilibrium was approached from both sides, for instance, by mixing equal molecular proportions of chloral *l*-amyl alcoholate, $[\alpha]_D^{20} + 1.19^\circ$, and ethyl alcohol and of chloral ethyl alcoholate and *l*-amyl alcohol. In the case of ethyl and of propyl alcohol, the equilibrium is reached when about 60% of chloral *l*-amyl alcoholate and 70% of *l*-amyl alcohol are present. With secondary alcohols, the proportion of *l*-amyl alcohol is smaller, and with tertiary alcohols it falls to less than 10%. Two molecular proportions of ethyl alcohol added to one of chloral *l*-amyl alcoholate raised the proportion of liberated *l*-amyl alcohol to 50% and 8 molecules to 84%. One molecule of *l*-amyl alcohol, added to chloral hydrate dissolved in chloroform, liberates water and forms 98% of *l*-amyl alcoholate. With cotarnine in benzene solution, similar results were obtained, indicating the existence of an (unstable) alcoholate.

Fourteen chloral alcoholates of the type $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OR}$ were prepared; the following were obtained crystalline and were analysed: from methyl alcohol, m. p. 38°; from ethyl alcohol, m. p. 50°; from isopropyl alcohol, m. p. 45°; from *n*-butyl alcohol, m. p. 49°; from trimethylcarbinol, m. p. 43°, and from cinnamyl alcohol, m. p. 42°.

G. B.

Preparation of Hexamethylenetetramine Borate. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 188815).—When one, two, and three molecular proportions of boric acid are mixed with hexamethylenetetramine (1 mol.), one, two, and three molecular proportions of water are eliminated respectively on drying at 70—80°. The residues consist of the three borates of hexamethylenetetramine: $\text{HBO}_2\cdot\text{C}_6\text{H}_{12}\text{N}_4$, $2\text{HBO}_2\cdot\text{C}_6\text{H}_{12}\text{N}_4$, and $3\text{HBO}_2\cdot\text{C}_6\text{H}_{12}\text{N}_4$. These salts, which also separate from the alcoholic solutions of their generators, are neutral or feebly acid crystalline powders, soluble in water and having useful antiseptic properties. G. T. M.

Reduction of Amino-acids to Amino-aldehydes. CARL NEUBERG (*Ber.*, 1908, 41, 956—963).—Fischer's method in the sugar series of

reducing lactones to aldehydes led the author to attempt the reduction of amino-acids in a similar manner, with negative results. When however, the esters of α -amino-acids or their hydrochlorides are reduced by sodium amalgam in a well-cooled aqueous or alcoholic solution, which is kept always acid by the addition of hydrochloric acid when necessary, amino-aldehydes are obtained, the amount of which is determined by isolating the amino-aldehyde in the form of the phenylosazone or of the *p*-nitrophenylosazone (ammonia and hydrogen being eliminated), or by converting it into the pyrazine derivative by means of alkaline mercuric chloride. In this way, the reduction of the esters of glycine, alanine, aminobutyric acid, leucine, aspartic acid, anilinoacetic acid, tyrosine, diaminopropionic acid, serine, isoserine, cystine, glycylglycine, and hippuric acid has been detected.

The hydrochlorides of the esters of β -amino-acids also undergo reduction, but the resulting solutions, whilst reducing alkaline solutions of silver salts, are not affected by Fehling's solution; this affords, therefore, a method of differentiating between α and β -amino-acids.

The *phenylosazone*, $C_{14}H_{14}N_4$, obtained from aminoacetaldehyde, forms yellow crystals and has m. p. $176-177^\circ$. The *p*-nitrophenylosazone, $C_{15}H_{14}O_4N_6$, m. p. 277° (decomp.), from α -aminopropaldehyde, is a scarlet, crystalline powder. C. S.

Physico-chemical Study of the Complex Copper-Glycine Sulphates. J. T. BARKER (*Trans. Faraday Soc.*, 1908, 3, 188-204).—Measurements of the relative concentrations of cupric ions in solutions containing copper sulphate and glycine (by means of the *E.M.F.* of concentration cells) lead to the conclusion that complex ions are formed containing 4 molecules of glycine to each atom of copper. The freezing point of a glycine solution is raised by addition of copper sulphate, and the results are in harmony with the view that the complex anions above mentioned are partly dissociated in solutions which do not contain a very large excess of glycine. The electrical conductivity of a copper sulphate solution increases when glycine is added to it, until 10 molecules of glycine have been added for each molecule of copper sulphate; further additions result in a decrease of conductivity. It is suggested that this is due to disturbance of the hydrolytic dissociation equilibrium in the copper sulphate solution, the cupric hydroxide combining with the glycine and so giving rise to the production of more free sulphuric acid. Zinc sulphate behaves in the same way. Measurements of the *E.M.F.* of a hydrogen electrode in zinc sulphate-glycine solutions and of the rate of inversion of sucrose by copper sulphate-glycine solutions show that the concentration of hydrogen ions is actually increased by the addition of glycine. By crystallisation of copper sulphate-glycine solutions, products were obtained consisting of mixtures of copper glycine, $(NH_2 \cdot CH_2 \cdot CO_2)_2Cu$, and basic glycine sulphate, $(NH_2 \cdot CH_2 \cdot CO_2H)_3H_2SO_4$. T. E.

Reduction of Glycine Ethyl Ester. EMIL FISCHER (*Ber.*, 1908, 41, 1019-1023).—Ethyl oxalate differs from other esters of aliphatic

and aromatic acids in that it can be reduced by sodium amalgam (Traube, this vol., i, 75). This behaviour results evidently from the direct union of the two strongly negative carbethoxy-groups. A similar, although more feeble, effect was observed previously as resulting from the accumulation of hydroxyl groups in the dibasic acids of the sugar group (Fischer, Abstr., 1890, 597). As an amino-group in the α -position has an influence similar to that of hydroxyl on the carboxylic group, it was to be expected that the esters of α -amino-acids would be capable of being reduced by sodium amalgam. This is now found to be the case with glycine ethyl ester, which, when treated with sodium amalgam in neutral or slightly acid solution, yields a liquid which reduces Fehling's solution, and must contain aminoacetaldehyde or its semiacetal, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{OEt}$. The reducing power of the solution shows that the ester is reduced to the extent of about 25%. On addition of hydrochloric acid to the reaction solution, evaporation almost to dryness under 10—15 mm. pressure, and treatment of the residue with hydrogen chloride in alcoholic solution at 0° , most of the unchanged glycine ester separates as the hydrochloride, whilst the reduction product is converted into aminoacetal, which is stable towards alkalis, and hence is readily separated from the remainder of the ester.

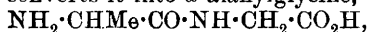
G. Y.

Walden's Inversion. II. EMIL FISCHER and HELMUTH SCHEIBLER (*Ber.*, 1908, 41, 889—893. Compare Abstr., 1907, i, 192).—*l*- α -Aminoisovaleric acid (*l*-valin) reacts with nitrosyl bromide yielding an active α -bromoisovaleric acid, which with ammonia yields the original valin and not its optical isomeride. This forms another example of the abnormal manner in which compounds containing an isopropyl group react (Fischer and Dilthey, Abstr., 1905, i, 35; *Annalen*, 1904, 334). The α -bromoisovaleric acid crystallises from well-cooled light petroleum in colourless prisms, m. p. 43.5° . In benzene solution it has $[\alpha]_D^{20} + 22.6^\circ$. It is only sparingly soluble in cold water, and has $[\alpha]_D^{20} + 9.0^\circ$.

J. J. S.

Synthesis of Polypeptides. XXIII. EMIL FISCHER (*Ber.*, 1908, 41, 850—864).—Fischer and Abderhalden (Abstr., 1907, i, 737, 990), by the hydrolysis of silk, obtained a soluble tetrapeptide, which is precipitated by ammonium sulphate and is composed of two molecules of glycine and one each of *d*-alanine and *l*-tyrosine. Attempts have now been made to synthesise this compound in the first place by the combination of tyrosine ester with chloroacetyl-*d*-alanylglycine, which led to a tetrapeptide differing from the above in being precipitated by ammonium sulphate with difficulty. In the second place, it was proposed to couple α -bromopropionylglycylglycine with tyrosine, but it was not found possible to obtain the chloride of this tripeptide in a pure state. *dl*-Alanyldiglycylglycine was obtained by coupling the raw product with glycine ester.

d-Bromopropionylglycine, prepared by coupling glycine with *d*-bromopropionyl chloride, crystallises from toluene in long needles, or from water in thin prisms, m. p. 122 — 123° (corr.), to a colourless liquid. Aqueous ammonia converts it into *d*-alanylglycine,

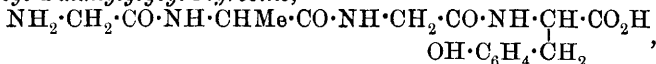


identical with that previously prepared (Abstr., 1905, i, 864). *Chloroacetyl-d-alanylglycine* crystallises in microscopic, globular aggregates of minute needles, m. p. 178° (corr. decomp.), and has $[\alpha]_D^{18} - 53.4^\circ$. *Glycyl-d-alanylglycine*,

$\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$,
crystallises in very minute needles, which darken at 220°, m. p. 245° (corr. decomp.), and has $[\alpha]_D^{20} - 64.3^\circ$; it is sparingly soluble in water, and is not precipitated by phosphotungstic acid.

Chloroacetyl-d-alanylglycyl chloride is obtained by the action of phosphorus pentachloride and acetyl chloride on the finely-divided substance as a yellow powder. It couples with tyrosine methyl ester in acetone solution to form *chloroacetyl-d-alanylglycyl-l-tyrosine methyl ester*, which crystallises in faintly yellow, lancet-shaped plates, m. p. 163—164.5° (corr.). The corresponding *acid*, obtained by hydrolysis of the ester with sodium hydroxide, crystallises in colourless, microscopic needles or thin prisms, m. p. 206—207° (corr.); it has an acid reaction, and gives a red coloration with Millon's reagent.

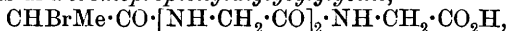
Glycyl-d-alanylglycyl-l-tyrosine,



is obtained by the action of ammonia on the above as a colourless, amorphous powder, which decomposes at 229° (corr.) without melting. It has $[\alpha]_D^{20} + 4.0^\circ$, and shows the biuret coloration and the red coloration with Millon's reagent. It is precipitated by phosphotungstic acid or by tannin, but only with difficulty by ammonium sulphate; it is rapidly hydrolysed by fresh pancreas extract, yielding tyrosine.

Chloroacetyl-d-alanylglycylglycine ester forms very minute, matted needles, m. p. 165—167° (corr.). *d-α-Bromopropionylglycylglycine*, prepared in the same manner as the antipode (Fischer and Warburg, Abstr., 1905, i, 692), has m. p. 172° (corr.), $[\alpha]_D^{20} + 29.7^\circ$. *d-Alanylglycylglycine* darkens at 206°, m. p. 220° (corr. decomp.); the antipode behaves similarly, and the m. p., 240° (corr.), previously given (*loc. cit.*) is an error. The tripeptide has $[\alpha]_D^{20} + 31.3^\circ$, and is easily soluble in water.

α-Bromopropionyldiglycylglycine ethyl ester, prepared by coupling *α*-bromopropionylglycylglycyl chloride with glycine ethyl ester, crystallises in very minute needles, decomposing at 189° (corr.). On hydrolysis, it yields *dl-α-bromopropionyldiglycylglycine*,



which has m. p. 176° (corr.). This acid is more conveniently prepared by coupling diglycylglycine with *α*-bromopropionyl bromide, when it has m. p. 180° (corr.).

dl-Alanyldiglycylglycine,



formed on treating the above substance with ammonia, becomes brown at 220°, m. p. 242° (corr.). E. F. A.

Conversion of *l*-Serine into the Natural Optically Active Cystine. EMIL FISCHER and KARL RASKE (*Ber.*, 1908, 41, 893—897). —*dl*-Cystine is obtained when *dl*-β-chloro-*α*-aminopropionic acid hydrochloride is heated with water and barium hydrosulphide at 100° for one

and a-half hours in sealed tubes, and the resulting product oxidised by atmospheric oxygen in the presence of ammonia (Erlenmeyer, Abstr., 1903, i, 792). When the optically active natural serine is used, an active cystine is obtained which is identical with the cystine from natural sources. The conclusion is drawn that natural cystine, serine, and alanine belong to the same genetic group. The configurations previously suggested for the last two compounds (Abstr., 1907, i, 393) cannot be regarded as rigidly established.

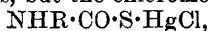
Full details for the preparation of barium hydrosulphide are given. J. J. S.

Preparations of Sodium Glycocholate. WILLIAM C. M. LEWIS (*Bio-Chem. J.*, 1908, 3, 119—128).—Strecker's formula for sodium glycocholate is confirmed. The ordinary methods of extraction of mixed bile salts do not yield a product consisting entirely of sodium glycocholate and taurocholate, but there is in addition a varying amount of sodium salts of fatty acids of much smaller molecular weight. This admixture may amount to as much as 50% of the total product. It is suggested that sodium myristate is the principal component of this admixture.

J. J. S.

A New Method of Forming *iso*Cyanates [Carbimides]. I. RICHARD ANSCHÜTZ (*Annalen*, 1908, 359, 202—216. Compare Freund and Asbrand, Abstr., 1895, i, 576).—An application of Hofmann's synthesis of thiocarbimides from carbon disulphide and primary amines to the formation of carbimides from carbonyl sulphide.

The action of primary amines on carbonyl sulphide leads to the formation of alkylammonium alkylthiolcarbimates, $\text{NHR} \cdot \text{CO} \cdot \text{S} \cdot \text{NH}_3\text{R}$, which react with metallic salts in aqueous or aqueous-acetone solution, forming the metallic alkylthiocarbimates. As Hofmann's method of decomposing the metallic alkylthiocarbimates in aqueous solution is inapplicable to the formation of carbimides, which react with water forming carbon dioxide and *s*-dialkylcarbimides, the author has studied the action of heat on the metallic salts of alkylthio- and alkylthiocarbimates, and finds that, whilst mercuric ethyldithiocarbamate decomposes at 150—160° forming only small amounts of ethyl thio-carbimide together with carbon disulphide, *s*-diethylcarbamide, and considerable quantities of mercuric sulphide, mercuric alkylthiolcarbimates, $(\text{NHR} \cdot \text{CO} \cdot \text{S})_2\text{Hg}$, when heated, yield mercuric sulphide, carbonyl sulphide, and *s*-dialkylcarbimides together with small amounts of the carbimides, but the chloromercuric salts,



decompose chiefly into mercuric sulphide, hydrogen chloride, and alkylcarbimides, the formation of carbonyl sulphide and the *s*-dialkylcarbamide taking place in this case to only a small extent. The decomposition of the mercuric alkylthiolcarbimates is considered to take place probably in two stages, the first leading to the formation of mercuric sulphide and the intermediate product, $\text{S}(\text{CO} \cdot \text{NHR})_2$.

Ethylammonium ethylthiolcarbamate, $\text{C}_5\text{H}_{14}\text{ON}_2\text{S}$, prepared by passing carbonyl sulphide into an ethereal solution of ethylamine, crystallises in white needles, m. p. 88—89°, is hygroscopic, decomposes in contact

with water, forming hydrogen sulphide and an oil, and yields the mercuric and chloromercuric salts as white precipitates on addition of the calculated quantities of mercuric chloride to its concentrated aqueous solution. *Mercuric ethylthiolcarbamate*, $(C_2H_5ONS)_2Hg$, has an odour of ethyl carbimide when moist or after drying; it commences to decompose at 90° , evolving carbonyl sulphide, and at 156 — 160° yields red mercuric sulphide, *s*-diethylcarbamide, and small amounts of ethylcarbimide. The *chloromercuric* salt, $C_2H_5ONClHg$, has an odour of ethylcarbimide, yields *s*-diethylcarbamide when boiled with water, and forms ethylcarbimide when heated. The *silver*, *copper*, and *lead* salts of ethylthiolcarbamic acid were also prepared.

isoButylammonium isobutylthiolcarbamate, $C_4H_{22}ON_2S$, crystallises in glistening leaflets, m. p. 102° , and is more stable than the ethyl compound. The *mercuric* and *chloromercuric* salts behave in the same manner as those of the ethyl compound. *isoButylcarbimide* (Brauner, Abstr., 1880, 228) is a colourless liquid, b. p. $101.5^\circ/760$ mm., has an odour resembling that of ethylcarbimide, and reacts with *isobutylamine*, forming *s*-diisobutylcarbamide. The *copper*, $C_{10}H_{20}O_2N_2S_2Cu$, and *cadmium*, $C_{10}H_{20}O_2N_2S_2Cd$, salts were analysed; when heated, these salts yield *s*-diisobutylcarbamide. G. Y.

Nitroacetonitrile. III. WILHELM STEINKOPF and LUDWIG BOHRMANN (*Ber.*, 1908, 41, 1044—1052).—After many unsuccessful attempts (compare Abstr., 1907, i, 490), nitroacetonitrile has at last been prepared by treating methazonic acid with thionyl chloride in ether. That the compound so obtained is nitroacetonitrile follows from the fact that it yields α -nitroethenylamino-oxime with hydroxylamine, and gives the nitrolic acid reaction and Konowloff's reaction. Its formation from methazonic acid proves the correctness of the formula assigned to this substance by Meister (Abstr., 1907, i, 885). Further, since the compound obtained by Steiner (*Trans.*, 1876, ii, 288) from fulminuric acid, and described by him as nitroacetonitrile, is not identical with nitroacetonitrile, this author's formulation of fulminuric acid as nitrocyanoacetamide becomes doubtful. Attempts are being made to prepare nitrocyanoacetamide.

Nitroacetonitrile, $NO_2 \cdot CH_2 \cdot CN$, is obtained as a fairly stable, yellow, limpid oil; when pure, it may be distilled under reduced pressure, b. p. $96^\circ/14$ mm.; it is not explosive, neither is the *ammonium* salt, which crystallises in slender, yellowish-white needles, decomposing at 130 — 135° ; the *silver* salt, obtained as a brown precipitate, is, however, very explosive. An aqueous solution of the ammonium salt when treated with a solution of diazobenzene nitrate yields *nitrocyanoformaldehydphenylhydrazone*, $CN \cdot C(NO_2) : N \cdot NHPH$; it forms glistening, reddish-brown crystals, decomposing at 108° , and is soluble in dilute alkalis.

α -Nitroethenylamino-oxime, $NO_2 \cdot CH_2 \cdot C(NH_2) : NOH$, obtained by the action of hydroxylamine on nitroacetonitrile, forms yellow crystals and decomposes suddenly at 108° . *Dibromonitroacetonitrile*,

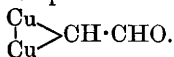


prepared by adding bromine to an aqueous solution of ammonium

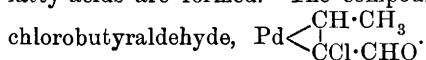
nitroacetoneitrile, is a pale yellow oil, b. p. 57—58°/12 mm., with an unpleasant odour; it solidifies to a crystalline mass at about -30°.

When nitroacetamide or its ammonium salt is warmed with thionyl chloride, it is converted into a compound which is probably *nitroacetimide chloride*, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CCl} \cdot \text{NH}$; it crystallises from water in white crystals with H_2O ; the anhydrous substance has m. p. 157—158°. When boiled with water for some time, it is converted into a substance, $\text{C}_2\text{H}_4\text{O}_5\text{N}_2$, decomposing violently at 121°. The nature of this compound is under investigation. W. H. G.

Metallic Acetylene Compounds. OSKAR MAKOWKA (*Ber.*, 1908, 41, 824—829. Compare Abstr., 1907, ii, 399, 403).—The copper acetylene compound, obtained by the precipitation of a cuprous salt by acetylene, is of constant composition, $\text{C}_2\text{H}_2\text{OCu}_2$, whether derived from chloride, nitrate, sulphate or acetate, or by precipitation in acetone solution. When oxidised with hydrogen peroxide, volatile products, showing an aldehyde reaction, are formed. In view of this, the compound is regarded as dicuproacetaldehyde of the constitution



The so-called palladium acetylene has the formula $\text{C}_4\text{H}_5\text{OClPd}$. It is non-explosive, and yields palladium when ignited. When heated with water or alkali hydroxides, butyraldehyde is produced, and, on fusion with potassium hydroxide, butyric acid and possibly also higher fatty acids are formed. The compound is considered to be pallado-



E. F. A.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1907, 77, 104—115).—This report deals with the action of reducing agents on 5-chloro-3-keto-1:1-dimethyl- Δ^4 -tetrahydrobenzene; the action of alcoholic potassium hydroxide on 3-bromo-1:1-dimethylhexahydrobenzene; recent work on hydroaromatic hydrocarbons, alcohols, ketones, and acids; steric hindrance in the formation of rings; optical influence of conjugated unsaturated groups, and velocity of chemical change in the polymethylene series. T. H. P.

Products of the Action of Aluminium Chloride and Hydrogen Chloride on Benzene; Phenylmethylcyclopentane. GABRIEL GUSTAVSON (*Compt. rend.*, 1908, 146, 640—642).—When a mixture of benzene and aluminium chloride saturated with hydrogen chloride is heated for some hours in hermetically sealed flasks on a water-bath, a dark brown liquid gradually separates, which on decomposition by water gives a mixture of benzene, hydrocarbons, b. p. up to 360°, and a resinous residue (*J. Russ. Phys. Chem. Soc.*, 1878, 10, 390). By treating the fraction b. p. 230—240° with fuming sulphuric acid and heating the sulphonic acid, isolated through its barium salt, with hydrochloric acid in sealed tubes at 180—200°, the author has obtained a hydrocarbon, $\text{C}_{12}\text{H}_{10}$, b. p. 230—232°.

n_D^{20} 1.5210, apparently identical with the 3-phenyl-1-methylcyclopentane described by Borsche and Menz (this vol., i, 149). It is not attacked by bromine, and not immediately by potassium permanganate solution. On oxidation by the latter or by chromic acid at 100° , benzoic and acetic acids are formed. When the dark brown liquid is extracted with light petroleum, a substance remains which will again combine with benzene, and the product on saturation with hydrogen chloride gives more phenylmethylcyclopentane mixed with more highly phenylated cyclic hydrocarbons. Amongst the latter, Kursanoff's diphenylcyclohexane (Abstr., 1902, i, 20) has been detected. Probably the cyclohexane is transformed into the methylcyclopentane, and the toluene observed by Friedel and Crafts arises from a transposition of the latter. E. H.

Transformations and New Nitrogenous Derivatives of Vinyltrimethylene. NICOLAUS J. DEMJANOFF (*Ber.*, 1908, 41, 915—920).—The constitution of Gustavson's vinyltrimethylene not having yet been finally established (compare Abstr., 1896, i, 699; Fecht, Abstr., 1907, i, 906), the action of nitrogen trioxide on the hydrocarbon was investigated, and by the reduction of the additive product so obtained cyclobutanone was formed. The *nitrosite*, $C_5H_8O_3N_2$, separates from an ethereal solution at 0° when the gas from arsenious oxide and nitric acid (D 1.36) is passed through it, and forms colourless, glistening leaflets, m. p. 145° to a deep blue liquid. A good yield of succinic acid is obtained by its oxidation with concentrated nitric acid. It is shown to be a ψ -nitrosite by its conversion into the weak base, $NO_2 \cdot C_5H_8 \cdot NHPh$, by aniline, nitrous oxide being liberated; this forms yellow leaflets, m. p. 98° ; the *hydrochloride*, $C_{11}H_{15}O_2N_2Cl$, is crystalline. Reduction of the nitrosite with tin and hydrochloric acid, as well as of the liquid product obtained simultaneously with the nitrosite, leads to the formation of a *diamine*, a colourless liquid, b. p. 180 — 185° . The *dihydrochloride*, $C_5H_8(NH_2HCl)_2$ forms colourless prisms; the *platinichloride*, $C_5H_{12}N_2H_2PtCl_6 \cdot 3H_2O$, orange-red prisms; the *aureichloride*, $C_5H_{12}N_2 \cdot 2HAuCl_4 \cdot H_2O$, yellow leaflets, and the *picrate*, $C_5H_8(NH_2)_2 \cdot 2C_6H_2(NO_2)_3 \cdot OH$, needles. These results show that in the nitrosite and liquid product the nitrogen atoms are directly united to carbon. In addition to the diamine a neutral product was obtained possessing aldehydic properties, b. p. 98 — 101° ; the semi-carbazone has m. p. 201 — 202° , and it is therefore identified as *cyclobutanone*, the formation of which is most easily explained by assuming the hydrocarbon to be methylene-cyclobutane, $CH_2:C \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} CH_2$, but the question requires further investigation. W. R.

Action of Nitric Acid on Saturated Hydrocarbons. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 184—192. Compare Konowaloff, Abstr., 1907, i, 1).—The formation of nitro-compounds is only the first stage in the action of nitric acid on hydrocarbons, and consequently the mass of the nitric acid employed influences greatly the final products obtained; thus, if the quantity of acid is small, only

nitro-compounds are obtained, but if the acid is increased, oxidation products are formed and the proportion of the nitro-compounds is diminished.

The nitration of hexahydro- ψ -cumene, b. p. 142—144°, can be carried out with equally good results, and more conveniently in open vessels than in sealed tubes if 75—150 c.c. of nitric acid, D 1.3, are used for 100 c.c. of the hydrocarbon, the chief products being mononitro-derivatives. Z. K.

The Study of Isomorphous Derivatives of Benzenesulphonic Acid. HENRY A. MIERS, HENRY E. ARMSTRONG, W. PALMER WYNNE, and WILLIAM J. POPE (*Brit. Assoc. Report*, 1907, 77, 272).—All the possible isomeric sulphonic chlorides and sulphonic bromides of the isomeric dichloro-, the isomeric dibromo-, and the isomeric chlorobromobenzenes are to be prepared and examined crystallographically so as to determine the extent of variation in the series of closely-related compounds. T. H. P.

Catalytic Reactions at High Temperatures and Pressures. XV. Reduction of Anthracene and Phenanthrene in Presence of Nickel Oxide. WLADIMIR N. IPATIEFF, W. JAKOWIEFF, and L. RAKITIN (*Ber.*, 1908, 41, 996—1000. Compare Godehot, *Abstr.*, 1904, i, 987; 1906, i, 76; Schmidt and Mezger, *Abstr.*, 1907, i, 1022).—When repeatedly heated with hydrogen in presence of nickel oxide at 260—270°/100—125 atmospheres for ten to fifteen hours, anthracene is reduced in three stages. The product of the first heating consists chiefly of tetrahydroanthracene; this is reduced in the second stage to decahydroanthracene, C₁₄H₂₀, which crystallises in odourless plates, m. p. 73—74° (52—53°: Lucas, *Abstr.*, 1888, 1201), and when again reduced yields a mixture of perhydroanthracene and a substance, m. p. -3°, having apparently the same composition. The yields are not quantitative, as part of the anthracene decomposes, forming carbon and methane.

The reduction of phenanthrene takes place in three stages in the same manner, but at higher temperatures. The reduction products are obtained in quantitative yields, as even at 400° carbon and methane are not formed. The product of the first stage is a mixture of dihydro- and tetrahydro-phenanthrene, and yields two *picrates*, m. p. 135—137°, and orange-red needles, m. p. 105—106°, respectively. The second reaction product, m. p. -4° to -5°, is octahydrophenanthrene, perhaps containing other hydrocarbons. The final reduction product consists of perhydrophenanthrene, C₁₄H₂₄, which is a colourless liquid, b. p. 266—276°, has an odour resembling caoutchouc, becomes slightly yellow on prolonged exposure to light, and is not attacked by nitric acid, bromine, or potassium permanganate at the ordinary temperature. G. Y.

Derivatives of Dihydroanthracene. LATHAM CLARKE (*Ber.*, 1908, 41, 935—936).—The reaction between anthraquinone and magnesium ethyl bromide in ethereal solution leads to the formation

of a substance, $C_{18}H_{16}O$, m. p. 159° , and of dihydroxydiethyldihydroanthracene, $C_6H_4 \begin{smallmatrix} \text{CEt(OH)} \\ \text{CEt(OH)} \end{smallmatrix} > C_6H_4$, m. p. 175° , which separates from ether in large, greenish-white needles containing 1 mol. of ether, and from alcohol in thick, white plates, which also contain alcohol of crystallisation, which is rapidly lost by exposure to the air. C. S.

Fluorene Parhydryde. LEOPOLD SPIEGEL (*Ber.*, 1908, 41, 884—886).—A repetition of the experiments of the author and Liebermann (*Abstr.*, 1889, 719) shows that, contrary to the statement of Schmidt and Mezger (this vol., i, 16), fluorene parhydryde, $C_{13}H_{22}$, is actually existent. C. S.

Attempt to Prepare Hexaphenylethane. RICHARD ANSCHÜTZ (*Annalen*, 1908, 359, 196—201).—It was observed previously (*Trans.*, 1885, 47, 898, 899) that phenyl fumarate, when heated, decomposes in two stages into carbon dioxide and stilbene, the intermediate product being phenyl cinnamate. Recently, Tschitschibabin has drawn attention to the instability of carboxyl and cyano-groups when attached to the same carbon atom as other negative groups (*Abstr.*, 1907, i, 27). These facts, together with the long-known formation of triphenylmethane by the decomposition of triphenylacetic acid, induced the author to study the action of heat on triphenylmethyl triphenylacetate, $CPh_3 \cdot CO_2 \cdot CPh_3$, triphenylmethyl fumarate, $CPh_3 \cdot CO_2 \cdot CH:CH \cdot CO_2 \cdot CPh_3$,

and phenyl triphenylacetate, $CPh_3 \cdot CO_2 Ph$, as these might be expected, in analogy with the formation of stilbene and triphenylmethane, to yield hexaphenylethane, *s*-bistriphenylmethylethylene, and tetraphenylethane respectively. Only in the case of the first of these esters, however, has any indication of the formation of such a product been obtained.

Triphenylmethyl triphenylacetate, $C_{39}H_{30}O_2$, prepared by the action of triphenylmethyl chloride on silver triphenylacetate in boiling benzene solution, crystallises in needles, m. p. 184 — 185° , is readily hydrolysed by alkalis, forming triphenylcarbinol and triphenylacetic acid, and, when heated at 185 — 200° in a vacuum, loses carbon dioxide and yields triphenylmethane, a white, crystalline substance, soluble in chloroform, a product, m. p. about 210° , insoluble in chloroform, but soluble in benzene, and an amorphous residue, m. p. about 300° , which dissolves in boiling ethylene dibromide and may be hexaphenylethane, $C_{38}H_{30}$.

Phenyl triphenylacetate, $C_{26}H_{20}O_2$, prepared from sodium phenoxide and triphenylacetyl chloride, crystallises in small needles, m. p. 122° , and when heated above its m. p. loses carbon dioxide and forms triphenylmethane and phenol.

Triphenylmethyl fumarate, $C_{42}H_{32}O_4$, prepared from triphenylmethyl chloride and silver fumarate, crystallises from carbon tetrachloride in needles containing CCl_4 , which is lost at 100° ; m. p. 152 — 153° . At 200° , the ester loses carbon dioxide, forming a mixture from which a pure product has not yet been obtained. G. Y.

Catalytic Reactions at High Temperatures and Pressures.
XIII. Reduction of Aromatic Amines and Quinoline in Presence of Nickel Oxide. WLADIMIR N. IPATIEFF (*Ber.*, 1908, 41, 991—993. Compare Abstr., 1907, i, 828).—Whilst the action of hydrogen on aromatic amines in presence of nickel oxide under the atmospheric pressure leads to the formation of large amounts of abnormal products, sometimes, as in the case of quinoline, even to the complete suppression of the normal reduction product (Padoa and Carughi, Abstr., 1906, i, 765), the reduction by means of hydrogen in presence of nickel oxide at high temperatures and under high pressures takes place more simply. When heated with hydrogen in presence of nickel oxide at 220—230°/115—120 atmospheres for forty to fifty hours, aniline forms aminocyclohexane in a 40—50% yield, together with dicyclohexylamine and phenylcyclohexylamine in 10% yields. Under similar conditions, diphenylamine yields dicyclohexylamine and traces of cyclohexylamine, whilst quinoline is reduced almost quantitatively to decahydroquinoline, or, on less prolonged heating, to tetrahydroquinoline. G. Y.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Report*, 1907, 77, 101—103).—A detailed study of the conditions governing the transformation of 2:4-dichloro-1-nitroaminobenzene into the isomeric 2:4-dichloro-6-nitroaniline and a study of the wandering of bromine in the chlorination of bromo-anilines.

T. H. P.

Preparation of *p*-Toluidine from Mixed Toluidines by means of *p*-Toluidine Hydrate. RICHARD J. FRISWELL (*J. Soc. Chem. Ind.*, 1908, 27, 258).—Referring to the recent publication of Walker and Beveridge (*Trans.*, 1907, 91, 1797), the author calls attention to the fact that, in 1889, he devised the mode of separating *p*-toluidine from mixed toluidines by means of *p*-toluidine hydrate, and successfully carried it out on a large scale. Technical details are given in the original. J. V. E.

Condensation of Chloral with Primary Aromatic Amines.
II. ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1908, 30, 136—142).—In an earlier paper (Wheeler and Weller, Abstr., 1903, i, 246), it was stated that chloral condenses with *o*- and *p*-nitroanilines to form trichloroethylidenedi-*o*- and -*p*-nitro-anilines.

An account is now given of the behaviour of chloral with other primary arylamines. The products crystallise well, and are decomposed by strong mineral acids with regeneration of the amine. They react readily with bromine at the ordinary temperature to form bromo-derivatives, in which the bromine atom probably replaces the hydrogen of the chloral residue.

[With C. W. MILLER.]—*Trichloroethylidenedi-p-bromoaniline*,



m. p. 140°, forms colourless needles and decomposes at 205°. The

bromo-derivative, m. p. 203° , crystallises in colourless plates, and the *chloro*-derivative, m. p. 93° , in long needles.

[With W. S. DICKSON.]—*Trichloroethylidenedi-o-methoxyphenylamine*, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe})_2$, m. p. 121° , forms large, pale yellow, rhombohedra or long, slender prisms, and is soluble in 100 c.c. of alcohol to the extent of 7 grams at the b. p. and 2.5 grams at 25° . The *bromo*-derivative crystallises in clusters of needles, and decomposes at about 230° .

Trichloroethylidenedi-p-methoxyphenylamine, m. p. 118 — 120° , forms brilliant, pink scales, and decomposes at 158° . By the action of bromine, a compound is obtained which blackens at about 198° .

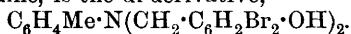
[With W. S. DICKSON.]—*Trichloroethylidene-o-aminobenzoic acid* (chloral-anthranilic acid) (Niementowski and Orzechowski, Abstr., 1896, i, 187), m. p. 152° , yields a *bromo*-derivative decomposing at 237° . When trichloroethylidenedi-o-aminobenzoic acid (chloral-dianthranilic acid) (Niementowski, Abstr., 1903, i, 91) is boiled with acetic anhydride, *o*-acetylaminobenzoic acid is produced. The *bromo*-derivative of chloral-dianthranilic acid has m. p. 236° (decomp.).

[With STROWD JORDAN.]—*Trichloroethylidenedi-o-tolylamine*, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Me})_2$, m. p. 80° , forms silky needles, and yields a *bromo*-derivative, m. p. about 268° . Physiologically, the compound produces a numbing effect.
E. G.

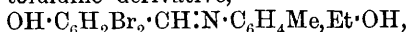
Condensation Products of Dibromo-*p*-hydroxybenzyl Bromide with Aromatic Bases. KARL AUWERS and ALFRED DOMBROWSKI (*Ber.*, 1908, 41, 1053—1058).—A further contribution to the study of the influence of the position of the methyl group on the chemical properties of benzenoid compounds (compare Auwers, Abstr., 1906, i, 258).

Although derivatives of dibromo-*p*-hydroxy- ψ -cumylaniline are readily obtained by the action of dibromo-*p*-hydroxy- ψ -cumyl bromide on an aromatic base in ethereal solution (compare Auwers and Dombrowski, Abstr., 1906, i, 380), it is found that when dibromo-*p*-hydroxybenzyl bromide acts on aniline, *p*-toluidine, or *m*-toluidine, instead of the expected substituted benzylaniline, the corresponding benzylidene derivative is obtained. However, the normal reaction product is obtained when *o*-toluidine, ψ -cumidine, *p*-xylydine, or *as*-m-xylydine is employed. It is therefore evident that the presence of the methyl group ortho to the amino-group prevents the oxidation of the substituted benzylaniline to the corresponding benzylidene derivative; further, since benzylidene derivatives have never been obtained when dibromo-*p*-hydroxy- ψ -cumyl bromide is employed, it follows that the same protective influence against oxidation is exerted by the methyl group when ortho to the $-\text{CH}_2\text{Br}$ group.

The nature of the solvent employed also influences the course of the reaction. Only in ethereal solution does the reaction take place in the manner above described; when benzene is used, the chief product formed, for example, by the action of dibromo-*p*-hydroxybenzyl bromide on *p*-toluidine, is the di-derivative,

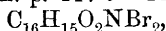


The benzylidene derivatives obtained by the action of dibromo-*p*-hydroxybenzyl bromide on aniline and *p*-toluidine were identical with those described by Paal and Kromschöder (Abstr., 1896, i, 225); the m. p. of the *p*-toluidine derivative,

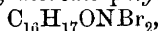


was found to be 187° , and not 157° as stated by these authors.

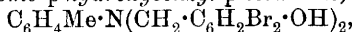
The following new compounds were prepared: *dibromo-p-hydroxybenzylidene-m-toluidine*, $\text{C}_{14}\text{H}_{11}\text{ONBr}_2$, a dark red, crystalline powder, m. p. $155.5\text{--}157^\circ$; *dibromo-p-hydroxybenzyl-o-toluidine*, $\text{C}_{14}\text{H}_{13}\text{ONBr}_2$, a white, crystalline powder, m. p. $117.5\text{--}119^\circ$; the *N*-acetate,



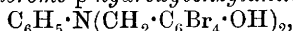
forms needle-shaped crystals; *dibromo-p-hydroxybenzyl-as-m-xylidine N-acetate*, $\text{C}_{17}\text{H}_{17}\text{O}_2\text{NBr}_2$, crystallises in very small leaflets, m. p. 175° ; the isomeric *p*-xylidine compound forms colourless crystals, m. p. $240\text{--}241^\circ$; *dibromo-p-hydroxybenzylidene-as-m-xylidine*, $\text{C}_{15}\text{H}_{13}\text{ONBr}_2$, is a red powder, m. p. 161° ; *dibromo-p-hydroxybenzyl-ψ-cumidine*,



crystallises in slender needles, m. p. $123\text{--}125^\circ$; the *N*-acetate has m. p. 205° ; *bisdibromo-p-hydroxybenzyl-p-toluidine*,



has m. p. $134\text{--}135^\circ$; *tetrabromo-p-hydroxybenzylaniline*, $\text{C}_{13}\text{H}_9\text{ONBr}_4$, crystallises in small, glistening, pearly leaflets, m. p. $126\text{--}127^\circ$; when its alcoholic solution is boiled for some time, it is partly converted into *bistetrabromo-p-hydroxybenzylaniline*,



a fine powder, m. p. 212° .

W. H. G.

Asymmetric Nitrogen. XXXII. Dependence of the Velocity of Racemisation of Optically Active Ammonium Salts on the Nature of the Anion. EDGAR WEDEKIND, OTTO WEDEKIND, and F. PASCHKE (*Ber.*, 1908, 41, 1029—1035. Compare E. Wedekind, Abstr., 1906, i, 161, 419).—The velocities with which *d*-phenylbenzylmethylpropylammonium iodide, bromide, and chloride undergo autoracemisation in chloroform solution at 35° have been measured, the velocity constants obtained being, for the iodide, $K=0.0065$, for the bromide, $K=0.0013$, and for the chloride, $K=0.00027$, that is, in the ratio Cl:Br:I=1:5:25. The rate of change of the bromide in bromoform solution was found to be the same as in chloroform solution.

Similar comparative measurements were made with *d*-phenylbenzylmethylallylammonium bromide and iodide in chloroform solution at 25° , 35° , and 45° , the K values obtained being, for the iodide, 0.0012 and 0.0040 at 25° and 35° respectively, and for the bromide, 0.00061 and 0.0024 at 35° and 45° respectively. From these values, it is seen that (1) the iodide undergoes racemisation about six times more rapidly than the bromide at the same temperature (35°); (2) the allylammonium salts are more stable than the corresponding propyl salts.

The effect of an increase in temperature on the rate of change is in several cases quite abnormal; for example, the K values for *d*-phenyl-

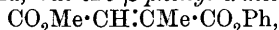
benzylmethylpropylammonium iodide at 25° and 35° are respectively 0.0013 and 0.0065.

1-Phenylbenzylmethylpropylammonium chloride has been prepared; it forms small, colourless crystals decomposing at 174—175°, $[\alpha]_D - 143.8^\circ$ (in chloroform). W. H. G.

Phenyl Mesaconates. ROSALIND CLARKE (*Annalen*, 1908, 359, 188—195).—The esters described in this paper were prepared in amplification of Anschütz's study of derivatives of mesaconic acid (Abstr., 1907, i, 468).

Phenyl mesaconate, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Ph}$, prepared by the action of mesaconyl chloride on sodium phenoxide in boiling toluene solution, crystallises from carbon disulphide in yellow leaflets, m. p. 66—67°; it resembles phenyl fumarate in that it evolves carbon dioxide when heated at high temperatures. On hydrolysis with 1 mol. of potassium hydroxide in boiling aqueous-acetone solution, it yields *α-phenyl hydrogen mesaconate*, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$, which crystallises from light petroleum in needles, m. p. 99°. *α-Phenyl β-methyl mesaconate*, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Me}$, m. p. 45—46°, b. p. 166°/13 mm., is obtained by gently heating sodium phenoxide with β-methyl mesaconyl α-chloride in ethereal solution.

β-Phenyl hydrogen mesaconate could not be obtained by partial esterification of the acid, but the β-phenyl α-methyl ester,



m. p. 23—25°, b. p. 176°/20 mm., is formed from sodium phenoxide and α-methyl mesaconyl β-chloride.

α-Phenyl mesaconyl β-chloride, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COCl}$, obtained as a crystalline mass on treatment of the α-phenyl hydrogen ester with phosphorus pentachloride in chloroform solution and distillation of the phosphoryl chloride and the solvent in a vacuum, yields the following three substances when treated with the corresponding bases in ethereal solution. *α-Phenyl mesacon-β-amate*, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from ether in white needles, m. p. 114—115°. *α-Phenyl mesacon-β-anilate*, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NHPh}$, white needles, m. p. 121°. *α-Phenyl mesacon-β-p-toluidate*, $\text{CO}_2\text{Ph}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, yellow needles, m. p. 129—130°.

β-Phenyl mesacon-α-anilate, white crystals, m. p. 114—115°, and the corresponding α-p-toluidate, yellow needles, m. p. 122°, are prepared by the action of mesacon-α-anilyl and mesacon-α-p-toluidyl chlorides on sodium phenoxide.

Whilst the β-alkyl mesacon-α-anilates and -α-p-toluidates melt at the same temperatures as, or at higher temperatures than, the corresponding β-anilates and β-p-toluidates, the α-phenyl mesacon-β-anilate and β-p-toluidate melt 7° higher than their isomerides. G. Y.

2:4:6-Trichlorophenol and its Transformation into Chlorinated Benzoquinones. EUGENE LEGER (*Compt. rend.*, 1908, 146, 694—697).—2:4:6-Trichlorophenol can be prepared readily and in quantity when concentrated eau de Javel is used instead of the dilute solution of hypochlorite employed by Chandelon (Abstr., 1883, 1108). It has m. p. 66—67° (corr.) [Chandelon (*loc. cit.*) gives 54°].

By the action of nitric acid, D 1.41, containing a small quantity of hydrochloric acid, trichlorophenol is converted into a mixture of tri- and tetra-chlorobenzoquinones, which can be separated by fractional crystallisation from alcohol; trichlorobenzoquinone softens at 166° and melts at 168° (corr.) (Graebe gives 164—166°, *Annalen*, 1868, 146, 1).

M. A. W.

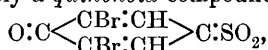
Basic Tri-iodophenoxide of Bismuth. ORESTE CARRASCO (*Boll. chim. farm.*, 1908, 47, 109—112).—The author gives an improved method for preparing 2 : 4 : 6-tri-iodophenol (compare Brenans, *Abstr.*, 1901, i, 322), from which he obtains a basic bismuth derivative possessed of therapeutic value.

By adding a potassium iodide solution of rather more iodine than is required by the equation $C_6H_5 \cdot OH + 3KHO + 6I = C_6H_2I_3 \cdot OH + 3KI + 3H_2O$ gradually to a solution of phenol in a large excess of potassium hydroxide (8 mols.) solution, a theoretical yield of 2 : 4 : 6-tri-iodophenol, free from di- or mono-iodophenol, is obtained.

Monohydrated bismuthyl 2 : 4 : 6-tri-iodophenoxide, $C_6H_2I_3 \cdot O \cdot Bi(OH)_2$, prepared by treating a solution of 2 : 4 : 6-tri-iodophenol (1 mol.) in alkali with a solution of bismuth nitrate (rather less than 1 mol.) in 45% aqueous glycerol, is obtained as a heavy, yellow, amorphous powder. The corresponding *anhydrous* derivative, $C_6H_2I_3 \cdot O \cdot BiO$, to which the name 'neoform' is given, is a yellow powder having a faint odour recalling that of xeroform, a similar compound containing bromine in place of iodine; it begins to decompose at 170—180°.

T. H. P.

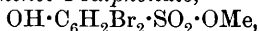
Quinonoid Sulpho-derivatives. THEODOR ZINCKE and R. BRUNE (*Ber.*, 1908, 41, 902—905).—An acetone solution of 2 : 6-dibromophenol-4-sulphonyl chloride (*Abstr.*, 1907, i, 698) becomes deep yellow when shaken with sodium acetate solution. Hydrogen chloride is eliminated, and probably a *quinonoid* compound,



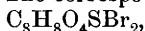
is formed. This compound has not been isolated, as the solution rapidly becomes colourless and deposits a colourless, crystalline compound, having the same composition, and probably representing the polymeric compound $C_6H_2Br_2 \begin{array}{c} \text{O} \cdot SO_2 \\ SO_2 \cdot O \end{array} > C_6H_2Br_2$. This behaviour is analogous to that of various ψ -bromides (*Abstr.*, 1907, i, 125). The polymeride readily reacts with methyl or ethyl alcohol and also with aniline, yielding the same derivatives as are formed when these substances react with the original sulphonyl chloride.

The polymeride is practically insoluble in the ordinary organic solvents, crystallises from hot nitrobenzene in rhombic plates and prisms, and is not readily oxidised.

Methyl 2 : 6-dibromophenol-4-sulphonate,



crystallises from benzene in rhombic plates, m. p. 196—197°, which dissolve readily in alkalis. The corresponding *ethyl* ester,

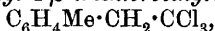


crystallises in prisms, m. p. 146—147°. The *sulphanilide*,
 $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{SO}_2 \cdot \text{NHPh}$,
 crystallises in colourless plates, m. p. 177°.

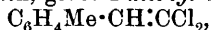
J. J. S.

4-Hydroxy-1:4-dimethyl-1-trichloromethyldihydrobenzene.

THEODOR ZINCKE and FR. SCHWABE (*Ber.*, 1908, 41, 897—902).—Zincke and Suhl's ketone, $\text{C}_8\text{H}_7\text{OCl}_3$ (*Abstr.*, 1907, i, 37), reacts readily with magnesium methyl iodide, yielding 4-hydroxy-1:4-dimethyl-1-trichloromethyleyclohexadiene, $\text{OH} \cdot \text{CMe} < \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix} > \text{CMe} \cdot \text{CCl}_3$, which crystallises from light petroleum in slender needles or plates, m. p. 131—132°. It is extremely unstable, and, when kept, rapidly gives up water, yielding 1-methyl-4-β-trichloroethylbenzene,

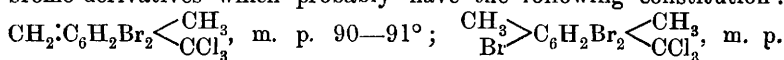


which crystallises from methyl alcohol in slender plates, m. p. 31—33°. When oxidised, this compound yields terephthalic acid, and when heated with alcoholic potash, gives 1-methyl-4-β-dichlorovinylbenzene,



colourless plates, m. p. 40—41°.

The carbinol reacts with a chloroform solution of bromine, yielding bromo-derivatives which probably have the following constitution:

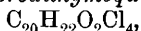


106—107° (decomp.), and $\begin{smallmatrix} \text{CH}_2\text{Br} \\ \text{Br} \end{smallmatrix} > \text{C}_6\text{H}_2\text{Br}_2 < \begin{smallmatrix} \text{CH}_3 \\ \text{CCl}_3 \end{smallmatrix}$, m. p. 133° (decomp.). The latter two readily lose bromine, yielding the dibromo-derivative.

J. J. S.

Action of Chlorine on Dithymol. HENRI COUSIN (*Compt. rend.* 1908, 146, 636—637. Compare this vol., i, 84, 162).—When dithymol (1 mol.), suspended in chloroform, is treated with slightly more than the theoretical quantity (2 mols.) of chlorine, *dichlorodithymol*, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Cl}_2$, is formed as brilliant, slightly yellow, prismatic crystals, m. p. 152—153° (corr.). By the continued action of chlorine, or, better, by the action of bromine (1 mol.) on its chloroform solution, dichlorodithymol is oxidised to *dichlorodithymoquinone*, $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Cl}_2$, which forms radiating groups of deep garnet-red, prismatic needles, m. p. 130—132° (corr. decomp.), insoluble in alkalis, and giving an intense blue colour with tincture of guaiacum.

Dithymol, suspended in chloroform, is converted by the prolonged action of chlorine into *dichlorodithymoquinone dichloride*,



a substance forming small, prismatic crystals of a sulphur-yellow colour, m. p. 176—178° (corr. decomp.), insoluble in alkalis. The latter substance on reduction gives dichlorodithymol.

E. H.

Styrene Oxide. MARC TIFFENEAU and ERNEST FOURNEAU (*Compt. rend.*, 1908, 146, 697—699).—Styrene oxide, obtained in a yield of 50% by the action of powdered potassium hydroxide on an ethereal solution of styrene iodohydrin (*Abstr.*, 1905, i, 591; this vol., i, 19),

has b. p. 191—192° (corr.) or 84—85°/15 mm., D^{20}_D 1.0633, $D^{16.4}_D$ 1.0523; it is not appreciably changed when heated in a sealed tube above its boiling point, and is only slowly converted into the isomeric phenyl-acetaldehyde on boiling with dilute mineral acids (Abstr., 1907, i, 404). Styrene oxide is reduced by sodium and water to benzyl alcohol, and combines with halogen acids to form halohydrins (Abstr., 1907, i, 404); when heated in a sealed tube with hydrocyanic acid, it yields the cyanohydrin of phenylacetaldehyde, which is converted into a mixture of ethylphenylhydracrylate and ethyl cinnamate by the action of an alcoholic solution of hydrogen chloride. Styrene oxide condenses with organo-magnesium derivatives to form the corresponding substituted benzylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{CHR}\cdot\text{OH}$, and not the alcohol, $\text{CH}_2\text{R}\cdot\text{CHPh}\cdot\text{OH}$, as previously stated (Abstr., 1907, i, 818), and is converted quantitatively into the corresponding amino-alcohol when heated in a sealed tube with amines (compare Krassusky, this vol., i, 139). M. A. W.

Oxidation of *m*-Nitrobenzoylcarbinol. WILLIAM L. EVANS and BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1908, 30, 404—412).—In an earlier paper (Evans, Abstr., 1906, i, 269), an account has been given of the behaviour of benzoylcarbinol towards oxidising agents. Further work is being carried out with the object of ascertaining whether the substituted benzoylcarbinols follow the same general course of reaction, and of determining the effect of substitution on the behaviour of these substances. The present paper deals with the oxidation of *m*-nitrobenzoylcarbinol.

An improved method is described for the preparation of bromo-*m*-nitroacetophenone. *m*-Nitroacetophenone acetate has m. p. 51°. On hydrolysis, it yields *m*-nitrobenzoylcarbinol, m. p. 92.5—93°, which forms pale yellow crystals, and, when heated with a mixture of glacial acetic acid and acetyl chloride, is reconverted into *m*-nitroacetophenone acetate. Aqueous solutions of the carbinol reduce ammoniacal silver nitrate and Fehling's solution.

When the carbinol is treated with freshly-precipitated mercuric oxide, freshly-precipitated silver oxide, or potassium permanganate, either alone or in presence of alkali hydroxide, it yields only *m*-nitrobenzoic acid and carbon dioxide. By the action of cupric hydroxide and alkali hydroxide on the carbinol, it is converted into *m*-nitro-mandelic acid, whilst, if treated with potassium ferricyanide and potassium hydroxide, it yields both *m*-nitrobenzoic and *m*-nitro-mandelic acids. E. G.

Preparation of Eugenyl *o*- and *m*-Aminobenzoates. J. D. RIEDEL (D.R.-P. 189333).—*Eugenyl o*-nitrobenzoate, pale yellow prisms, m. p. 60—62°, and *eugenyl m*-nitrobenzoate, well-defined, yellow prisms, m. p. 71—72°, are obtained by the action of the respective nitrobenzoyl chlorides on eugenol in the presence of aqueous sodium hydroxide. The corresponding amino-esters are produced on reducing the foregoing nitro-compounds with tin and hydrochloric acid or zinc and acetic acid; *eugenyl o*-aminobenzoate, yellowish-white, lustrous plates, m. p. 98—99°; *acetyl* derivative, yellowish-white needles, m. p.

102—103°; *eugenyl m-aminobenzoate*, yellow, lustrous prisms, m. p. 72—73°; *hydrochloride*, yellowish-white flakes, m. p. 160—162°; *acetyl derivative*, colourless plates, m. p. 102°. G. T. M.

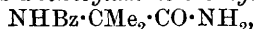
Benzoylaminoisobutyrolactimone. ERNST MOHR and THEODOR GEIS (*Ber.*, 1908, 41, 798—799).—Mohr and Köhler obtained an anhydride, termed a lactimone, by heating *o*-aminobenzoylanthranilic acid with acetic anhydride (*Abstr.*, 1907, i, 414). A similar anhydride,

$\text{CMe}_2 \begin{array}{c} \text{N}=\text{CPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{array}$, which contains the typical lactime and lactone groupings, $\cdot\text{O}\cdot\text{C}\cdot\text{N}\cdot$ and $\cdot\text{C}\cdot\text{CO}\cdot\text{O}\cdot\text{C}\cdot$, and is therefore a lactimone, has now been obtained in the same manner from α -benzoylaminoisobutyric acid. The lactimone group includes also such substances as the yellow

lactimide of benzylidenhippuric acid, $\text{CHPh}\cdot\text{C} \begin{array}{c} \text{N}=\text{CPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{array}$ (Erlen-

meyer, jun., *Abstr.*, 1899, i, 759), and the acylanthranils, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CR} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{array}$ (Anschütz, Schmidt, and Greiffenberg, *Abstr.*, 1903, i, 57).

α -Benzoylaminoisobutyric acid, $\text{NHBz}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, prepared in a 60—65% yield by the action of benzoyl chloride and potassium hydrogen carbonate on α -aminoisobutyric acid in cold concentrated aqueous solution, crystallises in colourless plates, m. p. 198°, decomp. above 220°. The *lactimone*, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$, crystallises in colourless plates, m. p. 34°, b. p. 123°/9 mm., and when treated with cold saturated alcoholic ammonia forms α -benzoylaminoisobutyramide,

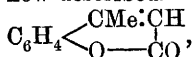


which crystallises in white needles, m. p. 201°. When boiled with aqueous sodium hydroxide, the amide evolves small amounts of ammonia and yields the *lactam*, $\text{CMe}_2 \begin{array}{c} \text{N}=\text{CPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array}$ (?), crystallising in white needles, m. p. 202°. G. Y.

Preparation of the Urethane of *m*-Amino-*p*-ethoxybenzoic Acid. AKTIENGESSELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 189838).—The *urethane*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CO}_2\text{H}$, of 3-amino-4-ethoxybenzoic acid is produced by dissolving the hydrochloride of this amino-acid in aqueous sodium carbonate and adding ethyl chlorocarbonate; it crystallises from alcohol in needles, m. p. 211—212°, and has a very soluble sodium salt. G. T. M.

4-Methylcoumarin. F. PETERS and HUGO SIMONIS (*Ber.*, 1908, 41, 830—837).—The synthesis of methylcoumarin from ethyl acetate and phenol by von Pechmann's method (*Abstr.*, 1884, 66, 1331) gives poor yields, owing probably to the concentrated sulphuric acid used acting rather to sulphonate the phenol than to cause condensation. Using a less concentrated acid (73% H_2SO_4) which no longer acts as a sulphonating agent and less phenol, and stirring the mixture rapidly, a more satisfactory yield is obtained. The proof of the constitution of 4-methylcoumarin is given by conversion into methylcoumarilic acid (Hantzsch and Lang, *Abstr.*, 1886, 706). A number

of halogen derivatives are now described. 4-Methylcoumarin,



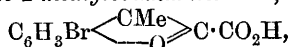
forms long, colourless needles, m. p. 90° ; the *dibromide* is unstable, and forms minute, red needles which lose hydrogen bromide on drying,

giving 3-bromo-4-methylcoumarin, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CMe} \cdot \text{CBr} \\ \diagdown \quad | \\ \text{O} \quad \text{CO} \end{array}$. This crystallises

in colourless prisms, m. p. 114° ; when heated with concentrated potassium hydroxide, it forms the *potassium* salt of 2-methylcoumarilic acid, crystallising in silky, glistening needles; the acid forms feather-like prisms, m. p. 188° (compare Hantzsch, *loc. cit.*); the copper salt forms green needles containing $3\text{H}_2\text{O}$, and the methyl ester, long, glistening needles, m. p. 70° .

4-Methyldihydrocoumarin crystallises in colourless, monoclinic prisms, m. p. 278° .

3 : 6-Dibromo-4-methylcoumarin, $\text{C}_6\text{H}_3\text{Br} \begin{array}{l} \text{CMe} \cdot \text{CBr} \\ \diagdown \quad | \\ \text{O} \quad \text{CO} \end{array}$, prepared by the action of bromine in carbon disulphide solution in sealed tubes at 140° , crystallises in yellow needles, m. p. 167° . Alkali converts it into 4-bromo-2-methylcoumarilic acid,



separating from benzene in aggregates of yellow needles, m. p. 155° , and forming a *copper* salt ($+2\text{H}_2\text{O}$), bright green needles, and a *potassium* salt ($+2\text{H}_2\text{O}$), silky, glistening needles.

3 : 6 : 8-Tribromo-4-methylcoumarin, prepared by heating with bromine under pressure at 175° , separates in colourless prisms, m. p. 196° . It yields, when heated with potassium hydroxide, 4 : 6-dibromo-2-methylcoumarilic acid, $\text{C}_6\text{H}_2\text{Br}_2 \begin{array}{l} \text{CMe} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{C} \cdot \text{CO}_2\text{H} \end{array}$, a yellow, flocculent precipitate, m. p. 96° ; the *copper* salt ($+2\text{H}_2\text{O}$) forms green, microscopic needles.

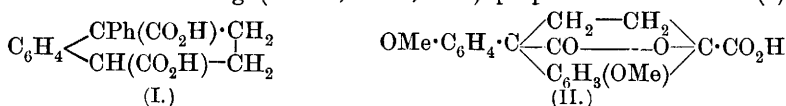
6-Bromo-4-methylcoumarin, $\text{C}_6\text{H}_3\text{Br} \begin{array}{l} \text{CMe} \cdot \text{CH} \\ \diagdown \quad | \\ \text{O} \quad \text{CO} \end{array}$, prepared from *p*-bromophenol and ethyl acetoacetate, forms colourless needles, m. p. 187° . It yields a mixture of 3 : 6- and 6 : 8-dibromomethylcoumarins when brominated, and the 3 : 6 : 8-tribromomethylcoumarin on further bromination. This last compound, when oxidised with permanganate in alkaline solution, gives 3 : 5-dibromosalicylic acid, thereby fixing the position of the bromine atom 3.

3 : 4-Dimethylcoumarin, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CMe} \cdot \text{CMe} \\ \diagdown \quad | \\ \text{O} \quad \text{CO} \end{array}$, prepared by condensing ethyl methyl acetoacetate with phenol, has m. p. 115° , and is isomeric with von Pechmann's 4 : 6-dimethylcoumarin (*Abstr.*, 1885, 56).

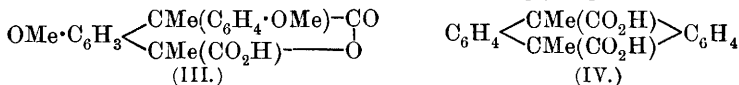
E. F. A.

Comparative Study of the Dehydration of Atrolactic and *p*-Methoxyatrolactic Acids. *p*-Methoxyatropic and Di-*p*-methoxyatropic Acids. J. BOUGAULT (*Compt. rend.*, 1908, 146, 766—769. Compare *Abstr.*, 1902, i, 452).—*p*-Methoxyatrolactic acid

is markedly different from atrolactic acid in its relation to dehydrating agents. Ladenburg found (Abstr., 1883, 670) that atrolactic acid is dehydrated by prolonged boiling with dilute hydrochloric acid, giving atropic acid and a little of Fittig's *isoatropic acid*; the author obtains the same transformation by heating for thirty minutes with concentrated hydrochloric acid on a boiling water-bath. By the very prolonged action (five to six months) of cold hydrochloric acid, however, β -chlorohydratropic acid, $\text{CH}_2\text{Cl}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, is the chief product, together with a small quantity of *isoatropic acid*. Atrolactic acid does not give appreciable quantities of atropic acid when boiled with acetic or very dilute mineral acids. On the other hand, *p*-methoxyatrolactic acid is rapidly dehydrated by boiling with these acids, giving good yields of *p-methoxyatropic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2$, shining spangles, m. p. $119-120^\circ$, which forms a *dibromide*, m. p. 142° . When *p*-methoxyatrolactic acid is left in contact with cold concentrated hydrochloric acid for forty-eight hours, the product is a mixture in almost equal parts of *p*-methoxyatropic acid and a dimolecular condensation derivative of this, called by the author *bis-p-methoxyatropic acid*, $(\text{C}_{10}\text{H}_{10}\text{O}_3)_2$. At the temperature of the water-bath, the latter acid is the sole product, and the reaction is complete in fifteen to twenty minutes. Bis-*p*-methoxyatropic acid has m. p. 215° , and by titration with standard alkali its molecular weight is found to be 356 (calculated as a monobasic acid). Re-titration after boiling with slight excess of alkali gives the result 178 (also calculated as a monobasic acid), indicating that the substance is a lactic acid. Fittig (Abstr., 1881, 425) proposed the formula (I)



for *isoatropic acid*, from which the formula (II) would be deduced for bis-*p*-methoxyatropic acid. The author, however, considers that a direct combination of the $\cdot\text{CH}_2\cdot$ groups is improbable, and prefers the formula (III) for the new acid, and accordingly represents Fittig's



isoatropic acid by (IV), which explains more easily than (I) its oxidation to anthraquinone. E. H.

Tyrosine. JULES ALOY and CHARLES RABAUT (*Bull. Soc. chim.*, 1908, [iv], 3, 391—393).—A study of the action of various reagents on tyrosine. The *hydrobromide* and *hydriodide* of the base, which are both crystalline, are described. Bromine vapour converts the base into dibromotyrosine hydrobromide, but with excess of bromine water an unstable, yellow perbromide is obtained, which is soluble in alkalis (and most organic solvents). Dry chlorine has no action on the base, but in presence of moisture a yellow, unstable, perchlorinated product is formed, which blackens on exposure

to air. No definite derivatives can be obtained by the action of iodine vapour on tyrosine.

Tyrosine suspended in water or dissolved in hydrochloric acid gives, on addition of chlorine water, followed by ammonia solution, a fine red colour. Bromine water may be used in place of chlorine water, but the colour formed is then less intense. Leucine does not give this reaction.

T. A. H.

Catalytic Reactions at High Temperatures and Pressures.

XVI. Reduction of Aromatic Ethers, Esters, and Acids in Presence of Nickel Oxide. WLADIMIR N. IPATIEFF and O. PHILIPPOFF (*Ber.*, 1908, 41, 1001—1007).—Phenyl ether is reduced by hydrogen in presence of nickel oxide at 230°/100 atmospheres in twelve hours, forming *cyclohexane*, *cyclohexanol*, and *cyclohexyl ether*, $O(C_6H_{11})_2$, which is formed also, together with *cyclohexanol*, by reduction of phenol in the same manner, and is obtained as a viscid oil, b. p. 275—277°/760 mm. Ethyl phthalate, when heated with hydrogen and nickel oxide under high pressures, yields methane, carbon dioxide, *o*-toluic acid, phthalic acid, and small amounts of benzoic acid.

Potassium phthalate remains unchanged when mixed with nickel oxide and heated in a current of hydrogen at 300°, or if heated with hydrogen alone under pressure, but, if heated with hydrogen and nickel oxide under pressure at 300°, it is reduced to *trans-cyclohexane-1:2-dicarboxylic acid*, together with small amounts of benzoic acid and methane; the amount of these by-products increases rapidly with the temperature of the reaction. This reduction is recommended as the most convenient method of preparing the *trans-cyclohexanedicarboxylic acid*.

Under the same conditions, potassium benzoate is reduced in nine hours to the extent of 40—50%, yielding potassium *cyclohexanecarboxylate*; at temperatures above 320°, the yield decreases in consequence of increased formation of methane. The *cyclohexanecarboxylic acid* is best prepared by heating sodium benzoate, which is more easily reduced than the potassium salt, with hydrogen and nickel oxide under pressure at 300° for two periods of four hours each.

G. Y.

Phthalides and Meconines. ERIC MERMOD and HUGO SIMONIS (*Ber.*, 1908, 41, 982—985).—The condensation of organo-magnesium compounds with phthalaldehydic acid and opianic acid has been continued (compare Abstr., 1906, i, 32, 303).

α -Ethylphthalide (compare Gottlieb, Abstr., 1899, i, 512) and α -phenylphthalide (Graebe and Juillard, Abstr., 1888, 1095) have been prepared from phthalaldehydic acid.

Anhydro - aa' - dimethylhydrophthalide, $C_6H_4 \begin{smallmatrix} \diagup C(:CH_2) \\ \diagdown CHMe \end{smallmatrix} O$ or

$C_6H_4 \begin{smallmatrix} \diagup CMe \\ | \\ \diagdown CMe \end{smallmatrix} O$, obtained by the action of magnesium methyl iodide on an ethereal solution of α -methylphthalide (Abstr., 1906, i, 32), crystallises from dilute alcohol in colourless needles, m. p. 153° (decomp.) after sintering at 140°.

α-Phenylmeconine, $C_6H_2(OMe)_2 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CHPh \diagup \end{smallmatrix} O$, crystallises from alcohol in glistening prisms, m. p. 112°. When warmed with alkalis, the ring is ruptured, but closes again on the addition of acid. The meconine dissolves in cold concentrated sulphuric acid to a colourless solution, which assumes a purple colour when warmed.

Magnesium alkyl or aryl bromides do not react with phthalaldehydic or opianic acid. Bromoalkylmeconines can be obtained either by the condensation of Grignard's compound with bromo-opianic acid or by the bromination of the alkylmeconines. *Bromo-α-methylmeconine*, $C_6HBr(OMe)_2 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CHMe \diagup \end{smallmatrix} O$, forms colourless plates, m. p. 77°, and the corresponding *ethyl* compound has m. p. 79°.

Nitro-α-ethylmeconine, $NO_2 \cdot C_6H(OMe)_2 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CHEt \diagup \end{smallmatrix} O$, obtained by the action of fuming nitric acid on ethylmeconine, crystallises from alcohol in yellow plates, m. p. 103.5°. When reduced, it yields *amino-α-ethylmeconine*, $C_{12}H_{15}O_4N$, in the form of colourless prisms, m. p. 158°. The *hydrochloride*, $C_{12}H_{15}O_4N \cdot HCl$, forms sparingly soluble, glistening needles, m. p. 196° (decomp.). The *platinichloride* forms a brown precipitate, which decomposes at 172°, and the *aurichloride* a dark green precipitate, decomposing at 200°.

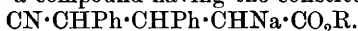
J. J. S.

Synthesis of Certain Aromatic Succinic Acids. SAMUEL AVERY and FRED W. UPSON (*J. Amer. Chem. Soc.*, 1908, 30, 600—604).—In order to compare the $\alpha\beta$ -diphenylglutaric acid obtained by Avery and McDole (compare following abstract) with its isomeride, *α-phenyl-β-benzylsuccinic acid*, $CO_2H \cdot CHPh \cdot CH(CH_2Ph) \cdot CO_2H$, the latter was prepared by the condensation of ethyl sodiobenzylmalonate with ethyl bromophenylacetate; it crystallises in slender, white needles, m. p. 176°; the *silver* salt is a white, amorphous precipitate. The investigation was then extended to see if sodium benzyl cyanide could be made to condense with aldehyde cyanohydrins in the same way as ethyl sodiocyanoacetate, as described by Higson and Thorpe (*Trans.*, 1906, 89, 1455). This was found to be the case; thus the nitrile of $\alpha\beta$ -diphenylsuccinic acid (compare Chalaney and Knoevenagel, *Abstr.*, 1892, 619) was obtained from sodium benzyl cyanide and benzaldehyde cyanohydrin. In some cases, one of the cyano-groups undergoes saponification during the reaction. This seems to depend on the nature of the adjacent groups; for example, *β-cyano-β-phenyl-α-isopropylpropionic acid*, $CN \cdot CHPh \cdot CHPr^i \cdot CO_2H$, is formed by condensing sodium benzyl cyanide with *isobutaldehyde* cyanohydrin; it forms white, feathery crystals, m. p. 126°, and when heated with strong hydrochloric acid under pressure is converted into *β-phenyl-α-isopropylsuccinic acid*, $CO_2H \cdot CHPr^i \cdot CHPh \cdot CO_2H$, crystallising in colourless, microscopic plates, m. p. 178°.

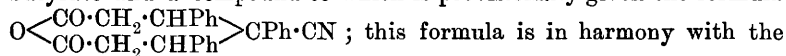
W. H. G.

Action of Sodium Benzyl Cyanide with Cinnamic Ester. SAMUEL AVERY and GUY R. MCDOLE (*J. Amer. Chem. Soc.*, 1908, 30, 595—600).—The action of benzyl cyanide on ethyl cinnamate was studied with the object of preparing certain aryl glutaric acids. It

was thought probable that the reaction would take place in a manner similar to that observed by Michael (Abstr., 1887, 672) in the action of ethyl sodioacetoacetate on the esters of unsaturated acids, namely, in the formation of a compound having the constitution



It was found, however, that the ester had undergone saponification, the two principal products formed being sodium γ -cyano- β -diphenylbutyrate and a compound to which is provisionally given the formula



observed facts, except in the following: the compound appears to be unchanged when boiled with sodium carbonate or ammonia in aqueous or alcoholic solution, and, although it is converted into a salt when boiled with alcoholic potassium hydroxide, the acid liberated from the salt has resisted all attempts to reconvert it into an anhydride. γ -Cyano- β -diphenylbutyric acid, $\text{CN} \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by the interaction of benzyl cyanide and ethyl cinnamate in the presence of solid sodium methoxide, crystallises in glistening, white needles, m. p. 161.5° . When heated with strong hydrochloric acid in a sealed tube at 150° for three hours, it is converted into $\alpha\beta$ -diphenylglutaric acid, $\text{CO}_2\text{H} \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallising in needles, m. p. $223-224^\circ$; the silver salt, $\text{C}_{17}\text{H}_{14}\text{O}_4\text{Ag}_2$, was prepared. The anhydride could not be obtained; the anilide, $\text{C}_{23}\text{H}_{21}\text{O}_3\text{N}$, crystallises in flat needles with a pearly lustre, m. p. $230-232^\circ$. The substance, $\text{CN} \cdot \text{CPh}(\text{CHPh} \cdot \text{CH}_2 \cdot \text{CO})_2\text{O}$ (?), is obtained when a mixture of benzyl cyanide and dry sodium methoxide heated to 140° is added to hot ethyl cinnamate, the whole being kept at 140° for ten minutes. It crystallises in long, obliquely pointed plates, m. p. $231-232^\circ$; when heated with a strong alcoholic potassium hydroxide solution, it is converted into the potassium salt of an acid; the free acid, $\text{C}_{26}\text{H}_{23}\text{O}_4\text{N}$, crystallises in rectangular plates, m. p. 213° ; the silver salt is a white, insoluble powder.

W. H. G.

Marrubiin. HENRY M. GORDIN (*J. Amer. Chem. Soc.*, 1908, 30, 265—271).—Marrubiin, the bitter constituent of horehound (*Marrubium vulgare*), was first investigated by Harms, and later by Kromayer, Hertel, Morrison, and Matusow.

Marrubiin, $\text{C}_{21}\text{H}_{28}\text{O}_4$, has m. p. $154.5-155.5^\circ$, b. p. $297-299^\circ/15 \text{ mm.}$, $[\alpha]_D + 45.68^\circ$, and when crystallised slowly from alcohol forms large, monoclinic prisms [$a : b : c = 1.5551 : 1 : 0.885$; $\beta = 61.17^\circ$], but, when crystallised rapidly, forms flat, tabular prisms, which also belong to the monoclinic system. The compound does not contain any methoxyl groups, and does not decolorise bromine solution. It has a bitter taste, a neutral reaction, and does not contain hydroxyl or carbonyl groups. When boiled with alcoholic potassium hydroxide, it is converted into *potassium marrubate*.

Marrubic acid, $\text{C}_{20}\text{H}_{29}\text{O}_3 \cdot \text{CO}_2\text{H}$, m. p. $173-174^\circ$ and $[\alpha]_D + 7.86^\circ$, forms long, white, silky needles, and when heated at $190-200^\circ$ under 15 mm. pressure is reconverted into marrubiin. The same change can be brought about by heating the acid at 50° with acetic anhydride containing a trace of zinc chloride, or by boiling it with alcoholic

hydrochloric acid. The acid reduces ammoniacal silver nitrate and Fehling's solution. The *barium* salt is described. The *ethyl* ester, m. p. 87° , forms lustrous scales, and, when heated at 100° under 28 mm. pressure, is converted into marrubiin.

The results of the investigation indicate that marrubiin is a lactone, $\text{O} \begin{smallmatrix} \diagup \text{C}_{20}\text{H}_{28}\text{O}_2 \\ \diagdown \text{CO} \end{smallmatrix}$, behaving like a γ -lactone in taking up a molecule of water to form a hydroxy-acid, marrubic acid, $\text{OH} \cdot \text{C}_{20}\text{H}_{28}\text{O}_2 \cdot \text{CO}_2\text{H}$.
E. G.

Synthesis of Optically Active Dibenzylaspartic and Dibenzylmalamic Acids. OSCAR LUTZ (*Ber.*, 1908, 41, 841—847). —Fischer and Raske (*Abstr.*, 1907, i, 381) have shown that under certain conditions *d*-aspartic acid is formed from *l*-bromosuccinic acid; the chief product, however, is malamic acid. It appears on further study of this reaction that, in addition to the influence of temperature, the strength and constitution of the base employed have also to be taken into account. By the action of dibenzylamine, a weaker base, on *l*-chloro- or -bromo-succinic acid, *d*-dibenzylaspartic acid is formed to the extent of 65—70%, and *l*-dibenzylmalamic acid to the extent of 8—15%. The former, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, forms thread-like, matted needles, m. p. 152 — 153° , is relatively stable towards heat and barium hydroxide, and forms a *silver* salt, $\text{C}_{18}\text{H}_{17}\text{O}_4\text{NAg}_2$. In ethyl alcohol, $[\alpha]_D = 0^{\circ}$; in sodium hydroxide solution, $[\alpha]_D = +23.2^{\circ}$; in presence of benzylamine, it has $[\alpha]_D + 43.8^{\circ}$ in ethyl alcohol, $+4^{\circ}$ in methyl alcohol, -10° in acetone, and -5.2° in acetic acid.

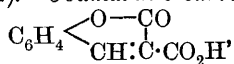
l-Dibenzylmalamic acid, $\text{CO}_2\text{H} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}(\text{C}_7\text{H}_7)_2$, forms minute prisms, m. p. 169 — 170° (decomp.); it loses water when heated, and forms an optically inactive unsaturated compound. It has $[\alpha]_D - 61.6^{\circ}$ in ethyl alcohol or -26.4° in presence of benzylamine.

E. F. A.

Action of Ozone on Santonin. GUIDO BARGELLINI and CESARE GIALDINO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 248—249). —The action of ozone on a chloroform solution of santonin or on a faintly alkaline solution of sodium santoninate yields an acid apparently identical with the ketonic acid, $\text{C}_{15}\text{H}_{20}\text{O}_7$, obtained by Angeli and Marino (*Abstr.*, 1907, i, 321) by the oxidation of santonin acid with potassium permanganate.

T. H. P.

Preparation of Coumarincarboxylic Acid. HAARMANN and REIMER (*D.R.-P.* 189252). —*Coumarin-3-carboxylic acid*,



m. p. 187 — 188° , was obtained by condensing cyanoacetic acid and salicylaldehyde in alkaline solution to *o*-hydroxybenzylidenecyanoacetic acid, and hydrolysing this intermediate product with steam and concentrated hydrochloric acid.

G. T. M.

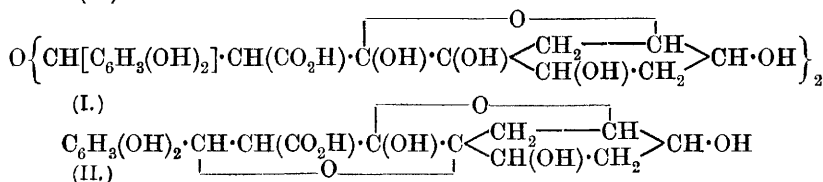
Coffee. II. K. GORTER (*Annalen*, 1908, 359, 217—244. Compare this vol., i, 186). —In continuation of his investigation of the constituents of coffee extract, the author has studied the decomposition

products of chlorogenic acid, and describes some further new substances obtained from the coffee beans.

When treated with aqueous potassium hydroxide at the ordinary temperature, chlorogenic acid yields caffeic and quinic acids, but, if boiled with dilute mineral acids, decomposes to the extent of 70%, forming carbon dioxide and a *product*, which is reddish-violet with blue fluorescence in solution, and to the extent of 30% is hydrolysed to caffeic and quinic acids. The colour reactions of these two acids, and the *zinc*, $(C_7H_{11}O_6)_2Zn$, and *calcium*, $(C_7H_{11}O_6)_2Ca \cdot 10H_2O$, salts of quinic acid, are described.

The action of acetic anhydride, containing small amounts of sulphuric acid, on chlorogenic acid at the ordinary temperature leads to the formation of *penta-acetylhemichlorogenic acid*, $C_{16}H_{13}O_9Ac_5$, which crystallises from dilute alcohol in white needles, m. p. $180.5-181^\circ$, and has a bitter taste; the *aniline* salt, $C_{16}H_{13}O_9Ac_5 \cdot NH_2Ph$, white crystals, m. p. $142-143^\circ$. On hydrolysis with acids or alkalis, the penta-acetyl compound yields *hemichlorogenic acid*; this is isolated as the *aniline* salt, $C_{16}H_{18}O_9 \cdot NH_2Ph$, crystallising in white needles, m. p. 173° . A mixture of this salt with the *aniline* salt of chlorogenic acid, $C_{32}H_{38}O_{19} \cdot 2NH_2Ph$, m. p. 174° , has m. p. $165-166^\circ$. The *benzidine* salt, needles, m. p. 161° , is more readily soluble than the corresponding chlorogenate.

The consideration of these facts leads to the formulation of the annexed constitutions for chlorogenic acid (I) and hemichlorogenic acid (II):



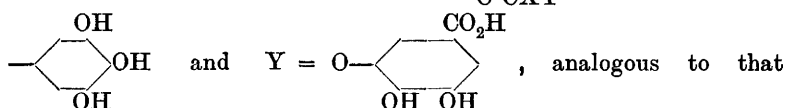
Addition of alcohol to the first extract of Liberian or Arabian coffee beans precipitates a *pectin substance*, $[\alpha]_D + 15^\circ$, which has a feeble acid reaction, dissolves slowly in water, when heated with dilute mineral acids yields galactose and a pentose, and on oxidation with nitric acid forms mucic acid.

Coffalic acid, $C_{34}H_{54}O_{15}$, is obtained on evaporation of the mother liquor from the preparation of potassium-caffeine chlorogenate; it crystallises in colourless, rhombic prisms, m. p. 255° , has a sweet taste, forms *precipitates* with silver nitrate, copper sulphate, and lead acetate and ammonia, and on hydrolysis with alkalis or acids yields *isovaleric acid* and an amorphous *substance*, which commences to soften at 160° , m. p. about 255° .

Liberian coffee beans contain an *oxydase*, which gives yellow, changing to yellowish-green and reddish-brown, coloration with potassium caffeine chlorogenate, and is therefore the cause of the colour gradually acquired by the colourless beans after plucking; the oxydase is destroyed at 70° , and gives a coloration with guaiacol solutions resembling, but less intense than, that given by laccase.

The caffetannic acid, described by previous authors, is a mixture of chlorogenic and coffalic acids with other substances. G. Y.

Preliminary Note on the Constitution of Gallotannic Acid and of Tannins in General. STEWART J. LLOYD (*Chem. News*, 1908, 97, 133).—From molecular weight determinations of crystalline compounds of gallotannic acid, notably the penta-acetyl derivative, it is concluded that natural gallotannic acid is composed of three digallic acid groups united to each other through three oxygen atoms to form a six-membered ring of the type $CXY \begin{smallmatrix} \diagup O \cdot CXY \\ \diagdown O \cdot CXY \end{smallmatrix} > O$, in which X =



found in trithio-ketones and trithio-aldehydes. Such a configuration admits of an inactive *cis*-form as well as the active *trans*-form which is assigned to natural gallotannic acid. P. H.

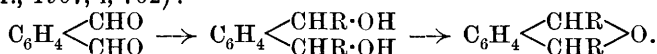
Catalytic Reactions at High Temperatures and Pressures.

XIV. Reduction of Benzaldehyde and Benzyl Alcohol in Presence of Iron. WLADIMIR N. IPATIEFF (*Ber.*, 1908, 41, 993—995. Compare Abstr., 1907, i, 5, 827).—It was shown previously that aliphatic aldehydes and ketones are reduced to the corresponding alcohols by hydrogen in presence of iron at high temperatures and pressures, and that, on the other hand, aromatic alcohols, aldehydes, and ketones under similar conditions, but in presence of nickel oxide, yield *cyclo*polymethylenes. It is now found that when heated with hydrogen in an iron tube for twelve hours at 280°/100 atmospheres, benzaldehyde yields water, toluene, dibenzyl, and resins. It is considered that the reduction must lead in the first place to the formation of benzyl alcohol; part of this is reduced directly to toluene, whilst another part forms water and benzyl ether, which on further reduction yields toluene and dibenzyl. In agreement with this view, it is found that benzyl alcohol under similar conditions yields toluene, benzaldehyde, and dibenzyl. Moreover, whilst reduction of the alcohol in a copper tube leads to the formation of toluene and small amounts of dibenzyl, benzaldehyde, which as previously shown does not form benzyl alcohol when heated with hydrogen in presence of copper, under these conditions also does not yield dibenzyl. In the absence of hydrogen, benzyl alcohol decomposes when heated in an iron tube at 400°, forming hydrogen and benzaldehyde, which partly decomposes further to benzene and carbon monoxide and partly is reduced by the hydrogen, forming toluene and dibenzyl. G. Y.

Reaction between Potassium Cyanide and *o*-Nitrobenzaldehyde. S. EKECRANTZ and A. AHLQVIST (*Ber.*, 1908, 41, 878—881).—The authors have examined the action of potassium cyanide on *o*-nitrobenzaldehyde under Popovici's conditions (Abstr., 1907, i, 628), and conclude that her so-called 2:2'-dinitrobenzoin

consists of *o*-nitrosobenzoic acid and *o*-azoxybenzoic acid, and that her 2 : 2'-dinitrobenzil is *o*-nitrobenzoic acid. C. S.

Action of Grignard Compounds on *o*-Phthalaldehyde. F. NELKEN and HUGO SIMONIS (*Ber.*, 1908, 41, 986—989).—*o*-Phthalaldehyde condenses with an excess of magnesium alkyl iodides, yielding *o*-dihydroxyalkylbenzenes, which when distilled form alkyl derivatives of isocoumaran or 1 : 3-dialkylphthalans (compare Ludwig, *Abstr.*, 1907, i, 702):



*Di- α -hydroxy-*o*-diethylbenzene*, $\text{C}_6\text{H}_4(\text{CHMe}\cdot\text{OH})_2$, is a yellow, viscid oil, which solidifies when placed in a freezing mixture. It dissolves readily in practically all solvents, and when distilled under reduced pressure yields 1 : 3-dimethylphthalan as a pale yellow oil, b. p. 122°/50 m.m.

*Di- α -hydroxy-*o*-dipropylbenzene*, $\text{C}_6\text{H}_4(\text{CHEt}\cdot\text{OH})_2$, is an oil, and the corresponding 1 : 3-diethylphthalan has b. p. 137°/50 mm.

1 : 3-Diphenylphthalan has b. p. 240°/14 mm., and forms a limpid, yellowish-red oil. J. J, S.

[Preparation of Vanillin from Guaiacol] A. ROESLER (*D.R.-P.* 189037).—The formation of an aldimide compound does not occur with guaiacol, hydrogen cyanide, and hydrochloric acid except when the reagents are brought together in the capillary interstices of infusorial earth. This earth is mixed with aqueous zinc chloride and heated to dryness, then treated with a benzene solution of guaiacol and hydrogen cyanide, and saturated with hydrogen chloride. The intermediate aldimide hydrochloride, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}\cdot\text{NH}\cdot\text{HCl}$, is decomposed with water, and the vanillin extracted with ether and purified by means of its bisulphite compound. G. T. M.

Synthesis of Trimethylgallaldehyde. FERDINAND MAUTHNER (*Ber.*, 1908, 41, 920—925).—The close relationships existing between gallaldehydes and some natural products suggested the above synthesis. Trimethylgallyl chloride (Perkin and Weizmann, *Trans.*, 1906, 89, 1655) was first condensed with hydrogen cyanide in ethereal solution in the presence of pyridine to form 3 : 4 : 5-trimethoxybenzoyl cyanide, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, which crystallises in yellow needles from light petroleum; m. p. 136—137°. It is hydrolysed on warming with dilute acids or alkalis to trimethylgallic acid, but the cyanide and hydrochloric acid (D 1·19) at the ordinary temperature after ten days yield a mixture of (1) trimethoxyphenylglyoxylamide, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, in small amount, crystallising from benzene in colourless needles, m. p. 149—150°, which on heating with acids or alkalis give trimethylgallic acid, ammonia and carbon monoxide, and (2) a good yield of trimethoxyphenylglyoxylic acid, $\text{C}_{11}\text{H}_{12}\text{O}_6$, separating from benzene in colourless needles, m. p. 155—156°; the phenylhydrazone, $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_2$, forms yellow needles, m. p. 213—214°.

Bouveault's method of converting this α -ketocarboxylic acid into the aldehyde by heating with aniline and then hydrolysing the anil

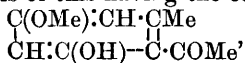
(Abstr., 1896, i, 649) was used. *Trimethylgallaldehyde*, $C_{10}H_{12}O_4$, crystallises from light petroleum in colourless leaflets, m. p. $74-75^\circ$. It has all the usual properties of an aldehyde; its *p*-nitrophenyl-hydrazone, $C_{16}H_{17}O_5N_3$, forms red needles, m. p. $201-202^\circ$, and the semicarbazone, $C_{11}H_{15}O_4N_3$, crystallises from water in colourless needles, m. p. $219-220^\circ$. W. R.

Formation of Mixtures of Isomerides of Constant Melting Point in Friedel and Crafts' Reaction. GUSTAVE PERRIER and H. CAILLE (*Compt. rend.*, 1908, 146, 769—770).—One of the authors (Perrier, *Thèse*, Paris, 1896) has described previously a method of separating the mixtures of isomeric ketones obtained by Friedel and Crafts' reaction, based on the differences in stability and solubility in carbon disulphide of their additive compounds with aluminium chloride. To effect a good separation by this method, the crystals first deposited must be collected separately, and when decomposed with water these give one isomeride in a pure state. If in the preparation of the phenyl naphthyl ketones this precaution is not observed, the product consists, not of the β -isomeride, but of a substance, m. p. 54° (sharp), also resulting from Friedel and Crafts' reaction as ordinarily carried out. This substance by (1) recrystallisation from light petroleum and mechanical separation of the crystals deposited, and (2) preparation of the picrates, can be separated into the α - (m. p. 75°) and the β -isomerides (m. p. 82°), and appears to be a eutectic mixture of the two. E. H.

isoOrcacetophenone Dimethyl Ether. JOSEF TAMBOR [and, in part, ST. BARANOWSKI, A. COMTESSE, and W. TOMI] (*Ber.*, 1908, 41, 793—798. Compare this vol., i, 358).—A substance, obtained occasionally as a by-product in the preparation of orcacetophenone dimethyl ether, is now found to be an isomeride. When heated with methyl benzoate, *m*-methoxybenzoate, or veratrate, and sodium, it forms substituted benzoylacetophenones, which are isomeric with those obtained under the same conditions from orcacetophenone dimethyl ether, and are converted in the same manner into substituted methylflavones. Hence the *isoorcacetophenone dimethyl ether* must have the constitution

$$\begin{array}{c} C(OMe):CH \cdot CMe \\ | \\ CH:C(OMe) \cdot C \cdot COMe \end{array}$$

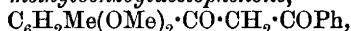
It is prepared by the action of acetyl chloride and aluminium chloride on orcinol dimethyl ether in presence of small amounts of glacial acetic acid, or of acetic anhydride and aluminium chloride on cooled orcinol dimethyl ether; it crystallises on evaporation of the light petroleum filtrate from orcacetophenone dimethyl ether in white needles, m. p. 48° . *isoOrcacetophenone monomethyl ether*, formed together with the dimethyl ether, must be a product of the hydrolysis of this having the constitution



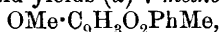
since in substituted acetophenones a methoxyl group in the ortho position is always more easily hydrolysed than one in the para position. The monomethyl ether crystallises in white needles, m. p. 79° , and is

converted into the dimethyl ether by the action of methyl sulphate and alkalis.

2 : 4-Dimethoxy-6-methylbenzoylacetophenone,

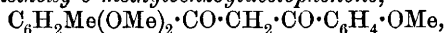


crystallises in white needles, m. p. 76—77°, and when boiled with concentrated hydriodic acid yields (a) 7-methoxy-5-methylflavone,



which crystallises in colourless needles, m. p. 115°, and is insoluble in alkalis, and (b) 7-hydroxy-5-methylflavone, $\text{OH} \cdot \text{C}_9\text{H}_3\text{O}_2\text{PhMe}$, which forms white needles, m. p. 297°, dissolves in dilute sodium hydroxide to a slightly yellow, or in concentrated sulphuric acid to a colourless, solution with blue fluorescence, and is converted by methyl sulphate and alkalis into 7-methoxy-5-methylflavone. 7-Acetoxy-5-methylflavone, $\text{C}_{18}\text{H}_{14}\text{O}_4$, forms colourless needles, m. p. 147°.

2 : 4 : 3'-Trimethoxy-6-methylbenzoylacetophenone,

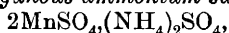


prepared from isooracetophenone dimethyl ether and methyl *m*-methoxybenzoate, crystallises in colourless prisms, m. p. 107°. 7 : 3'-Dihydroxy-5-methylflavone, $\text{OH} \cdot \text{C}_9\text{H}_3\text{O}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, colourless needles, m. p. 260°.

2 : 4 : 3' : 4'-Tetramethoxy-6-methylbenzoylacetophenone, $\text{C}_{20}\text{H}_{22}\text{O}_6$, prepared from the isodimethyl ether and methyl veratrate, crystallises in white needles, m. p. 134°. 7 : 3' : 4'-Trihydroxy-5-methylflavone, $\text{C}_{16}\text{H}_{12}\text{O}_5$, greenish-yellow needles, m. p. 258°. The triacetate, $\text{C}_{22}\text{H}_{18}\text{O}_8$, white needles, m. p. 188°.

The di-, tri-, and tetra-methoxymethylbenzoylacetophenones give red colorations with alcoholic ferric chloride. The di- and tri-hydroxymethylflavones form yellow or greenish-yellow solutions in concentrated sulphuric acid. G. Y.

Preparation of Aldehydes and Quinones. WALTHER LANG (D.R.-P. 189178).—*Manganous ammonium sulphate*,

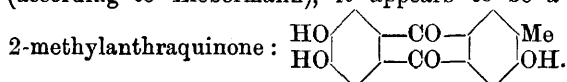


is obtained from a hot acid solution containing excess of ammonium sulphate; it forms yellow, anhydrous crystals, and is decomposed by water into the double salt, $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, and ammonium sulphate. The new double salt, dissolved in dilute sulphuric acid, is electrolysed into manganic ammonium alum, a lead-lined electrolytic cell serving as the anode. When benzene and toluene are oxidised with this manganic salt at 50°, *p*-benzoquinone and benzaldehyde are produced, whilst naphthalene, anthracene, and phenanthrene yield their respective quinones. G. T. M.

Trimethyl Ethers of Emodin from Frangula and from Aloes.

OTTO A. OESTERLE and ED. TISZA (*Arch. Pharm.*, 1908, 246, 112—116).—The above emodins have been methylated (with methyl sulphate in aqueous solution) with a view to determining whether any of the hydroxyl groups are in the α -position to a carbonyl group, and thus resist methylation (as found by Kostanecki and Drehe. Frangula-emodin readily gives a trimethyl ether, $\text{C}_{15}\text{H}_9\text{O}_2(\text{OMe})_3$, yellow needles, m. p. 225°, and, since this emodin is derived from β -methylantracene

(according to Liebermann), it appears to be a 3 : 6 : 7-trihydroxy-



The isomeric *trimethyl ether* of emodin from aloes forms orange-coloured needles, m. p. 163°, and is only formed very slowly ; from this and from the tinctorial properties, it is deduced that two, at least, of the hydroxyl groups are in α -positions. The substance thus appears to be connected with chrysazin. G. B.

Preparation of Dimethyl Dimethylene Ether. K. A. LINGNER (D.R.-P. 189331).—Dimethyl dimethylene ether, $O(CH_2 \cdot O \cdot C_{10}H_{19})_2$, formerly obtained from menthol, formaldehyde, and a mineral acid at low temperatures, has now been prepared by adding *s*-dichloromethyl ether to a toluene solution of sodium menthyl oxide, the yield being 76% of the calculated. G. T. M.

Preparation of Bornyl Borate. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 188703).—*Bornyl borate*, $B(OC_{10}H_{17})_3$, a white, tasteless powder, is prepared by heating borneol with boric acid or anhydride in xylene, or by melting together at 250° bornyl acetic anhydride and borneol. G. T. M.

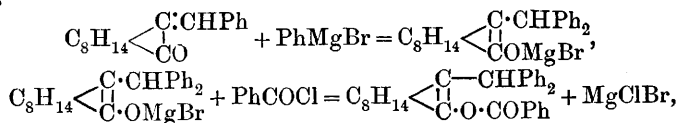
Preparation of *iso*Bornyl Esters of the Fatty Acids from Pinene Hydrochloride or Hydrobromide. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 189261).—*iso*Bornyl acetate results from the heating together of pinene hydrochloride, acetic acid, zinc chloride, and aluminium hydroxide or magnesium oxide. The presence of zinc chloride is essential ; in its absence, a portion of the pinene derivative remains unchanged. G. T. M.

Dynamic Isomerism. HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, JAMES J. DOBBIE, ARTHUR LAPWORTH, MARTIN O. FORSTER, and CECIL H. DESCH (*Brit. Assoc. Report*, 1907, 77, 270—272).—This report deals mainly with the influence of impurities on the velocity of mutarotation of nitrocamphor. T. H. P.

An Isomeride of Diphenylcamphorylmethane and the Conditions of its Formation. ALBIN HALLER and E. BAUER (*Compt. rend.*, 1908, 146, 718—722).—When diphenylcamphorylmethylene is reduced by sodium amalgam in acid-alcoholic solution, diphenylcamphorylmethane, m. p. 106—107°, is formed (*Abstr.*, 1906, i, 441), but, if the reduction is carried out in alkaline alcoholic solution, an *isomeride*, m. p. 136°, is obtained. The compound described previously is, moreover, transformed into its isomeride when boiled with alcoholic potash, or when heated with sodamide in the presence of toluene.

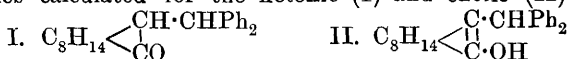
The product of the action of magnesium phenyl bromide on benzylidenecamphor reacts with benzoyl chloride, as has been described for

the benzylideneacetophenone derivative (Kohler Abstr., 1904, i, 595), thus :



forming *diphenylcamphorylmethane benzoate*. The latter compound, whether hydrolysed by boiling alcoholic potash, by cold sodium ethoxide solution, by ammonia at 180°, or by concentrated hydrochloric acid at 150°, invariably gives rise to the isomeride, m. p. 136—137°. But the benzoyl derivative cannot be prepared by the direct action of benzoyl chloride on either of the modifications of diphenylcamphorylmethane.

The observed molecular refractive powers of the isomerides, m. p. 106—107° and 136—137°, are 98·39 and 98·87 respectively, whilst the values calculated for the ketonic (I) and enolic (II) forms of



diphenylcamphorylmethane are 97·35 and 98·29. But, although the observed values approximate to the latter figure, it cannot be deduced that the isomerides have the enolic form, since it has been shown (Haller and Muller, Abstr., 1900, i, 182) that introduction of aromatic groups into the camphor molecule increases the molecular refractive power by as much as one unit.

It is stated in conclusion that hitherto no reaction or physical measurement has elucidated the constitution of these two isomeric compounds. E. H.

Preparation of Normal Alkyl Camphorates. J. D. RIEDEL (D.R.-P. 189840).—The methods hitherto employed have not given a satisfactory yield of dialkyl camphorates, as the normal ester was always mixed with the acid ester. It has now been found that the use of alkyl sulphates or aryl sulphonates readily leads to the normal ester.

Methyl *d*-camphorate was obtained by adding methyl sulphate to an alkaline solution of *d*-camphoric acid.

Ethyl *d*-camphorate was prepared either by adding ethyl sulphate to *d*-camphoric acid dissolved in alcoholic sodium ethoxide, or by mixing together ethyl benzenesulphonate and an aqueous solution of potassium *d*-camphorate. G. T. M.

Dimethylcampholide. GUSTAV KOMPPA (*Ber.*, 1908, 41, 1039—1044).—This investigation had as its object the preparation of *αα*-dimethylcamphor, in order that the properties of this compound might be contrasted with those of fenchone. If the latter compound has the constitution assigned to it by Semmler, then the two substances should closely resemble one another in chemical properties. In order to obtain the dimethylcamphor, dimethylcampholide was first prepared; it was then thought possible that by treating this with

potassium cyanide and hydrolysing the cyanide formed, that dimethylhomocamphoric acid would be obtained, from which dimethylcamphor could be prepared by the dry distillation of the calcium salt. This, however, could not be realised, since dimethylcampholide, when heated with potassium cyanide, yields an acid isomeric with dimethylcampholide, instead of the desired cyanide.

Dimethylcampholide, $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \text{---} \text{CMe}_2 \\ | \quad \quad \quad \diagup \text{CMe}_2 \quad \diagdown \text{O} \\ \text{CH}_3 \cdot \text{CMe} \text{---} \text{CO} \end{array}$, is prepared by treating

with dilute sulphuric acid the additive product formed by acting on camphoric anhydride with magnesium methyl iodide in ether; it crystallises in slender, white needles, m. p. 83.5–85°. When heated alone in a sealed tube at 285–300° or with potassium cyanide at 275–290°, or with 50% aqueous potassium hydroxide solution under pressure at 285–295°, it is converted into an unsaturated monobasic

acid, which probably has the formula $\begin{array}{c} \text{CH}_2\text{---CH---CMe:CH}_2 \\ | \qquad \qquad \qquad \text{>CMe}_2 \\ \text{CH}_3\cdot\text{CMe---CO}_2\text{H} \end{array}$ or

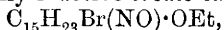
$$\begin{array}{c} \text{CH}_2 \cdot \text{C} \equiv \text{CMe}_2 \\ | \\ \text{CH}_3 \cdot \text{CMe} \text{---} \text{CO}_2\text{H} \end{array} \quad ; \text{ it crystallises in bent needles, m. p. } 68.5\text{--}70.5^\circ;$$

the ammonium salt crystallises in glistening, white leaflets. The acid decolorises bromine water and potassium permanganate solution, and is reconverted into dimethylcampholide by passing dry hydrogen chloride into its solution in absolute ether. W. H. G.

Sesquiterpene from Oleum Cadinum. IWAN SCHINDELMEISER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 181—184. Compare Lepeschkin, this vol., i, 278).—The sesquiterpene described by Lepeschkin is considered to be a mixture of a sesquiterpene described by Träger and Feldmann (*Abstr.*, 1899, i, 376) with considerable quantities of cadinene; and the isomeric sesquiterpene obtained by treating Lepeschkin's substance with hydrogen iodide is not identical with humulene, but consists of a mixture of tetrahydrocadinene, cadinene, and an optically inactive sesquiterpene. Z. K.

Sesquiterpenes. II. ERNST DEUSSEN and ARNOLD LEWINSOHN (*Annalen*, 1908, **359**, 245—261. Compare Abstr., 1907, i, 945).—**1. Caryophyllene Series.**—It is now found that, on repeated distillation, caryophyllene yields two hydrocarbons, one of which has b. p. 132—134°/16 mm., $[\alpha]_D^{20} - 4.67^\circ$, $D^{20} 0.90346$, $n_D^{20} 1.49973$, and yields 20.8% of nitrosochloride and 8.2% of blue nitrosite, whilst the other has b. p. 128—128.5°/17 mm., $[\alpha]_D^{17} - 23.57^\circ$, $D^{17} 0.91034$, $n_D^{17} 1.49899$, and yields only traces of nitrosochloride and 0.5% of nitrosite. This hydrocarbon is not identical with the sesquiterpene, b. p. 123—124°/14 mm., previously described (*loc. cit.*), as that forms 25% of nitrosochloride. A further fraction obtained from caryophyllene has $[\alpha]_D - 8^\circ$ to -9.6° , and gives 4.5—4.0% of nitrosochloride and 19.5—22% of nitrosite. The conclusion is drawn that the caryophyllenes, described in the literature, are mixtures of inactive caryophyllene with considerable amounts of a levorotatory hydrocarbon.

α-Caryophyllene nitrosobromide, $C_{15}H_{24}ONBr$, prepared by the action of ethereal hydrogen bromide on a mixture of caryophyllene, ethyl nitrite, ethyl acetate, and alcohol at -20° , separates from chloroform in crystals, m. p. $144-145^{\circ}$ (decomp.), is optically inactive, and when heated with sodium methoxide yields *i-α-nitrosocaryophyllene*, m. p. 116° . With bromine in carbon tetrachloride solution, this forms an *additive* compound, which, on recrystallisation from boiling alcohol, is converted into the optically inactive *bromo-ethoxy-compound*,



crystallising in colourless needles, m. p. $185-186^{\circ}$ (decomp.).

Caryophyllene nitrosate, m. p. 130.5° , is now found to be optically active, having $[\alpha]_D +56.91^{\circ}$. It is formed together with a *substance* crystallising in rosettes, m. p. $156-157^{\circ}$, by the action of chromic acid, equivalent to three atoms of oxygen, on the blue nitrosite in glacial acetic acid solution. When boiled with alcohol, the blue nitrosite yields a dicyclic hydrocarbon, $C_{15}H_{24}$, b. p. $125-125.5^{\circ}/14.5$ mm., $D^{19} 0.89941$, $[\alpha]_D^{19} -26.174^{\circ}$, $n_D^{19} 1.49665$, which is identical with the sesquiterpene, b. p. $123-124^{\circ}/14.5$ mm., previously described (*loc. cit.*), and forms two isomeric nitrosochlorides; the one of these has m. p. 122° , $[\alpha]_D +14.71^{\circ}$, and the other, m. p. 146° , $[\alpha]_D -33.69^{\circ}$. Both nitrosochlorides react with benzylamine, forming β -caryophyllenenitrol-benzylamine, m. p. $172-173^{\circ}$.

When the hydrocarbon, b. p. $123-124^{\circ}/14.5$ mm., is treated with nitrosyl chloride, the filtrate from the resulting nitrosochloride contains a tricyclic hydrocarbon, $C_{15}H_{24}$, b. p. $132-134^{\circ}/15$ mm., $D^{18} 0.9310$, $[\alpha]_D -22.28^{\circ}$, $n_D^{18} 1.50085$. This forms a white, crystalline *nitrosite*, m. p. 175° .

Clovene, prepared by Wallach and Walker's method (Abstr., 1893, i, 102) for the purpose of comparison with the preceding hydrocarbon, is obtained in two fractions: b. p. $131-139^{\circ}/15.5$ mm., $D^{19} 0.92223$, $\alpha +1.30^{\circ}$ (100 mm. tube), $n_D^{19} 1.4740$, and b. p. $139-143^{\circ}/15.5$ mm., $D^{19} 0.92786$, $\alpha +2.75^{\circ}$ (100 mm. tube), $n_D^{19} 1.50085$, respectively. It does not form a nitrosite, and is probably a mixture.

When oxidised with an amount of potassium permanganate, equivalent to four atoms of oxygen in dilute aqueous solution, caryophyllene, $[\alpha]_D -14^{\circ}$, obtained from clove oil, yields a *substance*, $C_{15}H_{22}O_4$, which crystallises in needles and leaflets, m. p. 120.5° , is strongly laevorotatory, has a persistent bitter taste, and appears to be derived from the laevorotatory hydrocarbon.

II. *Cadinene*.—If a current of chlorine is passed through a cooled solution of *l-cadinene* dihydrochloride exposed to sunlight, hydrogen chloride is evolved, and, on evaporation of the product, a white, sandy powder, $C_{15}H_{20}Cl_8$ or $C_{15}H_{18}Cl_8$, m. p. $65-70^{\circ}$, is obtained. This is probably a mixture of chloro-compounds, which cannot crystallise in presence of each other (compare Gladstone and Hibbert, Abstr., 1889, 1207).

The action of bromine on *cadinene* dihydrobromide in presence of a small amount of mercuric chloride leads to the formation of a grey, amorphous powder, $C_{15}H_{23}Br_5$, m. p. about 100° (evolving hydrogen bromide).
G. Y.

Long Leaf Pine Oil. JOHN E. TEEPLE (*J. Amer. Chem. Soc.*, 1908, 30, 412—414).—Long leaf pine oil, obtained by the distillation of lightwood (*Pinus palustris*) with steam, has a faint yellow colour, D^{155} 0.935—0.947, $[\alpha]_D$ about -11° , and n_D 1.483. When heated, it begins to distil at about 206 — 210° ; 75% collects between 211° and 218° , and 50% between 213° and 217° . The sp. gr. of the distillate increases regularly as the temperature rises, and becomes steady at about 0.947 at 217° . The oil consists essentially of terpineol, probably the *l*-modification of α -terpineol [Δ^1 -*p*-menthenol-(8)] of b. p. 217 — 218° .
E. G.

Constituents of Essential Oils. Derivatives of Santene, Santene Glycol, and the Unsaturated Ketone, $C_9H_{12}O$, derived from the Diketone, $C_9H_{14}O_2$. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, 41, 866—871. Compare Abstr., 1907, i, 1062; this vol., i, 38, 194, 195).—When the unsaturated

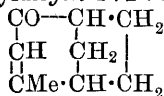
dicyclic hydrocarbon santene, $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ | \quad \text{CH}_2 \\ | \quad | \\ \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \end{array}$, dissolved in diluted

acetone, is oxidised by potassium permanganate, it yields a *glycol*, $\text{OH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2$

$\begin{array}{c} | \quad \text{CH}_2 \\ | \quad | \\ \text{OH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \end{array}$, m. p. 193° , b. p. $135^\circ/10$ mm., which is very stable

towards dehydrating agents and is converted by boiling dilute sulphuric acid into a *ketone*, $C_9H_{14}O$, b. p. 76 — $80^\circ/10$ mm., D^{20} 0.988, n_D 1.47980, which is not identical with camphenilone.

Oxidation of the glycol yields the saturated ketone, $C_9H_{14}O_2$, described previously, from which the unsaturated ketone, $C_9H_{12}O$, formerly obtained by the action of sodium ethoxide, is prepared in very much better yield by the action of alcoholic ammonia at 170° . This unsaturated ketone, b. p. 104 — $105^\circ/10$ mm., D^{20} 1.029, n_D 1.51390, is not a derivative of *dicyclo-2:2:2-octene*, as stated previously, but is 1-methyldicyclo-1:2:3- Δ^1 -octene-3-one,



By oxidation with potassium permanganate, it yields the *ketonic acid*, $\text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H}$

$\begin{array}{c} | \quad \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COMe} \end{array}$, b. p. 173 — $175^\circ/10$ mm, D^{20} 1.150, n_D 1.47936, the

semicarbazone of which has m. p. 182° . The constitution of the ketonic acid is proved by its oxidation by sodium hypobromite to *cis*-

$\text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H}$
cyclopentane-1:3-dicarboxylic acid, $\begin{array}{c} | \quad \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{array}$

The dioxime of the ketone, $C_9H_{14}O_2$, is reduced by sodium and alcohol to a *base*, $C_9H_{17}N$, b. p. 78 — $80^\circ/10$ mm., D^{20} 0.953, n_D 1.49856, the *picrate* of which has m. p. 192° .
C. S.

Resin Oil. WILLI SCHULTZE (*Annalen*, 1908, 359, 129—144).—The crude oil, obtained in a yield of about 60% on further distillation of American colophony after the resin essence, which forms about 5% of the resin, and the light oil, amounting to about 10%, have been removed, has been investigated by a number of authors, who have disagreed as to whether it is a simple substance or a mixture of hydrocarbons. A refined resin oil, obtained in a 60% yield on fractional distillation of the crude oil, is now found to be a mixture of saturated and unsaturated hydrocarbons. It is a wine-yellow liquid, having a strong violet fluorescence, b. p. about 300—350°, D^{15}_D 0.9693, $n_D - 39.96^\circ$ (100 mm. tube), has the ignition temperature 112°, the tenacity factor 6.97, and Engler's viscosity factor 2.12 at 50°. At -20°, it forms a viscid syrup, solidifies to a vitreous mass in a carbon dioxide-ether mixture, and distils unchanged under 12 mm. pressure, but evolves gas on prolonged boiling in a reflux apparatus. A pure substance could not be obtained by fractional distillation or solidification.

On treatment of the refined oil with concentrated sulphuric acid and repeated distillation of the product over sodium, a mixture of saturated hydrocarbons is obtained in a 36% yield as a transparent liquid, which has an odour faintly resembling petroleum, is not fluorescent, is stable towards alkaline permanganate or bromine water, and on distillation yields four fractions: b. p. 152—179°/10 mm., D^{15}_D 0.9486, $n_D - 3.23^\circ$ (100 mm. tube); b. p. 178.5—189°/10 mm., D^{15}_D 0.9550, $n_D - 4.14^\circ$; b. p. 191—194°/13.5 mm., D^{15}_D 0.9590, $n_D - 10.66^\circ$, and b. p. 196—202°/13.5 mm., D^{15}_D 0.9780, $n_D - 20.22^\circ$, respectively. A fraction, b. p. 195—197.5°/19 mm., gave on analysis figures agreeing only approximately with those required by octahydroretene. When boiled with manganese dioxide and dilute sulphuric acid, the saturated oil yields trimellitic acid and a saturated hydrocarbon, b. p. 198.5—200°/18.5—20 mm., which is volatile with steam and is not attacked by fuming sulphuric acid. The action of sulphur on the saturated oil, b. p. 178—210°/11—12 mm., leads to the formation of retene, m. p. 98.5—99°, and a substance, $C_{18}H_{16}S$, which is formed also by heating retene with sulphur at 230—240°. It crystallises in white leaflets, m. p. 225.5—226°, and gives an intense indigo-blue coloration with a mixture of fuming and concentrated sulphuric acids.

Trimellitic acid is best prepared by oxidation of ψ -cumene with potassium permanganate in boiling aqueous sodium hydroxide solution; the anhydride has m. p. 162.5—163° (157—158°: Baeyer, this Journ., 1873, 756).
G. Y.

Arbutin and Some of its Derivatives considered with Regard to their Rotatory Power and their Hydrolysis by Emulsin. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1908, 146, 764—766*).—Pure arbutin, that is, a glucoside which on hydrolysis gives one molecule of dextrose and one molecule of quinol, has not yet been obtained. According to Schiff and others, commercial arbutin is a mixture of arbutin (as above defined) and methylarbutin, whilst Habermann holds that arbutin is a complex glucoside, $C_{25}H_{34}O_{14}$, containing the elements dextrose, quinol, and quinol methyl ether. By a cryoscopic determination, the authors have found

* and *J. Pharm. Chim.*, 1908, 27, 421—427.

the value 268 for the molecular weight of the commercial glucoside, which is so nearly in accordance with the number 272 required by $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$ as to render Habermann's theory untenable. Undried commercial arbutin has $\alpha_D - 61.76^\circ$, which becomes -61.3° after purification. The purified glucoside loses 5.15% of water when dried at $120-125^\circ$, from which the value $\alpha_D - 64.7^\circ$ is deduced for the dry substance.

Arbutin methyl ether, prepared according to Schiff's directions, has m. p. $175-176^\circ$ (corr.) and $\alpha_D - 63.43^\circ$. Since the latter is very close to the value for purified arbutin, the specific rotatory power of true arbutin must approximate to -65° , and thus the glucoside is laevorotatory.

Arbutin benzyl ether, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$, has m. p. $161-162^\circ$ and $\alpha_D^{17} - 44.47^\circ$ (in alcohol). Dinitroarbutin, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5$, is laevorotatory. The compounds, arbutin methyl and benzyl ethers and dinitroarbutin, are hydrolysed by emulsin.

The conclusion is drawn that arbutin and its three derivatives follow the rule laid down by the authors that "all glucosides hydrolysed by emulsin are laevorotatory and are derived from dextrose."

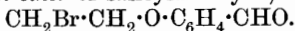
E. H.

Simple Method of Preparation of Phylloporphyrin. LEON MARCHLEWSKI [with PIASECKI] (*Ber.*, 1908, 41, 847—849*).—To prepare phylloporphyrin it is no longer first necessary to isolate phyllotaonin; the following method renders the former compound one of the easiest chlorophyll derivatives to prepare. A slight excess of barium hydroxide is added to an extract of dried acacia leaves. The precipitate is separated, washed, suspended in 96% alcohol, and carefully decomposed with concentrated sulphuric acid. The slightly acid solution is concentrated and heated with 10% alcoholic potash in an autoclave at 200° . The product is neutralised with acetic acid and warmed with alcohol, whereon phylloporphyrin dissolves, leaving a brown residue. The alcohol is evaporated, water added, and the phylloporphyrin and other chlorophyll derivatives extracted with ether. The ethereal solution is shaken with 5% hydrochloric acid, and the phylloporphyrin precipitated from this in the form of a reddish-brown mud by sodium acetate. This is dissolved in ether and the above process repeated, using 1% hydrochloric acid. The product is recrystallised twice from alcohol, and obtained as bright brown, narrow, rhombic plates pointed at both ends.

E. F. A.

An Attempt to Synthesise 1:2-Coumaran. MAXIMILIAN HELBIG (*J. pr. Chem.*, 1908, [ii], 77, 364—366).—The sodium derivative of salicylaldehyde is most readily prepared by adding the theoretical amount of sodium ethoxide solution gradually to the aldehyde dissolved in three times its weight of absolute alcohol.

When the sodium derivative is heated with bromosuccinic acid, hydrogen bromide is eliminated and fumaric acid formed. The sodium derivative condenses with ethylene dibromide at $130-140^\circ$, yielding the *bromoethyl ether* of salicylaldehyde,



* *Bull. Acad. Sci. Cracow*, 1908, 3, 127—129.

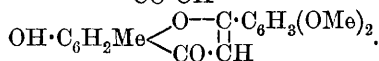
It has m. p. 52° , b. p. $184^{\circ}/11-12$ mm., and gives a red coloration with ferric chloride.

The *phenylhydrazone*, $C_{15}H_{15}ON_2Br$, crystallises in yellow needles, m. p. 114° .

Further condensation to the coumaran does not occur. J. J. S.

The Flavone Group. JOSEF TAMBOR [and, in part, B. ARONSTAMM, ST. BARANOWSKI, ST. CUKIER, and W. TOMI] (*Ber.*, 1908, 41, 787—792). —Tambor and Ludwinowsky found that oracetophenone dimethyl ether condenses with ethyl benzoate, forming 2 : 6-dimethoxy-4-methylbenzoylacetophenone (*Abstr.*, 1907, i, 75), which when boiled with hydriodic acid, D 2.00, yields 1-hydroxy-3-methylflavone. This reaction has now been extended to the condensation of oracetophenone with the three methyl methoxybenzoates and with methyl veratrate, which form the corresponding 2 : 6-dimethoxy-4-methylbenzoyl-methoxyacetophenones, $C_6H_2Me(OMe)_2 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OMe$, and -dimethoxyacetophenone, $C_6H_2Me(OMe)_2 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_3(OMe)_2$. These are converted by treatment with hydriodic acid, D 2.00, into the dihydroxy-, $OH \cdot C_6H_2Me \begin{smallmatrix} < O-C_6H_4 \cdot OH \\ | \\ CO \cdot CH \end{smallmatrix}$, and trihydroxy-7-methyl-

flavones, $OH \cdot C_6H_2Me \begin{smallmatrix} < O-C_6H_3(OH)_2 \\ | \\ CO \cdot CH \end{smallmatrix}$, respectively. When these are heated with potassium hydroxide and methyl iodide, the hydroxyl in position 5 remains unchanged, but the hydroxyls in the phenyl group are etherified, the resulting ethers having the constitution $OH \cdot C_6H_2Me \begin{smallmatrix} < O-C_6H_4 \cdot OMe \\ | \\ CO \cdot CH \end{smallmatrix}$ or



The results of the work now published confirm the view of Tambor and Ludwinowsky (*loc. cit.*) as to the constitution of oracetophenone.

Oracetophenone dimethyl ether crystallises in rhombic plates [$a : b : c = 0.7522 : 1 : 0.3932$].

2 : 6 : 2'-Trimethoxy-4-methylbenzoylacetophenone, $C_{19}H_{20}O_5$, prepared from methyl methylsalicylate, crystallises in rose-coloured needles, m. p. 118° , and gives a blood-red coloration with ferric chloride. 5 : 2'-Dihydroxy-7-methylflavone, $C_{16}H_{12}O_4$, forms greenish-yellow needles, m. p. $300-301^{\circ}$; the diacetate, $C_{20}H_{16}O_6$, white prisms, m. p. 108° . 5-Hydroxy-2'-methoxy-7-methylflavone, $C_{17}H_{14}O_4$, crystallises in yellow needles, m. p. 156° , and forms a sparingly soluble, yellow sodium salt.

2 : 6 : 3'-Trimethoxy-4-methylbenzoylacetophenone, prepared from methyl *m*-methoxybenzoate, crystallises in light brown prisms, m. p. 98° . 5 : 3'-Dihydroxy-7-methylflavone forms colourless needles, m. p. 227° , and forms a yellow solution in concentrated sulphuric acid, but does not dye mordanted threads; the diacetate crystallises in yellow, rhombic prisms, m. p. 137° . 5-Hydroxy-3'-methoxy-7-methylflavone forms yellow needles, m. p. 146° , yields a sparingly soluble, yellow sodium salt, and gives a yellow coloration with concentrated sulphuric acid.

2 : 6 : 4'-Trimethoxy-4-methylbenzoylacetophenone, prepared from methyl anisate, crystallises in colourless needles, m. p. 97—98°. 5 : 4'-Dihydroxy-7-methylflavone crystallises from alcohol in yellow needles, m. p. 295°; the *diacetate*, white needles, m. p. 148—149°. 5-Hydroxy-4'-methoxy-7-methylflavone crystallises in yellow needles, m. p. 274°, and forms an insoluble, yellow *sodium salt*.

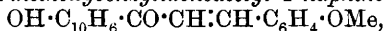
2 : 6 : 3' : 4'-Tetramethoxy-4-methylbenzoylacetophenone, $C_{20}H_{22}O_8$, from methyl veratrate, crystallises in white needles, m. p. 112°. 5 : 3' : 4'-Trihydroxy-7-methylflavone, $C_{16}H_{12}O_5$, yellow needles, m. p. 270°, gives with concentrated sulphuric acid a light yellow, or with sodium hydroxide solution an intense yellow coloration, and alumina mordant dyes a greenish-yellow. The *triacetate*, $C_{22}H_{18}O_8$, forms white needles, m. p. 169°. 5-Hydroxy-3' : 4'-dimethoxy-7-methylflavone, $C_{18}H_{16}O_5$, crystallises in yellow needles, m. p. 147°, forms an insoluble, yellow *sodium salt*, and gives a yellow coloration with concentrated sulphuric acid. G. Y.

Two Monohydroxy- α -naphthaflavonols. STANISLAUS VON KOSTANECKI [and, in part, J. W. ENGELSOHN and M. WURZELMANN] (*Ber.*, 1908, 41, 783—786).—In connexion with Bigler and Kostanecki's investigation of 3' : 4'-dihydroxy- α -naphthaflavonol (*Abstr.*, 1907, i, 76), 3'- and 4'-hydroxy- α -naphthaflavonols have been prepared and are now described.

4'-Methoxy- α -naphthaflavanone, $C_{10}H_6 \begin{smallmatrix} \text{O}-\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$, prepared by boiling 2-anisylideneacetyl-1-naphthol (*Abstr.*, 1899, i, 524) with hydrochloric acid in alcoholic solution, crystallises in white needles, m. p. 148°. The *isonitroso-derivative*, $C_{10}H_6 \begin{smallmatrix} \text{O}-\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{CO}\cdot\text{C}\cdot\text{N}\cdot\text{OH} \end{smallmatrix}$, crystallises from benzene in yellow needles, m. p. 169—170° (decomp.), and dyes orange with cobalt, but yellow with uranium, cadmium, and lead mordants. When boiled with 10% sulphuric acid in glacial acetic acid solution, the *isonitroso-derivative* is converted into 4'-methoxy- α -naphthaflavonol, $C_{10}H_6 \begin{smallmatrix} \text{O}-\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{CO}\cdot\text{C}\cdot\text{OH} \end{smallmatrix}$, which crystallises in yellow needles, m. p. 249°, dyes light yellow with alumina mordants, dissolves in concentrated sulphuric acid to a solution with intense light green fluorescence, and forms an insoluble, yellow *sodium salt*. The *acetate*, $\text{OMe}\cdot\text{C}_{19}\text{H}_{10}\text{O}_2\cdot\text{OAc}$, forms white needles, m. p. 196°.

4'-Hydroxy- α -naphthaflavonol, $C_{10}H_6 \begin{smallmatrix} \text{O}-\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OH} \\ \text{CO}\cdot\text{C}\cdot\text{OH} \end{smallmatrix}$, prepared by boiling the 4'-methoxy-compound with concentrated hydriodic acid, crystallises in yellow plates, m. p. 293°, dyes light yellow with alumina mordants, and dissolves in concentrated sulphuric acid or dilute sodium hydroxide to yellow solutions with green fluorescence. The *diacetate*, $\text{C}_{19}\text{H}_{10}\text{O}_2(\text{OAc})_2$, forms white needles, m. p. 181°.

The members of the isomeric series are prepared in the same manner, starting from 2-*m*-methoxybenzylideneacetyl-1-naphthol,



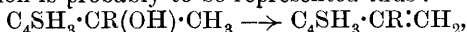
which is prepared by condensation of *m*-methoxybenzaldehyde with

2-acetyl-1-naphthol in the usual way. It crystallises in orange-red needles, m. p. 115°, and gives a red coloration with concentrated sulphuric acid.

3'-Methoxy- α -naphthaflavanone forms white needles, m. p. 130°. The isonitroso-derivative is a yellow, crystalline powder, m. p. 151° (decomp.), which dyes orange with cobalt mordants. 3'-Methoxy- α -naphthaflavonol, yellow needles, m. p. 185°, dyes light yellow with alumina mordants, and forms a yellow sodium salt; the acetate, white needles, m. p. 165°.

3'-Hydroxy- α -naphthaflavonol crystallises from alcohol in yellow, prismatic needles containing C_2H_6O , m. p. 248°, dyes light yellow with alumina mordants, and forms yellow solutions with green fluorescence in concentrated sulphuric acid or very dilute alkalis; the sodium salt forms yellow needles. G. Y.

Some Derivatives of Thiophen. VICTOR THOMAS (*Compt. rend.*, 1908, 146, 642—645).—In the presence of anhydrous ether, magnesium dissolves in 1-iodothiophen, giving magnesium thiophen iodide, which in general behaves like the corresponding phenyl derivative. With the aliphatic ketones, acetone, methyl ethyl ketone, methyl amyl ketone, and butyrone it reacts normally, giving tertiary alcohols, but the latter are difficult to isolate in a pure state, owing to the readiness with which they undergo dehydration, forming ethylenic hydrocarbons. Since the carbinol formed from acetophenone readily loses water, whilst the compound derived from benzophenone is remarkably stable, this dehydration is probably to be represented thus :



R signifying an aliphatic or aromatic radicle. Acetone condenses with magnesium thiophen iodide, giving a mixture of *thienyldimethylcarbinol*, $C_4SH_3 \cdot CMe_2 \cdot OH$, needles, m. p. 33°, which after a time liquefy to a viscous substance with a piquant odour, and β -*thienylpropylene*, $C_4SH_3 \cdot CMe : CH_2$, a colourless, agreeably smelling liquid, b. p. 166—167°/727 mm., which is easily polymerised when kept, finally giving a solid black mass. Methyl ethyl ketone gives a mixture of alcohol and hydrocarbon which could not be separated. The chief product of the action of methyl amyl ketone on magnesium thiophen iodide is β -*thienylheptylene*, $C_5H_{11} \cdot C(C_4SH_3) : CH_2$, a somewhat oily liquid, b. p. 165—168°/62 mm. Butyrone gives *thienyldipropylcarbinol*, $C_4SH_3 \cdot CPr_2 \cdot OH$, an agreeably smelling liquid, b. p. 160—163°/45—46 mm., which on distillation at ordinary pressure decomposes into the hydrocarbon and water. Acetophenone forms α -*phenyl- α -thienylmethylcarbinol*, $C_4SH_3 \cdot CPhMe \cdot OH$, needles, m. p. 50°, which gradually undergo partial liquefaction, probably forming the hydrocarbon. *Diphenylthienylcarbinol*, $C_4SH_3 \cdot CPh_2 \cdot OH$, hexagonal crystals, m. p. 125°, is formed from benzophenone; whilst yielding colourless solutions in neutral solvents, it resembles triphenylcarbinol in giving intensely yellow solutions in acids. E. H.

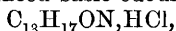
Preparation of 3-Hydroxy-(1)-thionaphthen. KALLE & CO. (D.R.-P. 188702).—It was formerly shown that phenylthioglycol-*o*-carboxylic acid when heated with sodium hydroxide gave 3-hydroxy-(1)-thionaphthen-2-carboxylic acid, which subsequently furnished

3-hydroxy-(1)-thionaphthen. It is now found that the two reactions can be effected in one stage by heating phenylthioglycol-*o*-carboxylic acid at 230°. G. T. M.

Acid Properties of Amino-ketones. PAUL RABE and WILHELM SCHNEIDER (*Ber.*, 1908, 41, 872—878. Compare Willstätter and Bode, *Abstr.*, 1900, i, 245; Miller and Rohde, *Abstr.*, 1901, i, 95; Rabe, *Abstr.*, 1907, i, 954; this vol., i, 100).—The amphoteric character of the α -, β -, and ϵ -amino-ketones, cinchoninone, piperidylacetophenone, dimethylaminocamphor, tropinone, and cinchotoxine is manifested, not only by the greater solubility (and the change of colour) in dilute sodium hydroxide than in water, but also in the formation of *O*-benzoyl derivatives. The two criteria are more pronounced in the methiodides than in the amino-ketones themselves.

The sodium *salt* of cinchoninone, $C_{19}H_{19}ON_2Na$, is obtained in clusters of yellowish-red crystals by the addition of ether to cinchoninone dissolved in a normal solution of sodium ethoxide; the sodium *salt* of cinchoninone methiodide, $C_{20}H_{22}ON_2INa$, obtained in a similar manner, forms deep yellow crystals.

[With FRITZ BRAASCH.]—Piperidylacetophenone (compare Schmidt and van Ark, *Abstr.*, 1900, i, 686), b. p. 180—181°/26 mm., is a colourless oil with a pronounced basic odour; the *hydrochloride*,



has m. p. 223°.

Piperidylacetophenone (2 mols.) and benzoyl chloride (1 mol.) in benzene solution deposit after fourteen days nearly the theoretical quantity of the hydrochloride; the *O*-benzoyl derivative, obtained as an oil after evaporation of the solvent, yields by hydrolysis benzoic acid and the products of the decomposition of piperidylacetophenone. Piperidylacetophenone methiodide by treatment with benzoyl chloride and normal sodium hydroxide yields the colourless *benzoyl* derivative, $C_{21}H_{24}O_2NI$, m. p. 146° (decomp.).

Dimethylaminocamphor methiodide, by the Schotten-Baumann method, yields a *benzoyl* derivative, $C_{20}H_{28}O_2NI$.

Tropinone methiodide, m. p. 273—275° (Willstätter gives m. p. 263—265°), forms a *benzoyl* derivative, $C_{16}H_{20}O_2NI$, m. p. 263—265°, which separates from alcohol in rhombic leaflets.

Methylcinchotoxine is more soluble in water than in normal sodium hydroxide. Methylcinchotoxine methiodide is not appreciably more soluble in dilute alkali than in water, but the change of colour in the alkaline solution is an indication of salt formation. It forms a *benzoyl* derivative, $C_{28}H_{31}O_2N_2I$. C. S.

Morphine. XVIII. Hydrolytic Products of α - and β -Chlorocodide. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1908, 41, 969—975. Compare Schryver and Lees, *Trans.*, 1900, 77, 1024; 1901, 79, 563; Lees and Tutin, *Proc.*, 1906, 22, 253; Lees, *Trans.*, 1907, 91, 1408; Knorr and Hörlein, this vol., i, 41).—The following constants for the halogen derivatives of morphine and codeine are given: α -Chloromorphide, m. p. 204° (decomp.); $[\alpha]_D - 375^\circ$. β -Chloromorphide, m. p. 188°; $[\alpha]_D - 5^\circ$. α -Chlorocodide, m. p. 152—153°;

$[\alpha]_D - 380^\circ$. β -Chlorocodide, m. p. $152-153^\circ$; $[\alpha]_D - 10^\circ$. Bromomorphide, m. p. $169-170^\circ$; $[\alpha]_D + 66^\circ$. Bromocodide, m. p. 162° ; $[\alpha]_D + 56^\circ$.

When hydrolysed by boiling with dilute acetic acid, the two chlorocodides yield the same products, but in different proportions. α -Chlorocodide gives ψ -codeine, 45%; *allo*- ψ -codeine (β -isocodeine), 15%, and isocodeine, 25%, whereas β -chlorocodide gives ψ -codeine, 10%; *allo*- ψ -codeine, 20%, and isocodeine, 55%. J. J. S.

Hydrolytic Products of α -Chloromorphide. ALFRED OPPÉ (*Ber.*, 1908, 41, 975—981. Compare Schryver and Lees, *Trans.*, 1900, 77, 1024; 1901, 79, 563; Lees, 1907, 91, 563; Knorr and Hörlein, preceding abstract).— α -, β -, and γ -isomorphines are obtained by the hydrolysis of α -chloromorphide with dilute acetic acid. γ -isoMorphine (neoisomorphine) is readily separated from the β -isomeride by extraction with boiling acetone, in which the γ -compound is very sparingly soluble. It separates from acetone in compact crystals, and has m. p. 278° (decomp.) and $[\alpha]_D^{15} - 94^\circ$. The hydrochloride has m. p. 314° (decomp.) and $[\alpha]_D^{15} - 76^\circ$ (Lees: -79.1°). The *hydrobromide*, $C_{17}H_{20}O_5NBr$, decomposes at 298° , and has $[\alpha]_D^{15} - 71^\circ$. Its *acetyl* derivative is oily, but yields a *methiodide*, $C_{22}H_{26}O_5NI$, which crystallises in needles, m. p. 267° (decomp.) and $[\alpha]_D^{15} - 24^\circ$.

The *methiodide* of diacetylmorphine crystallises in needles, decomposes at 252° , and has $[\alpha]_D^{15} - 107^\circ$. When methylated, γ -isomorphine yields ψ -codeine, and from this ϵ -methylmorphimethine (Knorr and Hörlein, *Abstr.*, 1907, i, 151) has been obtained. J. J. S.

Action of Ammonia on Methyl Ethyl Ketone. WILHELM TRAUBE (*Ber.*, 1908, 41, 777—782).—Sokoloff and Latschinoff (this *Journ.*, 1875, 353) found that acetone reacts with ammonia, forming diacetoneamine, together with small amounts of triacetoneamine. The present author has studied the action of ammonia on the first homologue of acetone, methyl ethyl ketone. This absorbs ammonia in only very small amounts, but, if an alcoholic solution of the ketone is saturated with ammonia and allowed to remain at the ordinary temperature for two or three weeks, 4-*keto*-2 : 3 : 6-*trimethyl*-2 : 6-*diethylpiperidine*, $CH_3 \cdot CMeEt \cdot NH$
 $CO \cdot CHMe \cdot CMeEt$, is formed in a 25% yield, and can be isolated as the oxalate. The free base is a colourless liquid, b. p. $157-159^\circ/30$ mm., or $247^\circ/760$ mm., and has a characteristic odour. The *nitrate*, $C_{12}H_{23}ON \cdot HNO_3$, crystallises in colourless needles, m. p. $169-172^\circ$ (decomp.). Reduction of the keto-base by alternate additions of sodium amalgam and dilute hydrochloric acid to the oxalate leads to the formation of 4-*hydroxy*-2 : 3 : 6-*trimethyl*-2 : 6-*diethylpiperidine*, $CH_3 \cdot CMeEt \cdot NH$
 $CH(OH) \cdot CHMe \cdot CMeEt$, which is obtained as a colourless oil, b. p. $140^\circ/20$ mm. This is a mixture of two isomerides, which can be separated by means of the difference in the solubilities of their oxalates. The more sparingly soluble *oxalate*, $C_{12}H_{25}ON \cdot C_2H_2O_4$, m. p. 208° (decomp.), when heated with benzoyl chloride at 160°

yields the *hydrochloride* of the benzoate, $C_{19}H_{29}O_2N \cdot HCl$, m. p. 230° ; the *benzoate*, $C_{19}H_{29}O_2N$, forms a colourless oil, which is partially decomposed on distillation in a vacuum, and forms, in addition to the preceding salt, a second highly soluble *hydrochloride*, obtained as a brittle mass on evaporation of the aqueous solution. The base, corresponding with the more soluble oxalate, is converted into the benzoate hydrochloride, m. p. 230° , when heated with benzoyl chloride. G. Y.

Nitrosopyrroles. E. MORELLI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 250—254).—The authors have studied the reactions of the trioxime, $NOH \cdot CMe \cdot CH_2 \cdot C(NO \cdot H) \cdot CMe \cdot NOH$, obtained by Angeli and Marchetti (*Abstr.*, 1907, i, 436) by the action of hydroxylamine on 3-nitroso-2:5-dimethylpyrrole or 3-nitroso-1-oxy-2:5-dimethylpyrrole.

The trioxime readily loses $1H_2O$, giving a furazan derivative, $O \begin{smallmatrix} N \cdot C \cdot CH_2 \cdot CMe \cdot NOH \\ | \\ N \cdot CMe \end{smallmatrix}$, and this, when boiled with dilute sulphuric acid, yields hydroxylamine and the *ketone*, $O \begin{smallmatrix} N \cdot C \cdot CH_2 \cdot COMe \\ | \\ N \cdot CMe \end{smallmatrix}$, which crystallises from ether in white needles, m. p. 19° , gives iodoform when treated with potassium hydroxide and iodine, and yields a *semicarbazone*, $C_6H_5ON_2 \cdot N_2H \cdot CO \cdot NH_2$, m. p. 188° . When reduced by means of sodium in alcoholic solution, the trioxime yields 3-amino-2:5-dimethylpyrrolidine, $NH \begin{smallmatrix} CHMe \cdot CH_2 \\ | \\ CHMe \cdot CH \cdot NH_2 \end{smallmatrix}$, which forms a *picrate*, $C_6H_{14}N_2 \cdot 2C_6H_3O_7N_3$, m. p. 242° (decomp.). T. H. P.

Action of Hydrazine Hydrate on Dinitrophenylpiperidine. LEOPOLD SPIEGEL (*Ber.*, 1908, 41, 886—888).—Hydrazine hydrate in boiling alcoholic solution hydrolyses 2:4-dinitrophenylpiperidine, the products being a piperidine salt and a substance, $C_6H_4O_3N_4$, m. p. 206° (decomp.), crystallising in yellowish-brown, glistening prisms, which is identical with Curtius and Mayer's 6-nitro-1-hydroxy-1:2:3-benzotriazole (this vol., i, 53). C. S.

Bz-Quinoline Mercaptans. ALBERT EDINGER (*Ber.*, 1908, 41, 937—943).—Quinoline-8-mercaptans have been prepared by the reduction of the corresponding quinolinesulphonyl chlorides with stannous chloride and hydrochloric acid.

Quinoline-8-sulphonyl chloride, $C_9NH_6 \cdot SO_2Cl$, m. p. 122° , prepared from phosphorus pentachloride and the sulphonic acid or its sodium salt at 136 — 140° , is reduced by stannous chloride and hydrochloric acid, yielding a *double salt* of tin and the mercaptan, which crystallises in stout, yellow prisms and decomposes at 270° . A cold alkaline solution of the double salt with benzoyl chloride yields the *benzoyl* derivative, $C_9NH_6 \cdot S \cdot CPh$, m. p. 110° , whilst benzyl chloride gives the *benzyl* derivative, $C_{16}H_{13}NS$, m. p. 112° . By hydrolysis with hot moderately concentrated hydrochloric acid and subsequent neutralisation at 0° ,

the benzoyl derivative yields the *mercaptan*, $C_9NH_6 \cdot SH \cdot 2H_2O$, m. p. 58—59°, which crystallises in glistening, red needles. By prolonged exposure to the air or by oxidation with alkaline potassium ferricyanide, the mercaptan yields the *disulphide*, $C_{18}H_{12}N_2S_2$, m. p. 206°, which separates from alcohol or glacial acetic acid in yellow prisms.

8-Thiocyanquinoline, $C_9NH_6 \cdot SCN$, m. p. 89°, prepared from the mercaptan, sodium methoxide, and cyanogen iodide in methyl-alcoholic solution, separates from dilute alcohol in white needles, and by warming with aniline forms a *substance*, $C_{16}H_{13}N_3S$, m. p. 142°. The *ethyl thio-ether*, $C_9NH_6 \cdot SEt$, m. p. 51°, crystallises in colourless needles.

5-Bromoquinoline, when heated at 130—140° with fuming sulphuric acid (40% SO_3), yields 5-bromoquinoline-8-sulphonic acid, the *chloride* of which, m. p. 124°, yields by reduction a tin double salt, from which a *benzoyl derivative*, $C_9NH_5Br \cdot S \cdot CPh$, m. p. 115°, is obtained. The corresponding *mercaptan*, $C_9NH_5Br \cdot SH$, m. p. 69°, crystallises in yellow needles. The *disulphide* has m. p. 193°. C. S.

Partial Racemism. VII. ALBERT LADENBURG and W. HERRMANN (*Ber.*, 1908, 41, 966—969. Compare Abstr., 1894, i, 208).—When quinaldine and an aqueous solution of tartaric acid are mixed at 60—63°, a crystalline acid tartrate is deposited, which yields an inactive base when decomposed with alkalis. The crystalline salt is not a mixture of *d*- and *l*-hydroquinaldine hydrogen tartrates, but a partially racemic salt.

The pure *l*-tetrahydroquinaldine was isolated in the form of the *l*-tartrate by the addition of *l*-tartaric acid to the mother liquor from the *d*-tetrahydroquinaldine *d*-tartrate.

The following data for the salts have been determined :

	M. p.	$D_{18.5}$	Water of crystallisation.
<i>n</i> -Tetrahydroquinaldine hydrogen tartrate...	72—73°	1.310	1.5H ₂ O
<i>d</i> -Tetrahydroquinaldine " " ...	90—91°	1.344	1H ₂ O
<i>l</i> -Tetrahydroquinaldine " " ...	62—63°	1.314	1.5H ₂ O

The transition temperature is 59°.

J. J. S.

Quinoline Derivatives. III. **Phenyl Quinolyl Ketone.** PERCY REMFRY and HERMAN DECKER (*Ber.*, 1908, 41, 1007—1009. Compare Abstr., 1905, i, 828; 1906, i, 984).—The action of magnesium phenyl bromide on ethyl cinchonate has been studied partly in connexion with the investigations of quinoline derivatives already published, and partly with a view to determining the applicability of carboxylic esters of the pyridine series to Grignard's synthesis. It is found that the action of 1 mol. of magnesium phenyl bromide on 2 mols. of ethyl cinchonate leads to the formation of diphenyl- γ -quinolylcarbinol together with considerable amounts of phenyl γ -quinolyl ketone, but that only traces of the ketone are obtained when 3 mols. of the organo-magnesium compound are added to 1 mol. of the ester.

Phenyl γ -quinolyl ketone, $C_6H_4 \begin{smallmatrix} \text{C(COPh) \cdot CH} \\ \text{N} \text{=====} \text{CH} \end{smallmatrix}$, separates from

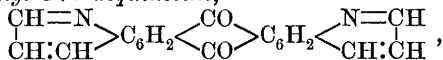
alcohol in crystalline aggregates, m. p. 294° , and is soluble in mineral acids.

Diphenyl- γ -quinolylcarbinol, $C_9H_6N \cdot CPh_2 \cdot OH$, separates from alcohol in small, white crystals, m. p. 247.5° , is soluble in dilute mineral acids, and gives with concentrated sulphuric acid a red coloration which disappears on dilution with water. The *hydrochloride*, yellow crystals, m. p. 223° ; the carbinol forms two crystalline *picrates*, the more soluble of which has m. p. $142-144^{\circ}$, whilst the other decomposes at high temperatures. The *methiodide* forms yellow crystals, becoming reddish-brown when dried, m. p. 159° , and gives with sodium carbonate in aqueous solution a white *precipitate*, which becomes violet on exposure to air, can be extracted by ether, and, on evaporation of the ethereal solution, is obtained as a violet residue, m. p. 234° . G. Y.

Preparation of Quinoline Derivatives of the Anthraquinone Series. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P.

189234).—*Anthraquinonyl-1-quinoline*, $\begin{array}{c} CH=N \\ | \\ CH:CH \end{array} > C_6H_2 : (CO)_2 : C_6H_4$, yellow crystals, m. p. 169° , is obtained by condensing 1-aminoanthraquinone and glycerol in the presence of concentrated sulphuric acid and nitrobenzenesulphonic acid.

Anthraquinonyl-1:5-diquinoline,



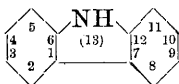
is an almost colourless base, m. p. 342° ; the *nitrate*, $C_{20}H_{10}H_2O_2, 2HNO_3$, is produced in a similar manner from 1:5-diaminoanthraquinone.

G. T. M.

Derivatives of Tetra- and Hexa-hydrocarbazoles and a New Synthesis of Carbazole. WALTHER BORSCHÉ [with A. WITTE and W. BOTHE] (*Annalen*, 1908, 359, 49–80).—It was shown by Dreschel (Abstr., 1888, 1276) that, when heated with dilute mineral acids, the phenylhydrazone of *cyclohexanone* yields only small amounts of phenylhydrazine and *cyclohexanone*, undergoing for the most part a reaction, analogous to Fischer's synthesis of indole from the phenylhydrazones of aldehydes and ketones, in which it loses ammonia and forms tetrahydrocarbazole (compare Baeyer, Abstr., 1894, i, 174). The present authors undertook the study of this little known reaction because it has become of importance in consequence of the ease with which *cycloketones* may now be obtained, and, on the other hand, of the increased interest attached to the hydrocarbazoles in connexion with their possible relation to the alkaloids of the strychnine series. The results obtained show that substituting groups in the meta- or para-position in the benzene nucleus of the phenylhydrazine do not, at least markedly, affect the reaction, but that tetracarbazoles are formed only from phenylhydrazones of simple saturated *cycloketones*, such as *cyclohexanone*, *d*-1-methyl-3-*cyclohexanone*, and *l*-menthone, and not from those of substances such as 1:3-dimethyl- Δ^6 -*cyclohexene-5-one*, *pulegone*, *d*-carvone, and *d*-camphor.

The tetracarbazoles are readily reduced by tin and hydrochloric acid, forming hexahydrocarbazoles (compare Graebe and Glaser, this Journ., 1872, 302), and, in so far as they are volatile, are converted into carbazoles by distillation over finely-divided lead oxide, which must be heated, but not too highly.

The annexed scheme has been adopted in the first part of this paper for the numbering of the positions in carbazole, as the usual method is insufficient for the naming of the new compounds now described.



The hydrazones were for the most part not purified, but heated in the crude state with dilute sulphuric acid on the water-bath.

The action of bromine on tetracarbazole in glacial acetic acid solution leads to the formation of a *hexabromo*-derivative, $C_{12}H_7NBr_6$ or $C_{12}H_3NBr_6$, obtained as a yellow, crystalline powder, unchanged at 300° or on prolonged heating with alcoholic potassium hydroxide or digestion with zinc dust and alcoholic hydrochloric acid, together with a more soluble *tetrabromo*-compound, $C_{12}H_5NBr_4$, m. p. 230° .

4-Methyl- $\Delta^{1(6)}$ -tetrahydrocarbazole, $C_{13}H_{15}N$, from phenylhydrazine and 1-methyl-3-cyclohexanone, separates from alcohol in crystals, m. p. 94° ; the *picrate*, $C_{19}H_{18}O_7N_4$, brownish-red leaflets, m. p. 155° .

9-Methyl- $\Delta^{1(6)}$ -tetrahydrocarbazole, $C_{13}H_{15}N$, from *p*-tolylhydrazine and cyclohexanone, crystallises from light petroleum in white needles, m. p. $141-142^\circ$.

4:9-Dimethyl- $\Delta^{1(6)}$ -tetrahydrocarbazole, $C_{14}H_{17}N$, from *p*-tolylhydrazine and 1-methyl-3-cyclohexanone, separates from methyl alcohol in transparent plates, m. p. 146° ; the *picrate*, dark red leaflets, m. p. 129° .

The *phenylhydrazone*, from menthone and phenylhydrazine, forms unstable needles, m. p. 53° , and yields 2-methyl-5-isopropyl- $\Delta^{1(6)}$ -tetrahydrocarbazole, $C_{16}H_{21}N$, which crystallises from dilute methyl alcohol in transparent prisms, m. p. 114.5° , b. p. about $150-200^\circ/15$ mm.

The α -naphthylhydrazone of cyclohexanone, colourless needles, yields $\Delta^{1(6)}$ -tetrahydrobenzo- α -naphthindole, $C_6H_8 \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{C} - \text{CH} \end{array} \text{CH}$, white needles, m. p. $139-140^\circ$.

$\Delta^{1(6)}$ -Tetrahydrobenzo- β -naphthindole, $C_6H_8 \begin{array}{c} \text{NH} \cdot \text{C} - \text{CH} \\ | \\ \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{CH}$, from β -naphthylhydrazine and cyclohexanone, forms white crystals, m. p. 152° .

9-Methoxy- $\Delta^{1(6)}$ -tetrahydrocarbazole, $C_{13}H_{15}ON$, from *p*-methoxyphenylhydrazine and cyclohexanone, crystallises in colourless needles, m. p. $94-95^\circ$. The 9-ethoxy-compound, $C_{14}H_{17}ON$, prepared in the same manner from *p*-ethoxyphenylhydrazine, forms colourless needles, m. p. $87-88^\circ$.

11-Chloro- $\Delta^{1(6)}$ -tetrahydrocarbazole, colourless prisms, m. p. $55-56^\circ$, 9-chloro- $\Delta^{1(6)}$ -tetrahydrocarbazole, $C_{12}H_{12}NCl$, needles, m. p. $54-55^\circ$, and 9-bromo- $\Delta^{1(6)}$ -tetrahydrocarbazole, colourless plates, m. p. 153° , are prepared from cyclohexanone and *o*-chloro-, *p*-chloro-, and *p*-bromophenylhydrazines respectively.

cycloHexanone-*p*-nitrophenylhydrazine, $C_{12}H_{15}O_2N_3$, forms yellow needles, m. p. 146—147°. 9-Nitro- $\Delta^{(6)}$ -tetrahydrocarbazole, $C_{12}H_{12}O_2N_2$, brownish-red crystals, m. p. 174°.

cycloHexanone-*o*-nitrophenylhydrazine, golden-brown needles, m. p. 74°. 11-Nitro- $\Delta^{(6)}$ -tetrahydrocarbazole, yellowish-brown leaflets, m. p. 148—149°.

cycloHexanone-*m*-nitrophenylhydrazine, red needles, m. p. 102—103°. 10-Nitro- $\Delta^{(6)}$ -tetrahydrocarbazole, red crystals, m. p. 151—152°.

1-Methyl-3-cyclohexanone-*m*-nitrophenylhydrazine, $C_{13}H_{17}O_2N_3$, separates from alcohol in crystals, m. p. 90°, and is unstable. 10-Nitro-4-methyl- $\Delta^{(6)}$ -tetrahydrocarbazole, $C_{13}H_{14}O_2N_2$, forms reddish-brown crystals, m. p. 147—148°.

The *m*-nitrophenylhydrazones of 1 : 3-dimethyl- Δ^6 -hexene-5-one, red prisms, m. p. 140°, and *d*-carvone, orange-red needles, m. p. 105—106°, and the *p*-nitrophenylhydrazine of *d*-carvone, reddish-brown needles, m. p. 174—175°, are described. Pulegone and *m*-nitrophenylhydrazine form a viscous condensation product.

4-Methylhexahydrocarbazole, prepared by reduction of the tetrahydrocarbazole with tin and alcoholic hydrochloric acid, crystallises in colourless prisms, m. p. 111°; the nitroso-derivative, $C_{13}H_{16}N \cdot NO$, needles, m. p. 62°; the carbamyl derivative, $C_{13}H_{16}N \cdot CO \cdot NH_2$, colourless crystals, m. p. 153—154°; the benzoyl derivative, $C_{13}H_{16}NBz$, colourless prisms, m. p. 89°.

2-Methyl-5-isopropylhexahydrocarbazole, $C_{16}H_{13}N$, obtained by reduction of the tetrahydrocarbazole, crystallises in white needles, m. p. 71°; the nitroso-derivative, $C_{16}H_{22}ON_2$, yellow prisms, m. p. 140—141°; the carbamyl derivative, $C_{16}H_{22}N \cdot CO \cdot NH_2$, colourless needles, m. p. 87—88°.

Carbazole is formed when tetrahydrocarbazole or 9-chloro- or 11-chloro-tetrahydrocarbazole is distilled over lead oxide. The following new substituted carbazoles have been prepared in the same manner from their tetrahydro-compounds. The positions occupied by the substituting groups are numbered in the usual manner.

2-Methylcarbazole, $C_{13}H_{11}N$, from 4-methyl- $\Delta^{(6)}$ -tetrahydrocarbazole, crystallises in colourless leaflets, m. p. 259°; the picrate, red needles, m. p. 167°. This methylcarbazole is formed also from 6-nitro-3-acetylaminotoluene by conversion of this successively into 4-nitro-m-toluidine, 4-nitro-3-anilinetoluene, and 1-phenyl-6-methylbenzotriazole, $N \begin{smallmatrix} \text{NPh} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6H_3Me$, which on distillation yields the 2-methylcarbazole.

2 : 6-Dimethylcarbazole is obtained as a white, crystalline powder, m. p. 208—209°; the picrate, light red needles, m. p. 153°.

1 : 3 : 7-Trimethylcarbazole, $C_{15}H_{15}N$, crystallises in white leaflets, m. p. 119°; the picrate, m. p. 177°.

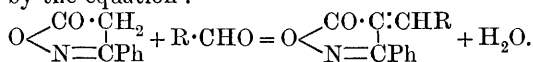
1 : 3 : 4 : 7-Tetramethylcarbazole, $C_{16}H_{17}N$, prepared from ψ -cumylhydrazine and *d*-1-methyl-3-cyclohexanone by way of the tetrahydrocarbazole, crystallises in nacreous leaflets, m. p. 153°; the picrate, dark red needles, m. p. 146—147°.

4-Methyl-1-isopropylcarbazole, $C_{16}H_{17}N$, is obtained as a colourless oil, solidifying to a mass of leaflets, m. p. 86°; the picrate, light red needles, m. p. 152°.

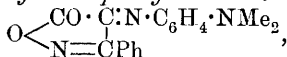
3-Methoxycarbazole, $C_{13}H_{11}ON$, crystallises in colourless needles, m. p. $138-139^\circ$; the *picrate*, m. p. 143° . G. Y.

Some Derivatives of Phenylisooxazolone. ANDRÉ WAHL and ANDRÉ MEYER (*Compt. rend.*, 1908, **146**, 638—640).—Schiff and his pupils have shown (Abstr., 1896, i, 83; 1897, i, 444, 493) that hydroxylamine hydrochloride and an aldehyde condense with ethyl acetoacetate in the presence of aniline, producing solid substances which are formed by the condensation of the aldehyde with the methylisooxazolone first formed. The authors find that phenylisooxazolone undergoes a similar reaction. Phenylisooxazolone, which is best prepared separately, condenses with most aromatic aldehydes on boiling in alcoholic solutions, and in the other cases piperidine is effective as a condensing agent. *Phenylbenzylidenesisooxazolone*, $C_9O_2NPh:CHPh$, forms bright yellow, shining spangles, m. p. 191° (decomp.).

Phenylcinnamylidenesisooxazolone crystallises from acetic acid in orange leaflets, m. p. 160° (decomp.). *Phenylfurylidenesisooxazolone* forms brown tablets, m. p. $132-133^\circ$ (decomp.). *Phenyl-p-dimethylaminobenzylidenesisooxazolone*, $C_9O_2NPh:CH \cdot C_6H_4 \cdot NMe_2$, crystallises in brick-red shining spangles, m. p. 184° ; it has a slight affinity for wool and cotton mordanted with tannin. The derivatives, *phenyl-o-hydroxybenzylidenesisooxazolone*, yellow needles, m. p. 187° , *phenyl-p-hydroxybenzylidenesisooxazolone*, yellow needles, m. p. $206-207^\circ$, *phenyl-4-hydroxy-3-methoxybenzylidenesisooxazolone*, golden-yellow needles, m. p. 213° , and *phenyl-β-hydroxynaphthylidenesisooxazolone*, m. p. 223° , which dissolve in alkalis to orange-red solutions, could not be examined for their tinctorial power, since their solutions lose their colour through hydrolysis. The readiness with which phenylisooxazolone condenses with aromatic aldehydes indicates that it probably contains a methylene group, and that the above reaction should be represented by the equation:



This is supported by the fact that phenylisooxazolone condenses with nitrosodimethylaniline (Sachs, Abstr., 1900, i, 362; 1901, i, 229), giving *phenyl-4-dimethylaminophenyliminoisooxazolone*,



violet-black needles, m. p. 184° (decomp.).

Relying on its formation by the action of hydroxylamine on ethyl ethoxycinnamate or on phenylpropiolamide, Moureu and Lazennec (Abstr., 1907, i, 716) have proposed the formula $O \begin{array}{c} \diagup \text{CO} \cdot \text{CH} \\ \diagdown \text{NH} \cdot \text{CPh} \end{array}$ for phenylisooxazolone. The present work and the preparation by Rabe (Abstr., 1897, i, 568) of two isomeric benzoyl derivatives of phenylisooxazolone indicate that the latter substance also reacts in the tautomeric methylene form. E. H.

Coloured Salts of Schiff's Bases. Colour as Related to Chemical Constitution. FORRIS J. MOORE and R. D. GALE (*J. Amer. Chem. Soc.*, 1908, **30**, 394—404).—In studying the com-

pound, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, obtained by the condensation of *p*-aminodimethylaniline with piperonal, it was observed that, on treating it with hydrogen chloride, a deep blood-red *hydrochloride* was formed at first and was afterwards converted into a bright lemon-yellow *dihydrochloride*.

It has now been found that *p*-benzylideneaminodimethylaniline (Calm, Abstr., 1885, 387) and the corresponding cinnamylidene, salicylidene, and anisylidene derivatives (Nuth, Abstr., 1885, 784) behave in a similar manner, except that the last-mentioned compound absorbs nearly 3 mols. of hydrogen chloride instead of 2. The *mono*- and *di-hydrochlorides* of these bases are described, and their possible constitution is discussed.

Piperonylidene-p-toluidine, m. p. 98° , forms cream-coloured prisms. *Piperonylidene-p-chloroaniline* has m. p. 78° . *Ethyl piperonylidene-p-aminobenzoate* has m. p. 109° . Piperonal condenses with *m*-nitroaniline and *p*-bromoaniline with formation of *substances* of m. p. 119° and 109° respectively. All these compounds and piperonylideneaniline form only *monohydrochlorides* which are of a yellow colour.

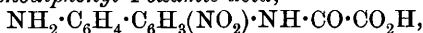
On treating piperonal with *p*-phenylenediamine and with benzidine, *compounds*, m. p. 216° and 241° respectively, are obtained, which are formed by the condensation of 1 mol. of the diamine with 2 mols. of piperonal; these substances form yellow scales with a bronze lustre.

E. G.

Substitution Products of *p*-Diaminodiphenylmethane and of *p*-Diaminodiphenyl. THEODOR NEUMÜLLER (*J. pr. Chem.*, 1908, [ii], 77, 353—363).—*p*-Diaminodiphenylmethane and its 3:3'-dinitro-derivative readily condense with monochloroacetic acid in the presence of sodium acetate, yielding diglycine derivatives. 4:4'-*Diphenylmethanediglycine*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, separates from water or dilute alcohol as a flocculent, crystalline mass, m. p. 175° . 3:3'-*Dinitro-4:4'-diphenylmethane diglycine*,

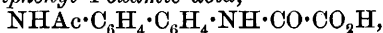
$\text{CH}_2[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}]_2$, crystallises in lemon-yellow needles, m. p. 164° (decomp.).

3-Nitro-4'-aminodiphenyl-4-oxamic acid,



is readily formed when 4'-aminodiphenyl-4-oxamic acid (D.R.-P. 95060) is nitrated at -5° to -10° with the theoretical amount of potassium nitrate dissolved in concentrated sulphuric acid. It crystallises from alcohol in small, chrome-red aggregates, which melt above 250° . Its *acetyl* derivative, $\text{C}_{16}\text{H}_{18}\text{O}_6\text{N}_3$, forms orange-red crystals, which also melt above 250° . The position of the nitro-group in the nitrated oxamic acid follows from the fact that on hydrolysis it yields *o*-nitrobenzidine, and on reduction yields a diamine which, with nitrous acid, gives a diazonium salt and not an azimino-compound, as would be expected if the two amino-groups were in the ortho-positions.

4'-Acetylaminodiphenyl-4-oxamic acid,



crystallises from dilute acetic acid in colourless needles, m. p. above 250° . The *calcium* salt, $\text{C}_{32}\text{H}_{26}\text{O}_8\text{N}_4\text{Ca}$, crystallises from dilute alcohol in slender needles. When nitrated, the acid yields 3'-nitro-4'-acetyl-

aminodiphenyl-4-oxamic acid, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, which separates from water as a pale orange-red, crystalline mass, m. p. 155°. When boiled with concentrated ammonia, it yields 3'-nitro-4'-aminodiphenyl-4-oxamic acid, in the form of slender needles, m. p. 206°. The fact that the nitro- and acetyl-amino-groups are in ortho-positions with respect to one another, follows from the readiness with which the acetyl group is eliminated. J. J. S.

Preparation of 5:5 Dialkylbarbituric Acids from the Corresponding Dialkylmalonylguanidines. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 189076).—The 5:5-dialkylbarbituric acids are obtained in good yield (90—100%) by treating with nitrous acid the dialkylmalonylguanidines produced by condensing the ethyl dialkylmalonates with guanidine, or by condensing the ethyl alkylmalonates with guanidine and alkylating the intermediate product. G. T. M.

Antipyrine Phosphate and Arsenate. P. AUBOUY (*Bull. Soc. chim.*, 1908, [iv], 3, 388—390).—These two salts have been prepared in extension of previous work on the preparation of the salts of pyrimidine with mineral acids (Abstr., 1906, i, 989). Both were obtained by the addition of the respective acids to antipyrine dissolved in alcohol.

Antipyrine phosphate, $[\text{C}_{11}\text{H}_{12}\text{ON}_2]_2 \cdot \text{H}_3\text{PO}_4$, m. p. 158—160°, forms colourless crystals, and is soluble in water, or alcohol, and insoluble in ether. *Antipyrine arsenate*, $[\text{C}_{11}\text{H}_{12}\text{ON}_2]_2 \cdot \text{H}_3\text{AsO}_4$, has m. p. 146—148°, and otherwise resembles the phosphate.

Aqueous solutions of either salt are acid to test paper, and the colour reactions of such solutions with various reagents are recorded.

T. A. H.

3-Hydroxy-1:2-dihydroquinoxaline and its Derivatives. SIGMUND MOTYLEWSKI (*Ber.*, 1908, 41, 800—805).—3-Hydroxy-1:2-dihydroquinoxaline, although not formed by the action of *o*-phenylenediamine on ethyl chloroacetate, may nevertheless be prepared by the condensation of *o*-phenylenediamine with chloroacetic acid; it crystallises from water in slender, colourless needles, m. p. 96—97°, containing 1 mol. H_2O ; the anhydrous substance has m. p. 132—133°; the *ferrocyanide*, $\text{C}_8\text{H}_8\text{ON}_2 \cdot \text{H}_4\text{Fe}(\text{CN})_6$, crystallises in silvery leaflets.

The *acetate*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} = \text{C} \cdot \text{OAc} \end{smallmatrix}$ or $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{Ac} \cdot \text{CO} \end{smallmatrix}$, crystallises in colourless needles, m. p. 166°; the *benzoate*, $\text{C}_8\text{H}_7\text{N}_2 \cdot \text{OBz}$, crystallises in microscopic, white needles, m. p. 210—211°. The parent substance is converted by nitrous acid into 1-nitroso-3-hydroxy-1:2-dihydroquinoxaline, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}(\text{NO}) \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$, crystallising in yellow, prismatic needles; it melts and partly decomposes at 164°, forming a white mass which becomes transparent at 210°.

Hydrated 3-hydroxy-1:2-dihydroquinoxaline when heated at 125° loses its water of crystallisation together with 2 atoms of hydrogen, being converted into a yellow, amorphous substance, m. p. 264° (decomp.); it probably has the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{CO} \end{smallmatrix}$ or

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{CH} \\ | \quad || \\ \text{N} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$ A substance, $\text{C}_8\text{H}_6\text{ON}_2$, isomeric with the latter compound, is obtained by the oxidation of 3-hydroxy-1:2-dihydroquinoxaline with potassium permanganate; it crystallises in colourless needles, m. p. 269° , and forms a white, amorphous silver salt,

$\text{C}_{16}\text{H}_{10}\text{O}_5\text{N}_4\text{Ag}_3$, and a green copper salt, $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_4\text{Cu}_5$. Oxidation of 3-hydroxy-1:2-dihydroquinoxaline with chromic acid leads to the formation of *o*-phenyleneoxamide, m. p. 410° (compare Seeliger and Meyer, Abstr., 1897, i, 45). The silver salt, $(\text{C}_{16}\text{H}_{10}\text{O}_5\text{N}_4\text{Ag}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, and copper salt, $\text{C}_{16}\text{H}_{10}\text{O}_7\text{N}_4\text{Cu}_4$, were prepared. The substance $\text{C}_8\text{H}_6\text{ON}_2$, obtained by the oxidation with potassium permanganate, and *o*-phenyleneoxamide are converted by phosphorus pentachloride into 2:3-dichloroquinoxaline, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{CCl} \\ | \quad || \\ \text{N} \cdot \text{CCl} \end{smallmatrix}$, crystallising in colourless needles, m. p. $149\text{--}150^\circ$.

W. H. G.

Preparation of Indoxyl and its Homologues and Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 188436).—The acylarylglycines when condensed with aluminium halides give rise to indoxyl derivatives.

Acetylphenylglycine, its potassium salt, or its ethyl ester when heated with aluminium chloride either in a vacuum or in a current of inert gas at $220\text{--}250^\circ$ furnishes indoxyl, which is isolated in the form of indigotin. Acetyltolylglycine gives rise to the methyl homologue of indigotin.

G. T. M.

Preparation of Indoxyl and its Homologues. LEON LILIENFELD (D.R.-P. 189021).—It is found that the yield of indoxyl or indigotin obtained by heating phenylglycine with alkali hydroxides in presence of an alkali metal is greatly increased by carrying out this operation under reduced pressure.

The potassium salt of phenylglycine, potassium or sodium hydroxide, and sodium when heated in a good vacuum at $200\text{--}250^\circ$ furnish 80—90% of indigotin.

G. T. M.

Indigoid Dyes. PAUL FRIEDLÄNDER (*Ber.*, 1908, 41, 772—777. Compare Abstr., 1907, i, 334).—The author applies the term “indigoid” to dyes which are related to indigotin in that the imino-groups of the latter are substituted by a sulphur or other bivalent atom or group. In continuation of the investigation of thioindigotin, now termed bisthionaphthenindigotin in conformity with Jacobson’s system of nomenclature (Abstr., 1906, i, 378), it has been found that asymmetric, as well as symmetric, indigoid dyes can be prepared by condensation of substances such as indoxyl, thioindoxyl, 1:3-diketohydrindene, α - and β -naphthols, and the more reactive phenols of the benzene series, which contain the grouping $\cdot\text{CO}\cdot\text{CH}_2\cdot$ or $\cdot\text{C}(\text{OH})\cdot\text{OH}\cdot$, with cyclic α -diketones, such as isatin, α -keto-halogen compounds, such as isatin chloride or dibromo-oxythionaphthen, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ | \quad | \\ \text{S} \end{smallmatrix} \text{CBr}_2$, and reactive anilinoketones and alkyl-oxyketones, such as the α -anilide and α -methyl ether of isatin. The

products are all coloured orange-red to greenish-blue. They vary in stability and in their behaviour towards alkalis with the nature of the two cyclic nuclei of which they are composed, but are in general stable towards acids, and on treatment with alkaline reducing agents yield colourless products mostly easily oxidised by the atmospheric oxygen with formation of the original dye. The following two new indigoid dyes are described.

Naphthalene-indole-indigotin, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} = \text{C} \cdot \text{CO} \\ \text{CH} : \text{CH} \quad \text{NH} \cdot C_6H_4 \end{smallmatrix}$, prepared

by the action of isatin chloride on α -naphthol in benzene solution, crystallises in copper-coloured prisms or needles, m. p. about 240° , and forms at higher temperatures a reddish-violet vapour which condenses to woolly needles. It is more easily soluble than indigotin, and is sulphonated with difficulty, yielding a *product* which is less stable towards alkalis than is indigo-carmin. When boiled with sodium carbonate solution, the indigotin forms a greenish-yellow, soluble *sodium* compound, readily decomposed by acids, and when boiled with sodium hydroxide dissolves and is rapidly decomposed. The solution obtained on reduction with alkaline hyposulphite is yellow.

2-Thionaphthen-2-indole-indigotin, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} \text{C} : \text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} C_6H_4$, pre-

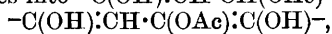
pared by heating indoxyl with dibromo-oxythionaphthen in glacial acetic acid solution, crystallises from nitrobenzene in reddish-violet needles, does not melt at 300° , sublimes at higher temperatures, and forms a slightly yellow reduction *product*, which dyes textile fibres bluish-violet. The *sulphonic acid* is blue and becomes yellow on addition of an excess of alkali.

The absorption spectra of thioindigotin and of the two new indigoid dyes are described. G. Y.

Behaviour of Indigoid Dyes and Indigotin towards Alkalis.

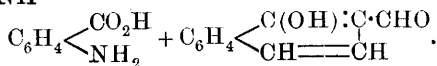
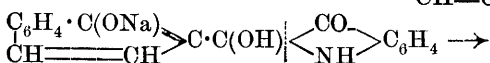
PAUL FRIEDLÄNDER (*Ber.*, 1908, 41, 1035—1039. Compare preceding abstract).—Binz has shown (*Abstr.*, 1906, i, 749) that indigotin forms an additive product with sodium hydroxide having the composition $C_{16}H_{10}O_2N_2NaOH$, in which he supposed the sodium hydroxide to be attached to a carbonyl group, thus: $>C \begin{smallmatrix} \text{ONa} \\ \text{OH} \end{smallmatrix}$. Since indigotin

and quinones contain the group $-\text{CO} \cdot \overset{|}{\underset{|}{\text{C}}} \cdot \text{CO}-$, which on the addition of acetic acid changes into $-\text{C}(\text{OH}) : \text{CH} \cdot \text{CH}(\text{OAc}) \cdot \text{CO}-$ or



the author considers it probable that the sodium hydroxide would combine in a similar manner. This view receives support from the fact that 2-naphthalene-2-indoleindigotin is decomposed by sodium hydroxide, yielding anthranilic acid and 1-hydroxy-2-naphthaldehyde,

the reaction being represented thus: $C_6H_4 \cdot \begin{smallmatrix} \text{CO} \\ \text{CH} = \text{CH} \end{smallmatrix} \text{C} : \text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} C_6H_4 \rightarrow$



1-Hydroxy-2-naphthaldehyde, $C_{11}H_8O_2$, crystallises in long, pale greenish-yellow needles, m. p. 59° ; it is very similar to salicylaldehyde, gives a crystalline *hydrazone*, and when treated with methyl sulphate in alkaline solution yields 1-methoxy-2-naphthaldehyde, crystallising in white, compact prisms, m. p. 47° .

2-Hydroxy-1-naphthaldehyde has been obtained by warming 1-naphthalene-2-indoleindigotin with 10% aqueous sodium hydroxide solution. Similarly, 1-hydroxy-4-methoxy-2-naphthaldehyde, lemon-yellow crystals, m. p. 100° , and 2-hydroxy-3-thionaphthaldehyde,

$C_6H_4 \begin{array}{c} \text{C(CHO)} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \gg C \cdot OH$, m. p. 130° , have been prepared from 4-methoxy-2-naphthalene-2-indoleindigotin and 3-thionaphthalene-2-indoleindigotin respectively. The *p*-quinonoid compounds which are formed together with the indigoid dyes by the condensation of isatin chloride with certain phenols and naphthols are also decomposed by alkali, yielding hydroxy-aldehydes; for example, 2-chloro-4-hydroxy-1-naphth-

aldehyde, $C_6H_4 \begin{array}{c} \text{C(CHO):CCl} \\ \diagup \quad \diagdown \\ \text{C(OH)=CH} \end{array}$, m. p. about 220° (decomp.), is obtained from the product which results on condensing isatin chloride with 2-chloro- α -naphthol.

W. H. G.

Action of Halogens on Aromatic Amines and their Use in the Synthesis of Certain Dyes. ADRIANO OSTROGOVICH and T. SILBERMANN (*Chem. Zentr.*, 1908, i, 266; from *Bul. Soc. Stiinte Bucuresti*, 1907, 16, 120—126).—Iodine, bromine, and chlorine react with aniline at 140 — 180° giving dyes of the induline class. If a mixture of aniline hydrochloride and α -naphthylamine is subjected to the action of iodine in presence of aniline, a substance of the nature of a rosinduline is produced. *p*-Toluidine when heated at 140 — 180° with aniline and iodine gives *p*-rosaniline hydriodide. J. V. E.

Oxidation of Aniline by Halogen Acids. ADRIANO OSTROGOVICH and T. SILBERMANN (*Chem. Zentr.*, 1908, i, 266; from *Bul. Soc. Stiinte Bucuresti*, 1907, 16, 127—133).—In the presence of mineral acids, chloric, bromic, and iodic acids oxidise aniline to aniline-black. In presence of acetic acid, aniline is scarcely attacked by chloric acid; with bromic acid it yields dianilinoquinoneanil, and with iodic acid, azophenine. When dianilinoquinoneanil is melted with aniline hydrochloride and aniline, a blue induline dye is obtained; by using *p*-phenylenediamine in place of aniline, a bluish-violet induline dye is obtained; *o*-aminophenol, *p*-aminophenol, and *p*-phenylenediamine react in this respect like aniline. J. V. E.

Explanation of the Formation of Induline. ADRIANO OSTROGOVICH and T. SILBERMANN (*Chem. Zentr.*, 1908, i, 266—267; from *Bul. Soc. Stiinte Bucuresti*, 1907, 16, 133—141).—When aniline-black is heated at 180° with excess of an aniline salt, induline is quantitatively formed; from this and other observations, the author concludes that aniline-black is an intermediate product in the oxidation of aniline to induline. J. V. E.

Glycine as a Product of Uricolysis. LYMAN B. STOOKEY (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxx.; *J. Biol. Chem.*, 4).—Although

in vitro uric acid may be readily degraded to glycine, it is unsettled whether glycine is an intermediary product in uricolysis. Minced liver and kidney were incubated with uric acid and benzoic acid; the greater portion of the uric acid was destroyed, but there was no corresponding increase of hippuric acid; hence glycine was not formed.

W. D. H.

Azoxy-compounds. TH. ROTARSKI (*Ber.*, 1908, 41, 865—866).—The liquid, crystalline modifications of azoxybenzene, *m*-azoxytoluene, *m*-azoxyanisole, and *p*-azoxyphenetole are reduced in acid solution to amino-compounds and in alkaline solution or by distillation with iron to azo-compounds, but differ from the solid forms in the following respects: (1) They respond to Liebermann's nitroso-reaction. (2) The solution in boiling glacial acetic acid is coloured red by hydrochloric acid, D 1.19. (3) The yellow colour is unchanged by sunlight. (4) Sulphuric acid does not convert them into hydroxyazo-compounds. (5) The additive compound with bromine, formed in chloroform solution, loses hydrogen bromide when melted.

The temperature at which the turbid liquid crystals become clear is unchanged by crystallisation or distillation.

m-Azoxyanisole, m. p. 51°, obtained from *m*-nitroanisole and sodium methoxide, becomes red on exposure to light, and by distillation with iron filings yields *m*-azoanisole, m. p. 73—74°. C. S.

Constitution of the Acetylated Condensation Products from Benzeneazo- α -naphthol and Tetramethyldiaminobenzhydrol. RICHARD MÖHLAU (*Ber.*, 1908, 41, 989—990. Compare Möhlau and Kegel, *Abstr.*, 1900, i, 56).—The author confirms Auwers and Eisenlohr's statement (this vol., i, 229) that, when the acetylated condensation product is reduced, acetanilide is not formed, but aniline; hence the argument for the hydrazone constitution for the condensation product is no longer valid. J. J. S.

Chloroamine Reaction of the Proteins. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*J. Soc. Chem. Ind.*, 1908, 27, 6, 260).—The reaction of chlorine and hypochlorites on nitrogenous colloids to form chloroamine derivatives is shown to take place in constant and characteristic quantitative proportions, the derivatives being formed without destructive actions. The bearing of the fixation of "active" chloroamine chlorine on bleaching processes and the application of chloroamine reactions to histological investigations are dealt with in detail. J. V. E.

Hydrolysis of Different Proteins in Pepsin-Acid Solutions. WILLIAM N. BERG (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xlv.; *J. Biol. Chem.*, 4).—Various proteins and various acids of strength equivalent to 0.2% hydrochloric acid were employed. Edestin digests most rapidly, then follow in the order given, alkali-albumin, acid-albumin, fibrin, egg-albumin, nucleo-protein, and elastin. The order of the acids in efficiency is hydrochloric, nitric, oxalic, phosphoric, sulphuric, tartaric, lactic, citric, acetic, and boric. W. D. H.

The Preparation of *iso*Leucine from the Hydrolysis Products of Proteins. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Biochem. Zeitsch.*, 1908, 9, 231—232).—The principal difficulty which has existed hitherto in the preparation of pure leucine and its isomeride consists in the separation of valine from the leucines. This can be best accomplished by precipitation of the latter substances by normal lead acetate and ammonia. The leucines were prepared from casein in the following way. The casein was hydrolysed with 33% sulphuric acid, and the latter separated by barium hydroxide. On evaporation of the filtrate from barium sulphate, a mixture of tyrosine and leucine separated. On addition of bromine, the bromo-compound of the former substance was obtained, and could be dissolved out with amyl alcohol. On further evaporation of the liquid after this treatment, the leucine-valine mixture separated. This was redissolved, and the crude leucine precipitated by lead acetate and ammonia. On decomposing the lead precipitate with hydrogen sulphide, a mixture of leucine and *isoleucine* was obtained, from which the constituents could be readily separated by treatment of the copper salts with methyl alcohol. S. B. S.

Influence of Electrolytes on the Coagulation-temperature of Egg-albumin. WOLFGANG OSTWALD (*Chem. Zentr.*, 1908, i, 89; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 108—113).—By using the figures of Bonamartini and Pauli (*Abstr.*, 1907, i, 802), the dependence of the coagulation-temperature of various solutions of egg-albumin on the concentration of an added salt, such as NaCl or NH_4Cl , is represented with great accuracy by the equation: $1/t = Kc^m$, where t = coagulation-temperature, c = salt concentration, and K and m = constants. By altering the coagulation-temperature to 16° and a salt concentration from 1% to 20%, m only varies between 0.08 and 0.21. The similarity of the above equation to the general adsorption equation apparently shows a connexion between the temperature of coagulation of egg-albumin in presence of electrolytes and adsorption phenomena in solution. The attempt of Freundlich (*Abstr.*, 1907, ii, 939) to connect the phenomena of coagulation with ion adsorption is criticised. J. V. E.

Adsorption of Acids by Casein. LUCIUS L. VAN SLYKE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1908, 4, 259—266).—In spite of criticisms by T. B. Robertson (this vol., ii, 89), the authors maintain that the relationship between casein and acids is one of adsorption rather than chemical combination. W. D. H.

Preparation and Some Properties of the Oxyhæmocyanin Crystallised from the Snail. C. DÉRÉ (*Compt. rend.*, 1908, 146, 784—786).—When snail's blood is dialysed in a collodion bag in the presence of distilled water, renewed morning and evening, at the temperature of melting snow, it remains perfectly limpid during the first seven days. In the course of the eighth day, the blood becomes cloudy, and soon deposits an abundant precipitate of oxyhæmocyanin, the azure colour of the liquid becoming paler. Microscopic

examination of the deposit shows that it consists entirely of crystals in the form of six-pointed stars, which are not birefringent. After sixteen days, the supernatant liquid has become practically colourless, and is not altered by agitation with air. If after seven days the dialysed blood is subjected to the action of a continuous current of 0.1 milliampere at 120 volts, the oxyhæmocyannin is deposited at the anode, whilst the liquid surrounding the cathode becomes colourless, but, on shaking the whole liquid, the crystals of oxyhæmocyannin redissolve to a blue-coloured solution.

Oxyhæmocyannin, after calcination, leaves a small quantity of a black residue, which dissolves in nitric acid and contains copper. It dissolves in water containing a trace of acetic acid. The absorption spectrum given by a layer 3 mm. thick of a solution containing 7.59 grams of oxyhæmocyannin per litre presents a band in the ultra-violet between λ 292.6 and λ 262.8. On increasing the thickness of the layer, a fresh band appears, and at 10 mm. extends from λ 364.0 to λ 328.2. The latter band seems to be characteristic; the most refrangible band is common to all albuminous substances. E. H.

Soluble Silver Compounds of Nucleic Acids and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 188435).—The silver compound of sodium nucleate from yeast is obtained as a thick paste by adding aqueous silver nitrate to a strong solution of the nucleate in water. A saturated solution of sodium chloride is added until the precipitate has redissolved, when the compound is reprecipitated with alcohol. The product is a yellowish-white powder containing 22% to 23% of silver.

Sodium nucleate from the thymus gland gives a similar derivative, as do also the formaldehyde derivatives of these acids. G. T. M.

Pyrimidine Derivatives in Nucleic Acid. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 21, 157—161).—The question has arisen whether or no the pyrimidine derivatives of nucleic acid originate from the purine substances in the presence of carbohydrates. In the present research, the purines were first removed by mild hydrolysis; severe hydrolysis then liberated the pyrimidine compounds. The fact that the mild hydrolysis completely removed the purine, is shown by no ammonia being liberated during the severe hydrolysis, for each molecule of pyrimidine which is formed from the purines involves the production of two molecules of ammonia. The further conclusion is drawn that uracil is not derived from cytosine, for this also involves the production of ammonia. W. D. H.

The Origin of Cytosine, obtained by the Hydrolysis of Nucleic Acids of Animal Origin. PHÆBUS A. LEVENE and JOHN A. MANDEL (*Biochem. Zeitsch.*, 1908, 9, 233—239).—The estimation of cytosine obtained in different stages of partial and also in complete hydrolysis of nucleic acid of spleen was carried out. The results lead to no definite conclusion as to whether the cytosine is of secondary origin or not, that is, whether it is derived from the hydrolysis of purine compounds or directly from the original nucleic acid molecule.

S. B. S.

Reducing Action of Animal Fibres. GUSTAV ULRICH [and, in part, THEODOR SCHMIDT] (*Zeitsch. physiol. Chem.*, 1908, 55, 25—41).—These investigations were carried out with the object of determining the action of wool on the mixture of chromium trioxide and formic acid, as employed in mordanting processes. The direct reducing action of the formic acid on the chromium trioxide appears to be but small. The formic acid acts on the fibres with the production of substances which bring about the reduction of chromium trioxide.

S. B. S.

Behaviour of Gelatin Solutions Towards Naphthols or Mixtures of Naphthols with Formaldehyde. ARTHUR WEIN-SCHENK (*Chem. Zeit.*, 1908, 32, 266—267).—A reply to Stiasny's statements concerning the author's observations on the tanning of hides by means of naphthols in the presence of aldehydes. The addition of formaldehyde to a solution obtained by adding β -naphthol dissolved in glycerol to a strong aqueous solution of gelatin, produces a thick, flaky precipitate which is quite insoluble in water, whereas no such precipitate is formed in the absence of β -naphthol.

P. H.

Some Oxides as Tanning Material. LÜPPO-CRAMER (*Chem. Zentr.*, 1908, i, 93—94; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 171—173).—The author found previously (Abstr., 1907, i, 1098) that gelatin absorbs soluble salts without becoming tanned, whereas colloidal silver oxide acts as a typical tanning material. Silver peroxide, prepared from silver nitrate and ammonium persulphate, is now shown to be a far more powerful tanning agent. The silver peroxide compound of gelatin is insoluble in boiling water and unchanged by sodium hydroxide, ammonia, sodium thiosulphate, or dilute sulphuric acid, but is decomposed when warmed with strong acids. Metol-soda developer darkens the yellow colour, partly reduces the peroxide to silver, and does not destroy the tanning. A photographic negative desilverised by ammonium persulphate behaves in a similar manner, and, since a 10% potassium cyanide solution removes the image but does not destroy the tanning, the photobromide remaining in the negative plays no part in the tanning. Silver peroxide itself coagulates concentrated solutions of gum arabic. Mercury and copper oxides tan gelatin, rendering it insoluble. The HgO -gelatin shows unusual hardness, and, like Ag_2O -gelatin, when warmed in water becomes intensely white. CuO -gelatin is green, and by washing out excess of salt the tanning is not destroyed.

In the coagulation of egg-albumin by silver nitrate solution, adsorption compounds of silver oxide with egg-albumin are formed which are not attacked by thiosulphates. In all albumin papers therefore, after fixing and washing, there remains some silver oxide which may cause the paper to become yellow.

J. V. E.

Lipoids. SIGMUND FRÄNKEL (*Biochem. Zeitsch.*, 1908, 9, 44—53).
Part I. Neottine, a Triaminophosphatide. CARLO BOLAFFIO.—Two substances have been prepared from egg-yolks containing nitrogen

and phosphorus, the one with the element in the ratio 8N : 1P, and the other, a triaminophosphatide, designated *neottine*.

The former was prepared by extracting egg-yolks with acetone, filtering, distilling off the acetone, and again extracting the residue left with ether. On distilling off the latter solvent, crystals were deposited, and were separated from the liquid fats by aid of a porous tile. They were only partly soluble in acetone; the solution in this solvent gave a precipitate with cadmium chloride in alcoholic solution, which was soluble in hot benzene and could be recrystallised from boiling 95% alcohol. The cadmium compound thus obtained was crystalline and readily darkened on exposure to air, and was therefore probably an unsaturated compound. It contained 1.84% N and 0.51% P.

The second compound, *neottine*, $C_{84}H_{172}O_{15}N_3P$, was obtained by extracting dried egg-yolks with acetone until a white residue was obtained; this was digested for two hours at 45° with double its weight of 95% alcohol. The filtered extract, on evaporation in a vacuum, gave a white residue, which showed little change on exposure to air; the subsequent alcoholic extract of the residue darkened, however. The substance from the first extract was recrystallised several times from hot alcohol, and a white substance was finally obtained which could be readily powdered; the powder consisted of a fine network of microscopic needles, m. p. 91°. The molecular weight was confirmed cryoscopically. The substance absorbs but a small quantity of iodine, the Hübl number being only 16.2, and is optically inactive. It was found by the Herzig and Mayer method that only one-third of the nitrogen is combined with methyl groups (that is, in the form of choline). On hydrolysis with barium hydroxide, three acids were obtained, presumably cerebronic, stearic, and palmitic acids.

S. B. S.

Synthetic Tryptophan and Some of its Derivatives. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1908, 55, 8—24).—By the reduction of *α*-benzoylaminoindolylacrylic acid, $C_8H_6N \cdot CH : C(NHBz) \cdot CO_2H$, with sodium and alcohol, racemic tryptophan has been obtained (Abstr., 1907, i, 737). For identification and comparison with the natural dextrorotatory substance, the *benzenesulphonyltryptophans*, $C_8H_6N \cdot CH_2 \cdot CH(NH \cdot SO_2Bz) \cdot CO_2H$, the corresponding *β*-naphthalenesulphonyltryptophans, and the *tryptophan-naphthylcarbimides* were prepared. The derivatives from the natural dextrorotatory substance and the racemic synthetical compound had identical melting points (185°, 180°, 158°). The naphthylcarbimide compound is very sensitive to light. The paper gives, in addition, the details of the preparation of the synthetical substance.

S. B. S.

Optical Behaviour of Tryptophan. H. FISCHER (*Zeitsch. physiol. Chem.*, 1908, 55, 74—76).—Tryptophan and its hydrochloride are levorotatory, whilst the sodium salt is dextrorotatory. The rotation in aqueous solutions shows considerable variations, which cannot be accounted for by polymerisation. There is no reason to alter the original designation of Hopkins and Cole of *l*- into *d*-tryptophan.

S. B. S.

Union of Carbon Dioxide with Amphoteric Amino-compounds. III. MAX SIEGFRIED and C. NEUMANN (*Zeitsch. physiol. Chem.*, 1908, **54**, 423—436. Compare Abstr., 1905, ii, 332; 1906, i, 324).—The amount of carbon dioxide absorbed in the formation of carbamic acids from amino-compounds is determined by adding to 0.1—0.5 gram of the substance, dissolved in 50 c.c. of ice-cold water, a few drops of phenolphthalein in lime-water, and then about 10 c.c. of milk of lime, containing 20% of calcium hydroxide. Carbon dioxide is passed in until the indicator is almost decolorised while the solution is gently shaken. The addition of milk of lime and its neutralisation by carbon dioxide is repeated three to four times. The solution of the calcium carbamate is filtered clear and boiled; the calcium carbonate which is thus precipitated is weighed, and the nitrogen in the filtrate is determined by Kjeldahl's method.

A number of amino-acids and other substances have been examined, and the molecular ratio of ammonia to carbon dioxide approximates in nearly all cases rather closely to a whole number (in accordance with the theory). The reaction has been applied fractionally to a gluco-albumose, first obtained by Pick. The purity of the substance is deduced from the constancy of the nitrogen content of the fractions.

G. B.

Union of Carbon Dioxide with Amphoteric Amino-compounds. IV. MAX SIEGFRIED and HANS LIEBERMANN (*Zeitsch. physiol. Chem.*, 1908, **54**, 437—447).—The method described in the preceding abstract has been applied to polypeptides. In the case of glycylglycine, the ratio N/CO_2 is 1.79; this seems to be due to the formation of the ammonium salt of glycylglycine-carboxylic acid, m. p. 206° (almost identical with that of the acid itself). Glycylglycine-carboxylic acid does not unite with carbon dioxide in the presence of lime.

For a number of dipeptides, the ratio N/CO_2 was 1.63—1.79; for tripeptides, 2.57; for a tetrapeptide, 3.29; for trypsin-fibrin-peptone- α and - β (Abstr., 1903, i, 782) it was 2.14—2.46. Since these peptones cannot be as simple as di- or tri-peptides, the explanation of the low value (2.14—2.46) is sought in the possible presence of hydroxyl groups in the peptones; small quantities of alcohol, when present in the reaction mixture (for instance, as alcoholic phenolphthalein), lower the ratio very considerably.

G. B.

Serum Containing Anti-amylase. C. GESSARD and JULES WOLFF (*Compt. rend.*, 1908, **146**, 414—416).—As was shown by Gessard (*Compt. rend. Soc. Biol.*, 1906, **61**, 425), a serum can be prepared inhibiting the action of malt-extract on starch. In the present experiment, the greatest degree of inhibition is 70%, as determined by the amount of maltose produced. At 50° , the inhibitory effect is only half as great as at 20° .

G. B.

Tyrosinase and Racemic Tyrosine. GABRIEL BERTRAND and M. ROSENBLATT (*Compt. rend.*, 1908, **146**, 304—306; *Bull. Soc. chim.*, 1908, [iv], **3**, 394—398).—The oxidation of *d*-tyrosine and of *l*-tyrosine

and of *dl*-tyrosine by tyrosinase (from *Russula*) takes place at the same rate. Accordingly, there is only one ferment for both antipodes.

G. B.

The Co-enzyme of Expressed Yeast in Juice. EDUARD BUCHNER and FRITZ KLATTE (*Biochem. Zeitsch.*, 1908, 8, 520—557).—Previous researches have shown that the fermentative activity of yeast is due to two substances, the zymase, which is destroyed by boiling the expressed juice, and a co-enzyme, which is not so destroyed; the latter only can dialyse through parchment, and can also be separated from the former by filtration through a Martin gelatin filter.

Further experiments have been carried out with a view of throwing light on the chemical nature of these substances. Considerable differences were noted in their activity in yeasts of different origin; the juice from Berlin yeast, for example, could be better regenerated by the addition of boiled juice after it had lost its activity, than could that from Munich yeast. This fact may account for some of the discrepancies in the observations of different observers.

This regeneration could be accomplished in some cases as many as six or seven times, and the zymase was still active even after twenty-seven days. These facts indicate that the co-enzyme is much more readily destroyed than the zymase.

Yeast juice, which has become inactive by keeping without sugar, cannot be regenerated; neither can a co-enzyme be prepared from it. It is known that the proteoclastic enzyme contained in yeast can destroy the zymase, and experiments were carried out to determine whether it exerted a similar action on the co-enzyme. It was found that the co-enzyme lost but little of its activity after treatment with trypsin; it is improbable, therefore, that the tryptic enzyme of the yeast is responsible for the destruction; furthermore, on mixing the co-enzyme (boiled yeast juice) with fresh juice without sugar, it rapidly loses its activity. If, however, the juice is six months old, it exerts no destructive action on a co-enzyme, even although it retains its proteoclastic activity. The tryptic enzyme presumably destroys the substance which acts on the co-enzyme. Boiled juice, however, on treatment with lipase from castor-oil seeds rapidly loses its co-enzymic activity, and this fact leads to the supposition that the co-enzyme is of the nature of a phosphoric ester. It was found, in fact, that sodium glycerophosphate has considerable power in regenerating the inactivated zymase.

S. B. S.

The Chemical Changes in Adrenaline produced by Enzymes. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 8, 383—386).—The extract from the ink bag of *Sepia officinalis* has the power of producing a black pigment from adrenaline, which is insoluble in alcohol but partly soluble in alkalis; it is an oxidation product. Other substances from the animal organism, which yield colours, were investigated, but only tryptophan and tyrosine yielded pigments. The action is due to an enzyme, as the boiled extract has no action.

S. B. S.

Organic Chemistry.

Relative Volatility of Certain Groups of Mixed Carbon Compounds. II. Mixed Methylenic Compounds. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1908, 6—17. Compare this vol., i, 305).—A continuation of the author's discussion of the volatility relations of carbon compounds, dealing with substances of the types $\text{CH}_2\text{XX}'$ and $\text{CH}_3\cdot\text{CHXX}'$. Numerous examples are quoted to show that in some cases the boiling point of a mixed compound is approximately the arithmetic mean of those of the two corresponding simple substances; thus dimethoxymethane, $\text{CH}_2(\text{OMe})_2$, has b. p. 42° , and diethoxymethane, $\text{CH}_2(\text{OEt})_2$, has b. p. 88° , whereas *methoxyethoxymethane*, $\text{OMe}\cdot\text{CH}_2\cdot\text{OEt}$, obtained by the action of sodium ethoxide in alcohol on chloromethoxymethane, $\text{CH}_2\text{Cl}\cdot\text{OMe}$, has b. p. 67° . In such cases, it is suggested that the liquids show no molecular association. In other instances, for example, in the group CH_2Cl_2 , b. p. 42° , $\text{CH}_2(\text{OMe})_2$, b. p. 42° , and $\text{OMe}\cdot\text{CH}_2\text{Cl}$, b. p. 59° , the boiling point of the mixed compound is above the arithmetic mean. A second illustration of this is afforded by the group diphenoxymethane, $\text{CH}_2(\text{OPh})_2$, b. p. 298° , which crystallises at -8° , dimethoxymethane, b. p. 42° , and the methoxyphenoxymethane, $\text{OMe}\cdot\text{CH}_2\cdot\text{OPh}$, b. p. 189° (compare Reychler, this vol., i, 159).

Similar illustrations of these two relationships are quoted from ethylidene compounds of the type $\text{CHMe}\cdot\text{XX}'$. T. A. H.

Volatility in the "Methylation" Series of Methyl Derivatives. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1908, 66—81. Compare this vol., i, 305, and preceding abstract).—A study of the effect of the continued substitution of CH_3- for $\text{H}-$ in simple methane derivatives.

Taking the four compounds MeCl , CH_2MeCl , CHMe_2Cl , CMe_3Cl , the difference in boiling point between each successive pair diminishes regularly by 9° , which is in agreement with the observation that the alkyl haloids are non-associated liquids, since in such a case the substitution of $-\text{CH}_3$ for $\text{H}-$ involves a simple gravimetric effect, and does not imply any simplification or otherwise in the molecule as a whole.

The case is quite different in the series $\text{H}\cdot\text{OH}$, $\text{CH}_3\cdot\text{OH}$, $\text{CH}_2\text{Me}\cdot\text{OH}$, $\text{CHMe}_2\cdot\text{OH}$, and $\text{CMe}_3\cdot\text{OH}$, where the differences in boiling point between each successive pair are -34° , $+12^\circ$, $+4^\circ$, $\pm 0^\circ$ respectively. Here the changes in boiling point are due to two causes operating simultaneously: (a) the gradual simplification of a complex associated molecule causing a diminution in boiling point, and (b) the increase in molecular weight due to the substitution of $\text{H}-$ by $-\text{CH}_3$ causing a rise in boiling point. The operation of the same two causes, but especially of the first, is also seen in the series $\text{HO}\cdot\text{H}$, $\text{MeO}\cdot\text{H}$,

$\text{Me}\cdot\text{O}\cdot\text{Me}$, where the differences between each successive pair are -34° and $+89^\circ$ respectively, methyl ether being much less associated than either water or methyl alcohol. Mercaptans are less associated than alcohols, and consequently the gradual substitution of methyl in compounds of this series has much the same effect as in the case of the haloids, for example, $\text{Me}\cdot\text{SH}$, $\text{CH}_2\text{Me}\cdot\text{SH}$, $\text{CHMe}_2\cdot\text{SH}$, $\text{CMe}_3\cdot\text{SH}$, where the difference between each successive pair diminishes regularly by 10° . Similar discussions of the corresponding bromides, iodides, ethers, esters, nitrites, cyanides, &c., are given, and each of these groups approximates more or less closely in its behaviour to one of the two types mentioned above.

T. A. H.

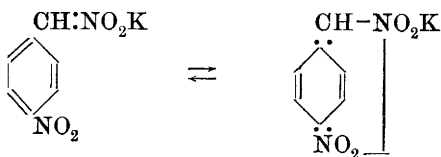
Spectroscopical Investigation of Isomerisable Nitro-compounds in Ultra-violet. EDGAR P. HEDLEY (*Ber.*, 1908, 41, 1195—1203).—Nitromethane, dinitromethane, trinitromethane, bromodinitromethane, dinitroethane, phenyldinitromethane, *o*-, *m*-, and *p*-nitrophenylnitromethane, and their alkali salts have been investigated in the ultra-violet by the method described by Hartley (*Trans.*, 1885, 47, 685).

The absorption curves of the colourless solutions of the mononitro-compounds in indifferent solvents are different from those of the colourless, alkaline solutions of the same compound, from which it follows, as has been shown by Ley and Hantzsch (*Abstr.*, 1906, i, 790), that the former solutions contain the true nitro-compound, $\text{R}\cdot\text{CH}_2\cdot\text{NO}_2$, whereas the latter contain the salts of the isomeric *aci*-nitro-compound, $\text{R}\cdot\text{CH}\cdot\text{NO}_2\text{M}$. Similarly, the absorption curves of the colourless solutions of dinitromethane, bromodinitromethane, and nitroform in ether, and of phenyldinitromethane in chloroform, are totally different from those of the yellow aqueous or alcoholic solutions of these compounds and of dinitroethane, which are very similar to the absorption curves of the solutions of the alkali salts of these compounds. The latter curves are analogous to those obtained by Baly with the nitroanilines (*Trans.*, 1906, 89, 514), and are totally different from those shown by the *aci*-mononitro-salts, $\text{R}\cdot\text{CH}\cdot\text{NO}_2\text{M}$. It is therefore evident that, as has been demonstrated by Hantzsch (*Abstr.*, 1907, i, 500), the coloured solutions of the dinitro-paraffins contain a highly isomerised form with a quinonoid grouping, which may be represented thus: $\text{R}\cdot\text{C}\begin{smallmatrix} \text{NO} \\ \diagdown \quad \diagup \\ \text{NO(OM)} \end{smallmatrix} > \text{O}$, and do not contain the

simple isomeric *aci*-form, $\text{R}\cdot\text{C}\begin{smallmatrix} \text{NO}_2 \\ \diagdown \quad \diagup \\ \text{NO}_2\text{M} \end{smallmatrix}$. The intensity of these solutions is proportional to the quantity of this form present in the solution; thus solutions of the alkali salts show a deeper band than the solutions of the substances in water, which in turn persists longer than that of a solution containing hydrochloric acid.

The colourless solutions of the nitrophenylnitromethanes in indifferent solvents do not show any absorption bands; the solutions of the alkali salts, however, show an absorption similar to that of dinitromethane salts, together with the characteristic benzene bands in the ultra-violet. It is probable that the colourless solutions contain

the true dinitro-compound, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NO}_2$, whereas the solutions



of the salts contain the benz-enoid and quinonoid salts in a state of equilibrium. It is also seen from the curves that the intensity of the benzene band is greatest in the case of the meta-salts,

and least with the para-salts, whilst the converse applies to the quinonoid band.

The colour of these similarly constituted compounds deepens with an increase in the molecular weight. W. H. G.

Densities of Solutions of Trimethylcarbinol and Phenol. EMANUALE PATERNÒ and ALDO MIELI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 396—400).—It has been found previously (compare Paternò and Ampola, *Abstr.*, 1897, ii, 476) that the equilibrium curve for mixtures of trimethylcarbinol and phenol exhibits two maxima, which should correspond with definite chemical compounds, and three minima, corresponding with three eutectic mixtures. The density-composition curves for mixtures of these two compounds at 25° and 46° exhibit no maxima, but are very nearly straight lines. T. H. P.

Reduction with Platinum and Hydrogen at the Ordinary Temperature. I. RICHARD WILLSTÄTTER and ERWIN W. MAYER (*Ber.*, 1908, 41, 1475—1480).—Reductions by means of hydrogen, which in presence of nickel or cobalt take place at high temperatures (Sabatier and Senderens, *Abstr.*, 1905, i, 333), may be accomplished at the ordinary temperature in presence of platinum (Fokin, *Abstr.*, 1907, i, 819). This method is of special importance for the reduction of olefines which are volatile only with difficulty. The application of the method to the reduction of a number of substances, including that of benzoic acid to hexahydrobenzoic acid, is described. The following facts are new.

Erucyl alcohol, $\text{C}_{22}\text{H}_{44}\text{O}$, m. p. 34·5°, prepared from erucic acid by Bouveault and Blanc's method (*Abstr.*, 1904, i, 642), forms a *di-bromide*, m. p. 45—45·5°, and on reduction yields *docosyl alcohol*, $\text{C}_{22}\text{H}_{46}\text{O}$, m. p. 71—71·5°. The *urethane* of the saturated alcohol has m. p. 86—86·5°.

Reduction of geraniol leads to the formation of the saturated alcohol in a 40% yield, and of $\beta\zeta$ -dimethyloctane, $\text{C}_{10}\text{H}_{22}$, in a 60% yield. The hydrocarbon is a colourless oil, b. p. 156·5—158°/724 mm., D_4^{20} 0·741, D_4^{20} 0·730, and is probably identical with Markownikoff and Reformatsky's hydrocarbon (*Abstr.*, 1893, i, 662).

Dihydrophytol, $\text{C}_{20}\text{H}_{42}\text{O}$, formed together with phytane by reduction of phytol, is a colourless oil, b. p. 201·5—202°/9·5 mm., D_4^{20} 0·849.

G. Y.

[General Method for the Preparation of Fatty or Aromatic Primary Ethers.] ALBERT REYCHLER (*Bull. Soc. chim.*, 1908, [iv], 3, 551).—A reply to Hamonet (this vol., i, 242), admitting the

accuracy of the latter's claim for priority in the discovery that the action of chlorodimethyl ether on magnesium alkyl haloids is capable of general application in the preparation of primary ethers.

T. A. H.

Glyceryl Nitrates. WILHELM WILL [with HAANEN and STÖHRER] (*Ber.*, 1908, 41, 1107—1125. Compare Mikolajczak, *Glückauf*, 1904, 629).—A comparative study of the mono-, di-, and tri-nitrates of glycerol. It is shown that, contrary to the statement of Mikolajczak, no advantages would accrue from the commercial employment of the dinitrate in place of the trinitrate, since the former in the anhydrous state is almost as explosive as the latter, and is as liable to freeze at low temperatures as the trinitrate, since it absorbs water from the air, forming a solid hydrate. The product formed by adding 100 parts of glycerol to 500 parts of a mixture of 45 parts of water, 342 parts of sulphuric acid, and 113 parts of nitric acid, or by adding glycerol to nitric acid (1·50), or by diluting a solution of glyceryl trinitrate in concentrated sulphuric acid with water, is a mixture of glyceryl $\alpha\beta$ -dinitrate and glyceryl $\alpha\gamma$ -dinitrate. The mother liquor from the action of nitric acid (1·50) on glycerol yields, on concentration and extraction with ether, an oil consisting of a mixture of glyceryl α -mononitrate and glyceryl β -mononitrate.

Glyceryl $\alpha\gamma$ -dinitrate, $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{O}\cdot\text{NO}_2)_2$, is an oil, b. p. $146\text{--}148^\circ/15$ mm. (decomp.), D_{15}^{20} 1·47, which solidifies at -40° and softens at -30° . It readily absorbs water from the air, forming a *hydrate*, $3(\text{C}_3\text{H}_6\text{O}_7\text{N}_2)\cdot\text{H}_2\text{O}$, crystallising in large, transparent, colourless prisms, m. p. 26° , b. p. $145^\circ/15$ mm. (decomp.). The anhydrous substance is almost as explosive as glyceryl trinitrate, but is far less sensitive to concussion in the hydrated form. Both forms detonate when heated on platinum foil. The *benzoate*, $\text{OBz}\cdot\text{CH}(\text{CH}_2\cdot\text{O}\cdot\text{NO}_2)_2$, is a crystalline substance, m. p. 67° ; the *p-nitrobenzoate*, $\text{C}_{10}\text{H}_9\text{O}_{10}\text{N}_3$, crystallises in small pyramids, m. p. 94° .

Glyceryl $\alpha\beta$ -dinitrate, $\text{NO}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{NO}_2)\cdot\text{CH}_2\cdot\text{OH}$, is an oil, b. p. about $145^\circ/15$ mm. (decomp.); the *hydrate* is also an oil; both forms are very similar in physical properties to the corresponding $\alpha\gamma$ -dinitrates. The *benzoate* and *acetate* could not be obtained in a crystalline form; the *p-nitrobenzoate* crystallises in yellow, rhombic leaflets, m. p. 81° . Both dinitrates yield on treatment with alkali hydroxides

the same *mononitroglycide*, $\text{O}\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2 \end{array}$, a colourless, limpid liquid, D_{20}^{20} 1·332, b. p. 174° (decomp.).

Glyceryl α -mononitrate, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, is formed when mononitroglycide is heated for some time with water; it crystallises in long prisms, m. p. $58\text{--}59^\circ$, b. p. about $155\text{--}160^\circ/15$ mm., and is very similar to glycerol in its general properties. It is not explosive, and yields on nitration a mixture of the trinitrate, $\alpha\beta$ -dinitrate, and $\alpha\gamma$ -dinitrate. It forms with calcium nitrate a crystalline *double salt*, $4\text{NO}_2\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2\cdot\text{Ca}(\text{NO}_3)_2$, m. p. 117° . The *diacetate*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, has m. p. $18\text{--}20^\circ$; the *dibenzoate*, $\text{OBz}\cdot\text{CH}_2\cdot\text{CH}(\text{OBz})\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, crystallises in colourless

needles, m. p. 68—69°; the *di-p-nitrobenzoate* forms yellowish-white crystals, m. p. 139°.

Glyceryl β-mononitrate, $\text{NO}_2 \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{OH})_2$, crystallises in slender leaflets, m. p. 54°, b. p. about 155—160°/15 mm. It is very similar in properties to the α -mononitrate, but does not form a double salt with calcium nitrate. It is converted on nitration into the trinitrate and the $\alpha\beta$ -dinitrate; the *di-p-nitrobenzoate* crystallises in yellow prisms, m. p. 152°.

W. H. G.

The Stability of Lecithin. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1908, 30, 881—895).—In the work of previous authors on the lecithins, it has generally been assumed that these substances readily undergo decomposition. In the course of an investigation, information was needed on this point, and experiments were therefore carried out which led to the following results.

Aqueous emulsions of egg and brain lecithin are very slightly affected by light, and are comparatively stable with respect to temperature. An increase of temperature or prolonged heating does not increase the dissociation as measured by acidity and electrical conductivity. Lecithin emulsions have an acid reaction. The residues, left after precipitating the emulsions with acetone, however, form neutral emulsions with water. On precipitating lecithin by the addition of acetone to an ethereal solution, in the process of preparation, a product is obtained which becomes acid when treated with water. The precipitation from water by means of acetone appears to cause some decomposition, as indicated by a change in the ratio of phosphorus to nitrogen in the residue. It is probable that the acidity is not due to the lecithin itself, but to decomposition products. Emulsions of both egg and brain lecithin are readily precipitated by dilute salt solutions, but no relation is observable between the precipitating powers of the salts and the valencies of their ions. E. G.

Behaviour of Emulsions of Lecithin with Metallic Salts and Certain Non-Electrolytes. JOHN H. LONG and FRANK GEHAERT (*J. Amer. Chem. Soc.*, 1908, 30, 895—902).—Solutions of many salts and acids cause precipitation when added to weak aqueous emulsions of lecithin. The completeness of the precipitation does not seem to bear any relation to the valency of the cations, but is connected in some way with the degree of dissociation of the various compounds. It has been found that ether and similar solvents extract very little lecithin from the pure emulsions, but that, after the addition of salt solutions, the lecithin is immediately taken up by the solvent; this action of the salts is related to their precipitating power. Certain non-electrolytes, such as glycerol, dextrose, sucrose, and carbamide, neither cause precipitation from the emulsions nor aid the solution of the lecithin by ether; on the addition of traces of salt solutions to the mixtures, however, the lecithin is immediately dissolved by the ether.

E. G.

Methods for the Preparation of Lecithin and other Phosphatides from Plant Seeds. ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1908, 55, 338—351).—The powdered material is extracted with 95%

alcohol at 50°, and the solvent is distilled off at the same temperature. The residue is treated alternately with water and ether, and the aqueous and ethereal extracts are brought (without shaking) into a separating funnel. The layers readily separate on addition of salt. The ethereal extract, after drying with anhydrous sodium sulphate, is evaporated down, and the residue taken up with acetone, in which the lecithin is insoluble; in this way, the fat is separated from the lecithin and phosphatides. The latter are then dissolved in ether, and precipitated from the concentrated solution by means of methyl acetate. The preparations thus obtained generally contain a certain amount of carbohydrates. S. B. S.

Action of Methyl Sulphate on Alkali Polysulphides. WILHELM STRECKER (*Ber.*, 1908, 41, 1105—1106).—Attempts to purify the hydrogen persulphides investigated by Bruni and Borgo (this vol., ii, 102) by distillation under reduced pressure having proved unsuccessful, the more stable methyl derivatives have been prepared by the action of methyl sulphate on alkali polysulphides.

Methyl trisulphide, Me_2S_3 (compare Klason, *Abstr.*, 1888, 356), is obtained by the distillation under reduced pressure of the products formed by the action of methyl sulphate on the alcoholic solutions of sodium pentasulphide, tetrasulphide, or trisulphide. It has not yet been definitely settled whether compounds are first formed having the composition Me_2S_5 or Me_2S_4 , and on distillation decompose, yielding the trisulphide. W. H. G.

Catalytic Reactions at High Temperatures and Pressures. XXII. **Catalytic Decomposition of Acids.** WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 514—518).—The author has investigated the decomposition of acetic acid which occurs when its vapour is passed over heated zinc, zinc oxide, zinc carbonate, calcium carbonate, strontium carbonate, barium carbonate, sodium hydroxide, sodium carbonate, or iron. The acid undergoes decomposition in two distinct ways, in one of which acetone, water, and carbon dioxide are formed, and in the other, hydrocarbons and hydrogen. At the moment of its formation, the acetone may undergo decomposition into carbon monoxide and saturated and unsaturated hydrocarbons. The carbonates of barium, strontium, calcium, and zinc, and also zinc oxide and metallic zinc, produce mainly the ketonic decomposition of acetic acid. The first action of the acetic acid may be to form metallic acetate, which then decomposes, giving acetone and the carbonate of the metal. When sodium hydroxide is used, the yield of acetone is small and that of methane large, whilst when sodium carbonate is employed, a considerable amount of acetone is formed. When iron is used as catalyst, only traces of acetone are obtained, the gases formed consisting of carbon dioxide and monoxide, hydrogen, methane, and ethylene hydrocarbons. T. H. P.

Preparation of Soluble Basic Acetates of Aluminium, Chromium, and Iron. E. DE HAËN (*D.R.-P.* 190451).—The

basic acetates of aluminium, chromium, and iron may be obtained in soluble stable form when to a strong solution of their sulphates and sodium acetate sufficient alkali is added to produce either of the following basic salts: $M'''_2(OH)_3(C_2H_3O_2)_4$ or $M'''_2(OH)_3(C_2H_3O_2)_3$. The solution should be sufficiently concentrated to keep the sodium sulphate produced in the form of a saturated solution at 34° .

A powdered mixture (19 parts) containing 71.3% of crystallised sodium acetate and 28.6% of anhydrous sodium carbonate is added to 64.7 parts of an aqueous solution of sodium alum (34°Bé) containing 17.6% of aluminium at 55° . After stirring for thirty minutes, the *basic aluminium acetate*, $Al_2(OH)_3(C_2H_3O_2)_3$, was centrifugalised and dried at moderate temperatures.

The *basic chromium* and *ferric acetates*, $Cr_2(OH)_3(C_2H_3O_2)_3$ and $Fe_2(OH)_3(C_2H_3O_2)_3$, are similarly prepared; the latter is a brick-red substance. G. T. M.

Certain Volatile and Non-volatile Compounds formed in Rancid Fats. ALBERTO SCALA (*Gazzetta*, 1908, 38, i, 307—327. Compare Abstr., 1899, i, 478).—Oil and lard which had been kept for some years until they had become thoroughly rancid were found to contain formic, butyric, hexoic, heptoic, and nonoic acids, and butaldehyde, hexaldehyde (?), heptaldehyde, and nonaldehyde. The odour and flavour of rancid fats are due, in some degree, to the hexaldehyde (?) and butaldehyde, but mainly to the heptaldehyde and nonaldehyde. The methods by which the various constituents were separated and characterised are fully described. T. H. P.

Action of Ozone on Triple Linkings. CARL D. HARRIES (*Ber.*, 1908, 41, 1227—1232).—Polemical (compare Molinari, Abstr., 1907, i, 1039; this vol., i, 244; Harries, this vol., i, 75). E. F. A.

Formation of Esters by Mass Action of Anions. BROR HOLMBERG (*Ber.*, 1908, 41, 1341—1346).—It has been already shown that the decomposition of ethyl diazoacetate by dilute acids is retarded by neutral salts, such as chlorides, sulphates, or nitrates (Fraenkel, Abstr., 1907, ii, 746), and Bredig and Ripley, from a study of the decomposition in the presence of chlorides, drew the conclusion that the ratio of the formation of ethyl chloroacetate to ethyl diazoacetate decomposition increased with the concentration of the chlorine ions, but was independent of the concentration of diazoacetate or hydrogen ions (Abstr., 1907, ii, 941).

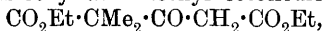
This view is supported by the isolation of ethyl glycollate and its nitric ester when the decomposition is carried out in the presence of sodium nitrate, and by fractional crystallisation of the liquid obtained after the decomposition of the diazoacetate in the presence of sodium sulphate and extraction with ether, when a salt was finally obtained which crystallised from alcohol in silky white leaflets, and proved to be *sodium ethyl glycollate sulphate*, $OEt \cdot CO \cdot CH_2 \cdot O \cdot SO_3Na$.

The reaction with nitrates and sulphates has also been studied quantitatively, with the result that the best yield of glycollic ester is obtained when the temperature is low and the concentration of anions is as great as possible. W. R.

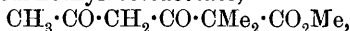
Condensations with Ethyl Acetoacetate and their Reversion.

WALTER DIECKMANN and ARTHUR KRON (*Ber.*, 1908, 41, 1260—1278).—In a previous communication (*Abstr.*, 1900, i, 623), the decomposition of $\alpha\gamma$ -dicarbonyl compounds by sodium ethoxide was shown to depend on their acidity. The stability of esters of β -ketocarboxylic acids, previously established, is now shown to extend to non-substituted $\alpha\gamma$ -diketones, as typified by benzoylacetone. The stability of cyclic ethyl succinylsuccinate towards sodium ethoxide illustrates how the increase in acidity raises the stability. The catalytic hydrolysis of esters of dialkylated β -ketocarboxylic acids has been confirmed in the cases of ethyl dibenzylacetoacetate and the alkylated propionylpropionic acid esters.

Compounds such as ethyl *as*-dimethylacetonedicarboxylate,



and methyl γ -acetyldimethylacetoacetate,



which contain an acid salt-forming group, $\text{CO}\cdot\text{CH}_2\cdot\text{CO}$, alongside a neutral, in itself decomposable, nucleus, $\text{CO}\cdot\text{CR}_2\cdot\text{CO}$, are hardly attacked by excess of sodium ethoxide even on boiling. On the other hand, when the strongly acid 1:3-dicarbonyl group, $\text{CO}\cdot\text{CH}_2\cdot\text{CO}$, is converted by alkylation into the less acid group, $\text{CO}\cdot\text{CHR}\cdot\text{CO}$, the stability towards sodium ethoxide disappears, as exemplified by the behaviour of ethyl trimethylacetonedicarboxylate. The group $\text{R}_2\cdot\text{CH}\cdot\text{CO}$ will permit of the ester condensation, provided salt formation takes place at the same time and opposes the decomposition in the reverse direction by the sodium alkoxide. Such condensations have been observed in the case of the interaction of sodium ethylmalonate and benzylidenemethyl *isopropyl* ketone and of ethyl sodioisobutyrylacetate and ethylcinnamic acid, when products which give colorations with ferric chloride are formed, but have not been isolated. In the case, however, of ethyl benzylidenemalonate and ethyl isobutyrylacetate, the product *ethyl 4-phenyl-1:1-dimethylcyclohexane-2:6-dione-3:5-dicarboxylate*, $\text{CMe}_2\left\langle\begin{smallmatrix} \text{CO}\cdot\text{CH}(\text{CO}_2\text{Et}) \\ \text{CO}\cdot\text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix}\right\rangle\text{CHPh}$, is formed. The same compound is obtained by methylation of ethyl phenylhydroresorcinoldicarboxylate, whereby the constitution is established.

Ethyl dibenzylacetoacetate, on boiling for three hours with alcoholic sodium ethoxide, yields ethyl dibenzylacetate, a colourless oil, b. p. 196—198°/14 mm., which could not be brought to crystallisation, but was identified by conversion into dibenzylacetic acid, m. p. 89—90°. *Methyl dibenzylacetate* forms colourless needles, m. p. 40—41°. The compound m. p. 88—89°, described as ethyl dibenzylacetate by Fichter and Schiess (*Abstr.*, 1901, i, 544), is regarded as more probably the ester $\text{CO}_2\text{Et}\cdot\text{C}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$.

Ethyl benzylidenebenzoylacetate is decomposed on heating for three hours with alcoholic sodium ethoxide into ethyl benzoate and ethyl cinnamate. On the other hand, benzoylacetone, ethyl succinylsuccinate, ethyl γ -acetyl- α -dimethylacetoacetate, and ethyl *as*-dimethylacetonedicarboxylate are all unchanged by boiling for three hours with sodium ethoxide.

Ethyl propionylpropionate is a colourless oil, b. p. 87—88°/16 mm.;

it can be alkylated by methyl iodide and sodium ethoxide to ethyl propionylethylpropionate, a colourless oil, b. p. 97—98°/16 mm. *Ethyl propionylbenzylpropionate*, $\text{COEt} \cdot \text{CMe}(\text{C}_7\text{H}_7) \cdot \text{CO}_2\text{Et}$, prepared by the action of benzyl chloride or bromide, is a colourless oil, b. p. 179—183°/20—21 mm. Boiling with sodium ethoxide converts this into *ethyl α -benzylpropionate*, $\text{CH}_3 \cdot \text{CH}(\text{C}_7\text{H}_7) \cdot \text{CO}_2\text{Et}$, a colourless oil, b. p. 142—143°/20—21 mm.

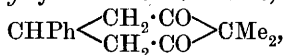
Ethyl sodioisobutyrylacetate in ethereal solution condenses with ethyl benzylidenemalonate to form *ethyl 4-phenyl-1:1-dimethylcyclohexane-2:6-dione-3:5-dicarboxylate*, crystallising in colourless prisms, m. p. 146°. This gives a bluish-violet coloration with ferric chloride, and forms a green, crystalline copper salt and a bisphenylpyrazolone derivative, $\text{C}_{28}\text{H}_{24}\text{O}_2\text{N}_4$, separating in colourless crystals which were not melted at 270°.

Ethyl isobutyrylacetate interacts with benzylideneacetophenone in presence of sodium ethoxide, forming *ethyl γ -benzoyl- α -isobutyryl- β -phenylbutyrate*, of which the colourless crystals have m. p. 112°.

Ethyl 4-p-methoxyphenyl-1:1-dimethylcyclohexane-2:6-dione-3:5-dicarboxylate, prepared from ethyl anisylidenemalonate, has m. p. 141°.

The above phenylcyclohexanedione ester compound dissolves in methyl-alcoholic potassium hydroxide, and separates in the form of a sparingly soluble crystalline dipotassium salt. If left in contact with the potassium hydroxide, this salt passes into solution, and separates again in the form of colourless crystals of a potassium salt of a tri-carboxylic acid, formed by opening the ring. Decomposed with mineral acids, the salt yields a thick, colourless oil, giving no coloration with ferric chloride. The ester is quite stable towards sodium ethoxide. Heating with mineral acids converts it into γ -isobutyryl- β -phenylbutyric acid, which crystallises in colourless needles, m. p. 106—107°. The amide forms colourless crystals, m. p. 126°; the semicarbazone has m. p. 165°.

4-Phenyl-1:1-dimethylcyclohexane-2:6-dione,



prepared by heating the above ester with 80% acetic acid, forms long, colourless needles, m. p. 86°; the dioxime has m. p. 235—236°; the bisphenylhydrazone forms faintly yellow prisms, m. p. 175—176°.

Ethyl 4-phenyl-1-ethylcyclohexane-2:6-dione-3:5-dicarboxylate forms colourless crystals, m. p. 146°, and gives an intense brownish-violet coloration with ferric chloride.

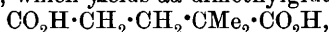
Ethyl 3-isobutyryl-2:6-diphenyl-4-isopropyl- Δ^3 -cyclohexene-1:1-dicarboxylate, prepared by the condensation of 2 mols. of benzylidenemethyl isopropyl ketone and 1 mol. of ethyl sodiomalonate, crystallises in colourless needles, m. p. 190°, and shows no coloration with ferric chloride.

The dibromide of benzylidenemethyl isopropyl ketone crystallises in prisms, m. p. 102—103°.

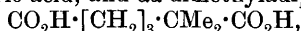
Ethyl 3-benzoyl-2:4:6-triphenyl- Δ^3 -cyclohexene-1:1-dicarboxylate, similarly prepared from benzylideneacetophenone, forms colourless crystals, m. p. 197°.

E. F. A.

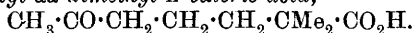
Condensations with Cinenic Acid. HANS RUPE and CARL LIECHTENHAN (*Ber.*, 1908, 41, 1278—1286).—By the action of concentrated sulphuric acid on cinenic acid, two products are formed: a liquid acid, $C_9H_{16}O_3$, which yields *aa*-dimethylglutaric acid,



on oxidation with nitric acid, and *aa*-dimethyladipic acid,



together with bromoform on treatment with sodium hypobromite, and is therefore a *δ*-acetyl-*aa*-dimethyl-*n*-valeric acid,



This change involves wandering of a methyl from carbon atom ζ to carbon atom α in cinenic acid, $\overset{CMe_2}{\underset{\text{O}}{\text{[CH}_2\text{]}_3}} \cdot CMe \cdot CO_2H$, and is

explained by the intermediate formation of a ring. The second product formed in small quantities is a cyclic lactone, $C_9H_{14}O_2$, probably the lactone of 1:3-dimethylcyclohexan-1-ol-3-carboxylic acid.

Cinenic acid is prepared from methylheptenone by Rupe and Schlochoff's method (*Abstr.*, 1905, i, 409), and fuller details of its preparation are now given. When dissolved in cooled concentrated sulphuric acid, it is converted into *δ*-acetyl-*aa*-dimethyl-*n*-valeric acid, a colourless liquid, which has b. p. 275—280°/739 mm., 168·8—169·4°/11·5 mm., D_4^{20} 1·0211, n_D^{20} 1·44883. The *ethyl* ester has b. p. 121·5°/12·5 mm. The *semicarbazone* forms large, colourless, many-faced crystals, m. p. 165°; the *oxime* separates in large, hard, prismatic prisms, m. p. 93—93·5°. By oxidation with nitric acid, *aa*-dimethylglutaric acid is formed, m. p. 84°, and is identified by means of the anhydride, *p*-toluidide, and anilide.

The *lactone* of 1:3-dimethylcyclohexan-1-ol-3-carboxylic acid has b. p. 102—114°/11 mm., and forms crystals, m. p. 50—51°. The *calcium* salt of the hydroxy-acid crystallises in hexagonal plates. With bromine, a crystalline product, m. p. 73·5—74°, is formed, which yields the original lactone when heated with alcoholic potassium hydroxide.

E. F. A.

Dehydracetic Acid. OSWALD HESSE (*J. pr. Chem.*, 1908, [ii], 77, 390—392).—An acid, m. p. 108°, obtained on recrystallising rhein from ethyl acetoacetate and thought to be a derivative of rhein (*Abstr.*, 1906, i, 280), has proved to be dehydracetic acid. A number of its salts are described. The *phenylmethylhydrazide*, $C_{15}H_{16}O_3N_2$, crystallises in light yellow needles, m. p. 148°.

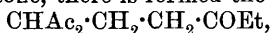
G. Y.

Syntheses by means of β-Chloroethyl and Vinyl Ketones. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 413—421, 421—427. Compare this vol., i, 418).—Vorländer has shown (*Abstr.*, 1897, i, 272) that it is possible to attach the sodium derivatives of β-ketonic esters to unsaturated acids. In the present paper, this work is extended to unsaturated ketones, and a number of products so obtained are described. When the vinyl ketones are employed directly, the yields of the products sought are unsatisfactory, and it is more convenient to condense the chloro-derivatives of the

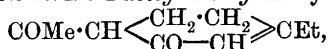
corresponding saturated ketones with the sodium derivatives of the β -ketonic substances used.

Ethyl α -acetyl- γ -propionyl-n-butyrate, $\text{COEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, b. p. $150^\circ/8$ mm. (decomp.), obtained by condensing the sodium derivative of ethyl acetoacetate with β -chloroethyl ethyl ketone, is a mobile liquid with a slight odour of mint, gives a bluish-violet colour with ferric chloride, yields a *disemicarbazone*, m. p. 195° (decomp.), and, unlike the δ -diketones described by Knoevenagel (Abstr., 1893, i, 419), is relatively stable, not undergoing ring condensation by the action of heat, sulphuric acid in alcohol, or sodium ethoxide, but only when its solution in ether is saturated with hydrogen chloride, yielding *ethyl 1-ethyl- Δ^1 -cyclohexene-3-one-4-carboxylate*, $\text{CO}_2\text{Et} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} - \text{CH} \end{smallmatrix} \text{CEt}$, b. p. $150^\circ/14$ mm., a liquid giving a blue coloration with ferric chloride, and possessing a pleasant mint-like odour. Its *semicarbazone*, m. p. 207° , crystallises from alcohol. When warmed with diluted sulphuric acid, the cyclic ester yields *1-ethyl- Δ^1 -cyclohexene-3-one*, b. p. $83^\circ/8$ mm., which is pungent and mint-like in odour, and gives a *semicarbazone*, m. p. 240° (decomp.). With 1 mol. of hydroxylamine hydrochloride, it furnishes a crystalline *oxime*, m. p. 106° , and with 2 mols. an oil (compare Hagemann, Abstr., 1893, i, 393). The ethylcyclohexenone reacts with magnesium ethyl bromide to form *1:3-diethylcyclohexadiene*, $\text{CEt} \begin{smallmatrix} \text{CH} - \text{CEt} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH}$, b. p. $68^\circ/9$ mm. pressure, and with magnesium phenyl bromide to form *1-phenyl-3-ethylcyclohexadiene*, b. p. $126-128^\circ/8$ mm. pressure, which has an odour like that of diphenyl.

When the sodium derivative of acetylacetone is condensed with β -chloroethyl ethyl ketone, there is formed the *triketone*,



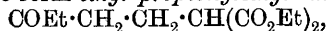
b. p. $154^\circ/16$ mm., a faintly yellow liquid, which gives a bluish-violet coloration with ferric chloride, and with 3 mols. of semicarbazide hydrochloride yields a *carbamyldipyrzolesemicarbazone*, which decomposes at 190° . On saturation of its solution in ether with hydrogen chloride, the triketone forms *4-acetyl-1-ethyl- Δ^1 -cyclohexene-3-one*,



b. p. $144^\circ/15$ mm., a faintly yellow liquid, giving a blue coloration with ferric chloride, and yielding a *carbamyldipyrzole*, m. p. 165° (decomp.), which separates from alcohol in dense crystals, and a *dioxime*, m. p. 216° (decomp.), which crystallises from ethyl acetate in brilliant needles.

The two δ -ketonic esters, referred to above, when undergoing cyclic condensation in presence of hydrochloric acid, form, in addition to substituted cyclohexenones of the type described, isomeric products of the type $\text{CO}_2\text{Et} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CMe} : \text{CMe} \end{smallmatrix} \text{CO}$, which are usually produced in too small quantities to be isolated.

The sodium derivative of ethyl malonate condenses with β -chloroethyl ethyl ketone to form *ethyl propionylethylmalonate*,



b. p. 166°/14 mm. pressure, a viscid liquid of peculiar odour, furnishing a *semicarbazone*, m. p. 90°, which crystallises in cottony needles from warm ether. The *free acid*, m. p. 83°, crystallises from cold benzene, and when heated at 160° furnishes *γ-propionylbutyric acid*, m. p. 50°, which crystallises from ether on addition of light petroleum, and yields a *semicarbazone*, m. p. 196°, and an *oxime*, m. p. 118°. *Methyl γ-propionylbutyrate*, b. p. 101–102°/10 mm., has but little odour. The *ethyl ester*, b. p. 116°/14 mm., on treatment by Vorländer's method (*loc. cit.*), furnishes a nearly theoretical yield of 1-methyl-Δ¹cyclohexen-2-ol-6-one, $\text{CMe} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{C(OH)} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, m. p. 210° approx. (decomp.). This forms

opaque crystals from alcohol, and furnishes with semicarbazide hydrochloride a *carbamylpyrazole*, which crystallises from formic acid on addition of alcohol and decomposes without melting, and a *dioxime*, m. p. 220° (approx.), which separates from alcohol in slender needles.

1-Methyl-Δ¹-cyclohexen-2-ol-6-one differs markedly in solubility from dihydroresorcinol, but comparison of the specific refractive powers of the two substances (respectively 0.28996 and 0.28516 in alcohol for sodium light) indicates that they are similarly constituted. The higher homologue gives a faint blue coloration with ferric chloride in the cold, but a much more intense colour is produced if the reagent is added to a hot saturated solution (0.3%) of the substance in water.

T. A. H.

Reactions of Mercuric Chloride with Organic Acids. WILLIAM OECHSNER DE CONINCK and DAUTRY (*Bull. Acad. roy. Belg.*, 1908, 55–56).—The authors confirm Becquerel and Marchand's observation that solutions containing mercuric chloride, oxalic acid, and water deposit mercurous chloride on exposure to sunlight for a few hours. When malonic acid is substituted for oxalic acid, traces of precipitation occur after about twelve days. It is suggested that this difference in reaction may be used as a method of distinguishing between the two acids.

T. A. H.

Some Cuprammonium Salts. VI. DAVID W. HORN and MINNIE A. GRAHAM (*Amer. Chem. J.*, 1908, 39, 505–513).—In an earlier paper (*Abstr.*, 1906, ii, 231), a stable cuprammonium oxalate, $\text{CuC}_2\text{O}_4 \cdot 2\text{NH}_3$, was described. It has now been found that a labile isomeric salt exists. The former is termed the α -, and the latter the β -compound.

The α -salt forms deep sapphire-coloured crystals, is saturated towards ammonia, has D_4^{25} 2.305, and dissociates at about 187°/30 mm. with production of a dark olive-green compound.

The β -salt is a sky-blue, amorphous substance, is unsaturated towards ammonia, has D_4^{25} about 2.230, dissociates at about 171°/30 mm. with formation of a green compound, and when heated at 100° is more or less completely transformed into the α -salt.

E. G.

Constitution of Carbon Suboxide. OTTO DIELS and PAUL BLUMBERG (*Ber.*, 1908, 41, 1233–1236).—Polemical (compare Michael, this vol., i, 316; also Diels and Blumberg, this vol., ii, 103; *Abstr.*, 1906, ii, 227; 1907, ii, 180). The following reasons are

given in favour of adopting the symmetrical allene formula $\text{CO}:\text{C}:\text{CO}$. (1) Boiling point $+7^\circ$, (2) similarity with the metal carbonyls, (3) high value of the molecular refraction and dispersion, (4) analogy to keten, (5) addition of 4 atoms of bromine and formation from dibromomalonyl bromide, (6) formation of malonic acid on the addition of water, and (7) improbable existence of a β -lactone containing a triple linking.

E. F. A.

Preparation of Adipic Acid and of Ethyl cyclopentanone-carboxylate. LOUIS BOUVEAULT and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1908, [iv], 3, 437—441).—Adipic acid may be prepared by the oxidation of cyclohexane (Aschan, *Abstr.*, 1899, i, 672), but the process is very slow, and cyclohexanol, which may be prepared in large quantity by reducing phenol by Sabatier and Senderens' method, is a more satisfactory starting point. A detailed description is given of the method of preparing adipic acid by oxidation of cyclohexanol with hot nitric acid, and of separating the acid from oxalic, glutaric, and succinic acids simultaneously formed. The yield of adipic acid is 52% of the theoretical. Ethyl adipate dissolved in benzene is readily converted by the action of sodamide (compare Haller, *Abstr.*, 1904, i, 600) into ethyl cyclopentanone-2-carboxylate, and the preparation of this substance and its separation from cyclopentanone, simultaneously formed, is described in detail.

T. A. H.

Bismuth Cholate. EMIL WÖRNER (D.R.-P. 191385).—Bismuth cholate is prepared by heating any basic bismuth salt with excess of an aqueous solution of an alkali cholate. The product is a yellowish-white insoluble basic salt, the composition of which depends on that of the bismuth salt employed in its production; alcohol decomposes it, withdrawing cholic acid.

G. T. M.

The Asymmetric Conjugation of Glycuronic Acid. PAUL MAYER (*Biochem. Zeitsch.*, 1908, 9, 439—441).—Inactive camphor was administered to a dog, and the excreted glycuronate was isolated from the urine. This on hydrolysis yielded a campherol, in which $[\alpha]_D^{17} = -5.91^\circ$. Pure *l*-campherol gives $[\alpha]_D -32.91^\circ$. Hence the campherol in the urine contained 17.9% of the active variety, and an asymmetric conjugation with glycuronic acid had taken place in the organism.

S. B. S.

Formaldehyde Solutions. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1908, [iv], 3, 411—413).—The author asserts that certain of the conclusions regarding the constitution of aqueous solutions of formaldehyde drawn by Auerbach and Barschall from the results of their investigations (*Abstr.*, 1905, i, 860; 1908, i, 131) are merely confirmatory of views already published by him (*Abstr.*, 1897, i, 504, 505; ii, 359).

T. A. H.

A Simple Reaction for Producing a Disinfectant Gas. [Formaldehyde Vapour.] G. CARTERET (*Compt. rend.*, 1908, 146, 819—820).—Reactions hitherto described for the production of form-

aldehyde by the action of peroxides or per-salts on trioxymethylene or paraformaldehyde suffer under the disadvantage of being either too violent or too slow. But by the action of water (3 parts) on a mixture of bleaching powder (2 parts) with paraformaldehyde (1 part), a rapid evolution of formaldehyde vapour is produced, the temperature of the mixture rising to 108°. The gas evolved contains only traces of chlorine, and does not attack objects placed in it, except certain aniline dyes which react with formaldehyde. Its bactericidal power is very great. Sporulated charcoal placed under two thicknesses of cloth is sterilised in seven hours in the atmosphere produced by 125 grams of paraformaldehyde in a space of 20 cubic metres. In this and similar reactions, the author considers the production of formaldehyde to be due to the elevation of temperature in the presence of water vapour.

E. H.

Keten. HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1908, 41, 1516—1517).—A reply to Wilsmore and Stewart (this vol., i, 318).

G. Y.

Saccharin and Alkali Saccharinates. EBERHARD RIMBACH and EDMUND HEITEN (*Annalen*, 1908, 359, 317—335).—Tables are given of the optical rotation and rotatory dispersion of saccharin in water, methyl and ethyl alcohols, and acetone, and of alkali saccharinates in water, the influence of concentration and temperature being also observed. The crystallographic constants are also given, as well as the electrical conductivity of the aqueous solutions of the potassium and rubidium salts.

J. V. E.

The Relation of the Cyclic Inosite to the Aliphatic Sugars. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 9, 551—556).—Inosite on distillation with phosphoric oxide or boron trioxide yields furfuraldehyde, which was identified by the isolation of its condensation products with thiosemicarbazide and *p*-nitrophenylhydrazine. This reaction indicates a relationship with the aliphatic sugars.

S. B. S.

Constitution of "Phytin." CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 9, 557—560).—Phytin is a condensation product of inosite and phosphoric acid, not of formaldehyde and phosphoric acid, since on distillation with glacial phosphoric acid it yields a liquid which, on rectification, gives the ordinary furfuraldehyde reactions (preceding abstract).

S. B. S.

Action of Anhydrous Nitric and Sulphuric Acids on Cellulose. BERTHOLD RASSOW and WALDEMAR VON BONGÉ (*Zeitsch. angew. Chem.*, 1908, 21, 732—737).—The mixture of nitric and sulphuric acids employed for the commercial nitration of cellulose always contains a certain amount of water. In the present communication, the action of a mixture of anhydrous acids has been studied; by keeping the acids in large excess, the influence of the water formed by the reaction was as far as possible eliminated. It was found that esters of nitric acid, insoluble in water, were only formed when the nitrating mixture contained at least one part of

nitric acid to seven of sulphuric acid; the resulting nitrocellulose is short fibred and contains 37.79% of unchanged cellulose. By increasing the proportion of nitric acid, the percentage of nitrogen in the resulting product was raised until it corresponded with a mixture of penta- and hexa-nitrocelluloses, but it never reached the figure attained with the use of the diluted acids. A sudden diminution in the nitrogen content of the nitrocellulose was observed when the proportions of acid were one of sulphuric to three of nitric, but by increasing the amount of nitric acid the percentage rose, and finally dropped again to 10.98 when nitric acid alone was employed. The nitrocellulose formed by the action of anhydrous nitric acid alone on cellulose is slimy, but on treatment with water it becomes tough. The solubility of the esters in a mixture of ether and alcohol is, on the whole, low. Contrary to the usually accepted view, it was found that nitrocelluloses are completely soluble in Schweizer's reagent on prolonged shaking.

P. H.

Preparation of Amylamine. CHEMISCHE WERKE FORM. HEINRICH BRY (D.R.-P. 193166).—Leucine, when distilled under reduced pressure, furnishes amylamine, the yield depending on the degree of vacuum employed. The product contains at least two isomerides, *iso*amylamine, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, and active amylamine, $\text{CHMeEt} \cdot \text{CH}_2 \cdot \text{NH}_2$. Owing to racemisation at the high temperature, the externally compensated form is also present. *iso*Leucine behaves similarly on distillation.

G. T. M.

Preparation of Choline from Lecithin. J. D. RIEDEL (D.R.-P. 193449).—Lecithin is heated with two parts of 40% sulphuric acid, and the mixture shaken until a clear solution is obtained. On cooling, the fatty acids separate and solidify, the aqueous solution and washings are almost neutralised with barium hydroxide. The filtrate is concentrated, and the choline precipitated as its mercurichloride. This compound is suspended in water and decomposed with hydrogen sulphide, and the filtrate evaporated. The residue of choline solidifies on cooling to a yellow, crystalline mass; the melting points of the aurichloride and platinichloride from this preparation agree with those obtained formerly for these choline double salts.

G. T. M.

The Quantitative Recovery of Choline from Lecithin. G. MORUZZI (*Zeitsch. physiol. Chem.*, 1908, 55, 352—359).—By the hydrolysis of the cadmium chloride compound of lecithin with fifty times its weight of 10% sulphuric acid for four hours, scission took place of practically all the basic nitrogen (99.8%). Under these conditions, the maximum yield was obtained. Experiments were carried out with the object of quantitatively isolating the base after hydrolysis, chiefly by means of the phosphotungstate; the base was set free from the phosphotungstate, and precipitated and weighed in the form of the platinichloride. As a rule, only 77% of the choline, calculated on the nitrogen content of the scission product obtained by acid, was obtained.

S. B. S.

The Quantitative Recovery of Choline from Lecithin. HUGH MACLEAN (*Zeitsch. physiol. Chem.*, 1908, 55, 360—370).—The hydrolysis was carried out by means of barium hydroxide both in aqueous solution and in solution in methyl alcohol. All the original nitrogen, except about 8%, dissolved in the alcohol. In most cases, the choline was precipitated by mercuric chloride, recovered from this precipitate, and reprecipitated as platinichloride. The amount of platinichloride recovered was only about 77% of the quantity theoretically possible (compare preceding abstract). By means of experiments carried out with pure choline, mixed with glycerophosphate and other substances, it was found that the loss is due to the incompleteness of the platinichloride precipitation, which, in the presence of substances derived from lecithin hydrolysis, amounts to about 9—10%.
S. B. S.

Compounds of Amino-acids and Ammonia. III. PETER BERGELL and JOHANNES FEIGL (*Zeitsch. physiol. Chem.*, 1908, 55, 173—176).—By hydrolysis of diglycinimide, $\text{NH}(\text{CO}\cdot\text{CH}_2\text{NH}_2)_2$ (this vol., i, 140), with sodium hydroxide, iminodiacetic acid, $\text{NH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, is obtained. This acid was isolated as the crystalline β -naphthalenesulphonyl derivative, $\text{C}_{14}\text{H}_{13}\text{O}_6\text{NS}$, m. p. 230° (uncorr.), yielding a very sparingly soluble barium salt, $\text{C}_{14}\text{H}_{11}\text{O}_6\text{NSBa}$.
G. B.

Synthesis of isoLeucine. FELIX EHRLICH (*Ber.*, 1908, 41, 1453—1458*).—The synthesis of *d*-isoleucine described previously (Abstr., 1907, i, 592) is incomplete in so far as the initial substance is *d*-amyl alcohol, and, moreover, presents difficulties arising from the fact that commercial amyl alcohol is not an individual substance.

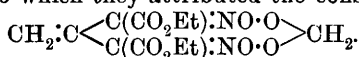
Bouveault and Locquin's synthesis (Abstr., 1906, i, 938) is remarkable in that, starting from inactive substances, they obtained only the racemic form of *isoleucine*, whereas theoretically the racemic form of *allo-isoleucine* should also be produced.

Taking into account the close analogy between the chemical behaviour of leucine and *isoleucine*, the author has succeeded in synthesising the racemic modification of the latter by the method successfully employed by Fischer and Schmitz (Abstr., 1906, i, 182) in the synthesis of leucine. *sec*-Butyl iodide and ethyl sodiomalonate yield van Romburgh's *sec*-butylmalonic acid (Abstr., 1888, 446), which by bromination by Fischer's method (Abstr., 1904, i, 890) gives *a*-bromo-*sec*-butylmalonic acid, $\text{CHMeEt}\cdot\text{CBr}(\text{CO}_2\text{H})_2$, m. p. 114 — 115° (decomp.). By distilling the latter in a vacuum, *a*-bromo- β -methylvaleric acid, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, is obtained, b. p. 139 — $140^\circ/22$ mm., which is converted by 25% ammonium hydroxide at the ordinary temperature in five days, or by concentrated ammonium hydroxide at 100° in two hours, into inactive *isoleucine*, the resolution of which by yeast will be described subsequently.
C. S.

Action of Formaldehyde on the Ammonium Derivative of Ethyl Nitromalonate. A. BATTAGLIA (*Gazzetta*, 1908, 38, i, 356—360).—Ulpiani and Pannain (Abstr., 1903, i, 863), by the

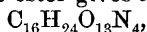
* and *Zeitsch. Ver. deut. Zuckerind.*, 1908, 528—533.

action of formaldehyde on ethyl nitromalonate in presence of ammonia, obtained an ester to which they attributed the constitution



The results of the author's examination of this product are, however, best explained by the structure $\text{NH}[\text{CH}_2\cdot\text{C}(\text{NO}_2)(\text{CO}_2\text{Et})_2]_2$.

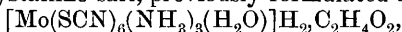
The ester has the normal molecular weight in freezing benzene or boiling ether, and yields the ammonium derivative of ethyl nitromalonate when treated with dry ammonia in ethereal solution. The action of nitrous acid on the ester gives a true *nitrosoamine*,



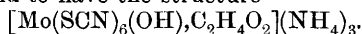
which is obtained as a pale yellow oil, whilst with diethylamine the ester forms the *diethylamine* salt of ethyl nitromalonate, $\text{C}_{11}\text{H}_{22}\text{O}_6\text{N}_2$, m. p. 123° . The ester contains no double linking, and forms an unstable, crystalline compound with bromine. T. H. P.

Hexathiocyno-salts of Molybdenum. JOHANNA MAAS and JULIUS SAND (*Ber.*, 1908, 41, 1500—1514. Compare Abstr., 1906, i, 487; this vol., i, 11; Chilesotti, Abstr., 1906, ii, 263, 365).—The relation of the complex salts of molybdenum to the aquo-salts of the cobalt series is discussed.

The yellow, crystalline salt, previously formulated as



is now considered to be an additive compound of acetic acid and an ammonium salt, and to have the structure



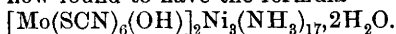
It crystallises in rhombic pyramids [$a:b:c=0.7255:1:0.6338$], and has the electrolytic conductivity $\mu_{25}=299.9$ with $v=34.47$. The conductivity increases on addition of 1 mol. of sodium hydroxide to the aqueous solution, in consequence of the formation of sodium acetate and the ammonium salt, $[\text{Mo}(\text{SCN})_6(\text{OH})](\text{NH}_4)_3$; as on addition of a further 3 mols. of sodium hydroxide the sodium salt, $[\text{Mo}(\text{SCN})_6(\text{OH})]\text{Na}_3$, and free ammonia, which has only feeble conducting powers, are formed, the effect of the addition of the alkali does not differ greatly from that of dilution with water, and hence the conductivity of the solution diminishes, but on further addition of sodium hydroxide the conductivity again increases, as the alkali is then present in excess.

The *potassium* salt, $[\text{Mo}(\text{SCN})_6(\text{OH})]\text{K}_3\cdot 4\text{H}_2\text{O}$, prepared by electrolysis of potassium molybdate and thiocyanate in hydrochloric acid solution, forms yellow crystals, loses $4\text{H}_2\text{O}$ over sulphuric acid in a vacuum, has the conductivity $\mu_{25}=355$ with $v=64$, and when treated with acetic acid yields the *salt*, $[\text{Mo}(\text{SCN})_6(\text{OH})(\text{C}_2\text{H}_4\text{O}_2)]\text{K}_3$. This crystallises in rhombic pyramids, [$a:b:c=0.7124:1:0.6318$], and has the conductivity $\mu_{25}=334$ with $v=64$.

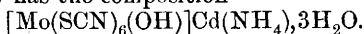
The salt, $\text{Mo}(\text{SCN})_6(\text{OH})(\text{HC}_2\text{H}_8\text{N}_2)_3$, formed by the action of ethylenediamine on the ammonium salt, crystallises in quadratic prisms, m. p. 128° (decomp.).

The zinc salt, previously formulated as $\text{Mo}(\text{SCN})_6\text{Zn}(\text{NH}_3)_4$, is now found to have the formula $[\text{Mo}(\text{SCN})_6(\text{OH})_2]\text{Zn}_3(\text{NH}_3)_{11}$; the

ammonia groups are co-ordinated with the zinc atoms. Similarly, the nickel salt is now found to have the formula



The corresponding cadmium salt, $[\text{Mo}(\text{SCN})_6(\text{OH})]_2\text{Cd}_3(\text{NH}_3)_{13}$, forms yellow crystals. A crystalline salt, $[\text{Mo}(\text{SCN})_6(\text{OH})]\text{HCd}\cdot 2\text{H}_2\text{O}$, is formed as a red precipitate on addition of cadmium sulphate to a concentrated aqueous solution of the additive compound of the ammonium salt and acetic acid, whilst in the presence of sulphuric acid the precipitate has the composition



A complex salt, $[\text{Mo}(\text{SCN})_6(\text{OH})]_3\text{Cd}_3\cdot [\text{Mo}(\text{SCN})_6(\text{OH})]\text{CdK}\cdot 18\text{H}_2\text{O}$, is formed from the acetate of the potassium series. G. Y.

Fixation of Amines on the Ethylenic Linking of Alkyl Vinyl Ketones. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 543—551).—A more detailed account is given of the substances obtained by the addition of primary or secondary amines to alkyl vinyl ketones (Abstr., 1906, i, 142; 1907, i, 241).

Ethyl β -diethylaminoethyl ketone, $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$, obtained by simple addition of diethylamine to ethyl vinyl ketone dissolved in ether, is a liquid of feebly basic odour and is readily soluble in water. The *semicarbazone*, m. p. 100° , and the *picrate*, m. p. 78° , are crystalline. On reduction, the amino-ketone furnishes the corresponding *amino-alcohol*, b. p. $80^\circ/8$ mm., which is liquid, has a feebly basic odour, and furnishes a *benzoate hydrochloride*, m. p. 75° , and a *phenylurethane hydrochloride*, m. p. 134° , both of which are crystalline.

Ethyl β -piperidinoethyl ketone, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$, b. p. $100^\circ/7$ mm., is liquid, possesses a piperidine-like odour, is slightly soluble in water, and yields a crystalline *semicarbazone*, m. p. 146° , *picrate*, m. p. 97° , *platinichloride*, m. p. 135° (approx.), and *oxime*, m. p. 50° . The oxime, on reduction by sodium amalgam in acetic acid, yields 1- γ -aminoamylpiperidine, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{NH}_2$, b. p. $100^\circ/9$ mm., which is liquid, has a strongly basic odour, is soluble in water, and furnishes a *hydrochloride*, m. p. 212° (approx.), *picrate*, m. p. 167° , and a *monohydrated platinichloride*, m. p. 216° (approx.), all of which are well crystallised. With potassium cyanate, the diamine yields the corresponding *carbamide*, m. p. 145° , which separates from benzene in colourless crystals, and with phenylcarbimide the corresponding *phenylcarbamide*, m. p. 104° , crystallising from benzene on addition of light petroleum. The diamine reacts with ethyl oxalate to form the corresponding *oxamide*, m. p. 128° , which crystallises from boiling acetic acid.

The interaction of primary amines and alkyl vinyl ketones is less simple than is that of the *sec.*-amines, since the former can react (1) with the ketone group, or (2) may simply add on to the ethylenic linking, forming a secondary amine, which may in its turn react with a second molecule of the alkyl vinyl ketone. The simple additive reaction is the principal one which occurs in presence of acetic or formic acid.

Ethyl β -propylaminoethyl ketone, $\text{NHPr}^a\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$, b. p. $85^\circ/12$ mm., the chief product of the action of propylamine on ethyl

vinyl ketone in presence of formic acid, is an unstable liquid of basic odour, and furnishes a *phenylcarbamide*, m. p. 115° , which separates from alcohol in brilliant lamellæ. In addition to the amino-ketone, a viscous *liquid* boiling at $156^{\circ}/12$ mm. is obtained in the above reaction, which may be the product of the further action of ethyl β -propyl-aminoethyl ketone on ethyl vinyl ketone, and has the constitution $\text{COEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NPr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COEt}$, but no definite semicarbazone could be obtained from it. The interaction of ammonia and ethyl vinyl ketone seems to be very complex, and no definite product could be isolated.

T. A. H.

"Neuronal" (Bromodiethylacetamide). CARL MANNICH and F. ZERNIK (*Arch. Pharm.*, 1908, **246**, 178—186).—A continuation of work undertaken with a view to the determination of the constitution of neuronal. The results now recorded confirm the constitution previously suggested for the drug by Zernik (*Apoth. Zeit.*, 1904, 88).

When neuronal, $\text{C}_2\text{H}_5\text{Br}\cdot\text{CO}\cdot\text{NH}_2$, is boiled with a solution of sodium hydroxide in water, it decomposes in two ways, yielding in the one case diethyl ketone with hydrobromic and hydrocyanic acids, and in the other, diethylglycollamide, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, and hydrobromic acid. *Diethylglycollamide*, m. p. 85 — 86° , crystallises in colourless leaflets from benzene, dissolves moist mercuric oxide on warming, is not attacked by alkaline permanganate, and yields neither diethyl ketone nor hydrogen cyanide when heated with alkali hydroxides, so that it is not an intermediate product in the first reaction. Neuronal dissolved in ether is decomposed by metallic sodium, yielding diethylcarbinol and hydrobromic and hydrocyanic acids. When boiled with water, neuronal loses 1 mol. of hydrogen bromide and furnishes *α -ethylcrotonamide*, $\text{CHMe}\cdot\text{C}_2\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, m. p. 99° , which crystallises in colourless needles, is readily soluble in alcohol or ether, slightly so in light petroleum, is not hydrolysed by alkalis, but is slowly attacked by boiling dilute sulphuric acid, forming ammonia and an indefinite oily product. It forms a *dibromide*, m. p. 128° , which crystallises from alcohol in colourless needles, and is readily soluble in chloroform or alcohol, but scarcely so in water. None of the three new substances described is physiologically active.

T. A. H.

Preparation of α -Chloroisovalerylcarbamide. KNOLL & Co. (D.R.-P. 191386. Compare Abstr., 1907, i, 1017).— α -Chloroisovalerylchloride and the corresponding bromide, prepared from α -chloroisovaleric acid and phosphoryl chloride and phosphorus tribromide respectively, react with carbamide, giving rise to α -chloroisovalerylcarbamide, m. p. 139° , a substance having marked hypnotic properties.

G. T. M.

Double Compounds of Hydrogen Peroxide with Organic Compounds. SIMEON M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 376—380).—Like inorganic compounds (compare Tanatar, Abstr., 1902, ii, 11; Willstätter, Abstr., 1903, ii, 537), a large number of organic compounds combine with hydrogen peroxide, forming compounds similar to those containing water of crystallisation. In

certain cases, compounds which do not crystallise with water of crystallisation form crystalline compounds with hydrogen peroxide. The following compounds were prepared by evaporating, either on the water-bath or in a desiccator, solutions of the various substances in more or less concentrated hydrogen peroxide solutions.

Carbamide forms the moderately stable *compound*, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$, which is deposited in large, transparent crystals, resembling those of potassium nitrate, and retains more than 15% (instead of 36.15%) of hydrogen peroxide after six months. Acetamide and urethane also unite with hydrogen peroxide, but no definite compounds could be obtained. Succinimide yields the *compound*, $\text{C}_4\text{H}_5\text{O}_2\text{N} \cdot \text{H}_2\text{O}_2$, which is appreciably less stable than that formed by carbamide. Asparagine gives the viscous *compound*, $\text{C}_4\text{H}_8\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}_2$; mannitol, the moderately unstable *compound*, $\text{C}_6\text{H}_{14}\text{O}_6 \cdot \text{H}_2\text{O}_2$, and pinacone, the syrupy *compound*, $\text{C}_6\text{H}_{14}\text{O}_2 \cdot \text{H}_2\text{O}_2$, which evaporates completely on the water-bath and gives a distillate containing 8.93%, instead of 22.36%, of hydrogen peroxide. Erythritol forms an unstable, crystalline compound. Sucrose does not combine with hydrogen peroxide, whilst parabanic acid and ammonium oxalate yield crystalline compounds of indefinite composition.

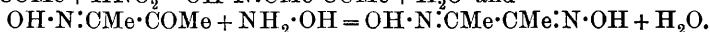
T. H. P.

Synthesis of Ammonia and of Hydrogen Cyanide. HERMAN C. WOLTERECK (*Compt. rend.*, 1908, 146, 929—931. Compare Abstr., 1904, ii, 115; this vol., ii, 174).—When heated moist air is blown through an apparatus containing incandescent charcoal, the escaping gases contain hydrogen cyanide and ammonia in quantities increasing with the temperature of the air and of the charcoal. If instead of air a mixture of air and ammonia is employed, hydrogen cyanide is also formed, together with ammonia, corresponding with an excess of 44% of the original quantity. The probable course of the reaction is the formation of hydrogen cyanide in the zone of highest temperature according to the equation $2\text{N} + \text{O} + \text{H}_2\text{O} + 4\text{C} = 2\text{HCN} + 2\text{CO}$, and the subsequent decomposition of part of the hydrogen cyanide to form ammonia and carbon monoxide, $\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{CO}$.

In one experiment of an hour's duration, 97.70 grams of hydrogen cyanide and 71.53 grams of ammonia were obtained by passing 820 kilos. of air at 300° over heated charcoal at 1260—1340°.

M. A. W.

Preparation of Dimethylglyoxime. A. GANDARIN (*J. pr. Chem.*, 1908, [ii], 77, 414—416).—Since dimethylglyoxime has become of importance as a reagent for nickel and cobalt (Kraut, Abstr., 1906, ii, 858; Brunck, Abstr., 1907, ii, 582; Tschugaeff, *ibid.*, 989), an easy and cheap method of preparation was highly desirable. Such a method is now described. Methyl ethyl ketone is shaken with amyl nitrite and hydrochloric acid, D 1.19, at 40—50°; the product is treated with ice and sodium hydroxide, and the resulting alkaline solution of the isonitroso-compound is heated with hydroxylamine hydrochloride. The reaction takes place according to the equations: $\text{C}_2\text{H}_5 \cdot \text{COMe} + \text{HNO}_2 = \text{OH} \cdot \text{N} : \text{CMe} \cdot \text{COMe} + \text{H}_2\text{O}$ and



The pure dioxime is obtained in a yield of 650—700 grams from 850 c.c. of the ketone. The original should be consulted for details of the process. G. Y.

Synthesis by means of Organo-metallic Compounds. JOSEPH ZELTNER (*J. pr. Chem.*, 1908, [ii], 77, 393—402; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 381—391).—A résumé of the work of various authors on organo-metallic compounds. The capacity to form such compounds, which commences with the metals of the first group of the periodic system, reaches its maximum in the metals of the second group, and diminishes in the metals of groups III, IV, and V. The elements of groups VI and VII show no tendency to form organo-metallic compounds, but this tendency reappears in the transition group VIII. The stability of organo-metallic compounds of metals of the same group increases with the atomic weight of the metal and with the size of the organic radicle. If a reaction takes place in several stages, and it is desired to obtain the product of the first stage, it is advantageous to employ zinc rather than magnesium; conversely, if the final product is desired, or the reaction takes place in one stage, magnesium is to be preferred to zinc. The influence of the weight of the alkyl groups is seen in the formation of primary in place of secondary, and of secondary in place of tertiary, alcohols from zinc dipropyl and zinc compounds of higher alkyls (compare Bogomoletz, *Abstr.*, 1881, 401). G. Y.

cycloOctane and cycloHeptane. RICHARD WILLSTÄTTER and TOKUHEI KAMETAKA (*Ber.*, 1908, 41, 1480—1486).—Willstätter and Bruce found that *cyclobutane* is reduced to butane by Sabatier and Senderens' method at 180—200° (*Abstr.*, 1907, i, 1018), and that (*loc. cit.*) the reduction of *cyclopropane* to propane takes place still more easily at 80—120°. Sabatier and Senderens, on the other hand, have shown that *cyclohexane*, when heated with nickel and hydrogen, does not form hexane, but at 270—280° decomposes, yielding methane and benzene. The behaviour of *cycloheptane* and *cyclooctane* under similar conditions has now been studied.

When reduced with hydrogen and nickel at 235°, *cycloheptane* is converted chiefly into methyl*cyclohexane*, at the same time forming small amounts of dimethyl*cyclopentane*. If the reduction is carried out at 250°, the product contains traces of aromatic hydrocarbon in consequence of the decomposition of methyl*cyclohexane*, which commences at 240° (Sabatier and Senderens, *Abstr.*, 1905, i, 401).

cycloOctane, prepared by Willstätter and Veraguth's method (*Abstr.*, 1907, i, 303), is obtained in a series of fractions: b. p. 142—144°/737 mm.; b. p. 144—147°/737 mm.; and m. p. 5—6°, b. p. 147·2—148·8°/737 mm. The first two fractions, when oxidised by nitric acid, yield suberic acid and a more easily soluble acid, m. p. 82—85°, which may be β -methyladipic acid. The fraction with the highest boiling point is probably pure *cyclooctane*. When reduced with nickel and hydrogen at 205—210°, it yields a product consisting chiefly of dimethyl*cyclohexane*, together with, perhaps, alkylated *cyclopentanes*

dicycloOctane, C_8H_{14} , prepared by reduction of *dicyclooctene* (Willstätter and Veraguth, *loc. cit.*) by Sabatier and Senderens' method at $145-150^\circ$, has b. p. $139.5-140.5^\circ$ (corr.), D_4^0 0.8775, D_4^{20} 0.8604, n_D^{20} 1.46148, is stable towards permanganate, and is coloured by bromine in traces. On reduction with hydrogen and nickel at $200-205^\circ$, *dicyclooctane* yields a mixture of hydrocarbons identical with the product obtained from *cyclooctane*, which may be formed intermediately.

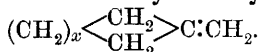
G. Y.

Constitution of cycloButene. RICHARD WILLSTÄTTER and JAMES BRUCE (*Ber.*, 1908, 41, 1486—1488. Compare Abstr., 1907, i, 1018; Willstätter and Schmaedel, Abstr., 1905, i, 514).—Zelinsky and Gutt's suggestion that *cyclobutene* has a dicyclic structure (this vol., i, 14) is discussed and rejected. The formation of *cyclobutene* from trimethylcyclobutylammonium hydroxide and by the action of zinc on *cyclobutene* dibromide are in agreement with the monocyclic structure. *cycloButene* decolorises permanganate instantaneously, and forms an *additive* compound with bromine at -20° , whereas dicyclic hydrocarbons are stable towards these reagents. *cycloButene* dibromide is a 1:2-dibromide and not a 1:3-dibromide, as only 1 mol. of hydrogen bromide can be split off; the resulting bromocyclobutene on oxidation yields succinic acid, and has therefore the constitution $\begin{array}{c} CH_2 \cdot CBr \\ | \\ CH_2 \cdot CH \end{array}$, and

not $\begin{array}{c} CH_2 \cdot CHBr \\ | \\ CH=CH \end{array}$, as would be the case if *cyclobutene* had a dicyclic structure.

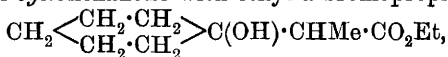
G. Y.

Terpenes and Ethereal Oils. XCII. Preparation of Cyclic Hydrocarbons with Semicyclic Linkings and their Use in New Syntheses. OTTO WALLACH (*Annalen*, 1908, 360, 26—81).—As has been shown previously, the unsaturated hydrocarbons, formed by loss of water from tertiary alcohols, $(CH_2)_x \begin{array}{c} < CH_2 \\ > \\ CH_2 \end{array} CR \cdot OH$, which are prepared from cyclic ketones by Grignard's reaction, usually have the ethylene linking in the cyclic nucleus. If, on the other hand, the cyclic ketone is condensed with ethyl bromoacetate and zinc, the resulting hydroxy-esters, $(CH_2)_x \begin{array}{c} < CH_2 \\ > \\ CH_2 \end{array} C(OH) \cdot CH_2 \cdot CO_2Et$, when treated with potassium hydrogen sulphate, yield unsaturated acids of the type $(CH_2)_x \begin{array}{c} < CH_2 \\ > \\ CH_2 \end{array} C:CH \cdot CO_2H$, which on distillation form unsaturated hydrocarbons with semicyclic ethylene linkings,

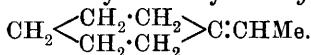


Such hydrocarbons have been obtained also on distillation of unsaturated acids having an ethylene linking in the cyclic nucleus, molecular transformation taking place along with the loss of carbon dioxide. It is now found that unsaturated hydrocarbons with semicyclic ethylene linkings are obtained also from acids having the

carboxyl group situated in a longer side-chain. Thus the condensation product of *cyclohexanone* with ethyl α -bromopropionate,



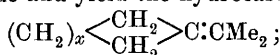
on hydrolysis and distillation yields ethylidenecyclohexane,



Of special interest is the behaviour of the condensation products of ethyl α -bromoisobutyrate, $(\text{CH}_2)_x \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{C}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$. The

removal of water from such substances can lead to the formation only of unsaturated esters containing a nucleus ethylene linking,

$(\text{CH}_2)_x \begin{array}{c} \text{CH}_2 \\ \text{OH} \end{array} \text{C} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$. The corresponding acids on distillation lose carbon dioxide and yield the hydrocarbons,



in this case, also, the ethylene linking wanders to the side-chain. In this manner, *o*-, *m*-, and *p*-menthenes with semicyclic ethylene linkings have been synthesised from the corresponding methylcyclohexanones.

The reverse transmigration of an ethylene linking from the semicyclic position into the nucleus has been observed previously as taking place under the influence of boiling mineral acids in the case of *p*-menthene (Abstr., 1906, i, 682) and of isopropylidenepentane (Abstr., 1907, i, 616). This is now found to be a general reaction, the ethylene linking being stable in the nucleus in aqueous acid solution, but in the semicyclic position in the absence of water and at high temperatures.

I. *Condensation of cyclohexanone with Ethyl α -Bromopropionate.*—[With EDGAR EVANS.]—Ethyl cyclohexanol-1-*a*-propionate,



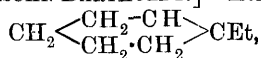
prepared in the usual manner from cyclohexanone and ethyl α -bromopropionate, has b. p. 125—127°/12 mm. or 135—136°/20 mm., and when heated with potassium hydrogen sulphate at 150° yields the unsaturated ester, b. p. 108—112°/12 mm. This on hydrolysis forms cyclohexene-*a*-propionic acid, b. p. 148—150°/13 mm.; the silver salt, $\text{C}_9\text{H}_{13}\text{O}_2\text{Ag}$, was analysed. On distillation under the ordinary pressure, the acid yields cyclohexene-ethane (ethylidenecyclohexane), $\text{C}_8\text{H}_{10} \cdot \text{CHMe}$, b. p. 137—138°, D^{20}_D 0.8220—0.8225, n^{20}_D 1.4626—1.4631. This hydrocarbon readily forms a nitrosochloride in an 88% yield. The nitrolpiperidide, $\text{C}_5\text{H}_{10} \cdot \text{N} \cdot \text{C}_6\text{H}_{10} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$, has m. p. 116—117°.

The methoxyloxime, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{OMe} \\ \text{CMe} \cdot \text{N} \cdot \text{OH} \end{array}$, m. p. 85—86°, is formed from the nitrosochloride by the action of sodium methoxide. When heated successively with dimethylaniline and sulphuric acid, the nitrosochloride yields a mixture of acetophenone and cyclohexenyl methyl ketone, $\text{CH}_2 \begin{array}{c} \text{CH}_2 - \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \cdot \text{COMe}$. This is obtained

by heating the nitrosochloride with sodium acetate and acetic acid, and distilling the product with steam in presence of sulphuric acid; it has b. p. 201—202°, D 0.9655, n^{20}_D 1.4881. The semicarbazone,

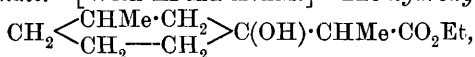
$C_9H_{15}ON_3$, m. p. 220—221°; the *oxime*, m. p. 99°. When reduced with sodium in alcoholic solution, the tetrahydro-ketone yields hexahydroacetophenone (*cyclohexyl methyl ketone*), which forms a *p-nitrophenylhydrazone*, m. p. 154°.

[With PAUL MENDELSON-BARTHOLDY.]—Ethyl- Δ^1 -cyclohexene,



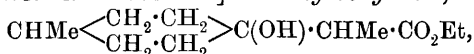
prepared by boiling ethylidenecyclohexane with alcoholic sulphuric acid, is identical with Sabatier and Mailhe's hydrocarbon (Abstr., 1904, i, 666). It has b. p. 134—136°, D^{19}_D 0.8235, and n_D 1.4591. It forms a *nitrosochloride* readily, but in smaller yield than its isomeride. The *nitrolpiperidide*, m. p. 149°. When heated with sodium acetate and glacial acetic acid, the nitrosochloride yields a *ketone*, b. p. 195—200°, which has an odour resembling *cyclohexanone*, and forms an *oxime*, m. p. 57°, and a *semicarbazone*, m. p. 175°.

II. Condensation of Active 1-Methylcyclohexane-3-one with Ethyl α -Bromopropionate.—[With EDGAR EVANS.]—The *hydroxy-ester*,



prepared in the usual manner from 1-methylcyclohexane-3-one, ethyl α -bromopropionate, and zinc, has b. p. 133—135°/13 mm. The unsaturated *ester*, b. p. 115—117°/13 mm. The unsaturated *acid*, b. p. 155—157°/17 mm., forms a *silver salt*, $C_{10}H_{15}O_2Ag$, and on distillation yields 1-methyl-3-ethylidenecyclohexane, $C_6H_9Me \cdot CHMe$, which has b. p. 153°, D 0.813, n_D 1.4584, and is laevorotatory. The *nitrosochloride* forms a *nitrolpiperidide*, m. p. 100—101°.

III. Condensation of 1-Methylcyclohexane-4-one with Ethyl α -Bromopropionate.—[With EDGAR EVANS.]—The *hydroxy-ester*,



has b. p. 134—136°/13 mm. The unsaturated *ester*, b. p. 114—116°/13 mm. The unsaturated *acid*, b. p. 152—154°/13 mm., forms a *silver salt*, $C_{10}H_{15}O_2Ag$.

1-Methyl-4-ethylidenecyclohexane, $C_{10}H_{16}$, has b. p. 156°, D^{20}_D 0.811, n^{20}_D 1.4571. The *nitrosochloride*, formed in an 83% to 85% yield, was converted into (a) the *nitrolpiperidide*, $C_{14}H_{26}ON_2$, which is obtained in two fractions, m. p. 127—128° and 133—134°, and (b) the *oxime*,

$CHMe \begin{array}{c} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2-CH \end{array} \cdot C \cdot CMe \cdot NOH$, m. p. 117°, which on hydrolysis is converted into 4-acetyl-1-methyl- Δ^1 -cyclohexene, $C_6H_8Me \cdot COMe$, b. p. 212—214°, D^{20}_D 0.942, n^{20}_D 1.4782. This forms a *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 220°. On reduction with sodium and alcohol, the tetrahydro-ketone is converted into a saturated *ketone*, which on treatment with hypobromite yields bromoform and an acid having the composition of hexahydrotoluic acid.

IV. Condensation of cycloHexanone with Ethyl α -Bromo-n-butyrate.—[With J. B. CHURCHILL and MAHLON RENTSCHLER.]—The *hydroxy-ester*, $OH \cdot C_6H_{10} \cdot CHEt \cdot CO_2Et$, has b. p. 145—150°/16 mm. The unsaturated *ester*, b. p. 122—127°/14 mm. The unsaturated *acid*, b. p. about 150°, forms a *silver salt*, $C_{10}H_{15}O_2Ag$; this acid reacts with

hydrogen bromide in glacial acetic acid solution, forming a *bromo-acid*, $C_{10}H_{17}O_2Br$, m. p. 107—108°.

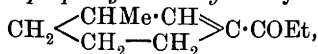
Propyridenecyclohexane, $C_8H_{10} \cdot CHEt$, formed by distillation of the preceding unsaturated acid, has b. p. 157—158°, D 0·8210, n_D^{19} 1·4631. The *nitrosochloride*, $(C_8H_{10}ONCl)_2$, crystallises from benzene in prisms, m. p. 119°; the *nitrolpiperidide*, $C_8H_{10}N \cdot C_6H_{10} \cdot CEt \cdot NOH$, m. p. 123°; the *methoxyl-oxime*, $OMe \cdot C_8H_{10} \cdot CEt \cdot NOH$, m. p. 100—101°. Δ^1 -cyclo-Hexenyl methyl ketone, $C_6H_9 \cdot COEt$, prepared by the action of dimethylaniline or of sodium acetate and hydrogen chloride in glacial acetic acid solution on the nitrosochloride, has b. p. 218°; the *semicarbazones*, obtained by the two methods of preparation, have m. p. 160—170° and 179—180° respectively.

n-Propyl- Δ^1 -cyclohexene, $CH_2 \begin{smallmatrix} \diagup CH_2-CH \\ \diagdown CH_2-CH_2 \end{smallmatrix} CPr^a$, prepared by boiling propyridenecyclohexane with alcoholic sulphuric acid, is identical with the hydrocarbon prepared by Sabatier and Mailhe's method (*loc. cit.*). It has b. p. 154—156°. The *nitrosochloride*, m. p. 104°; the *nitrolpiperidide*, m. p. 126—128°. The action of sodium methoxide on the *nitrosochloride* leads to the formation of an *oxime*; the corresponding *semicarbazone* has m. p. 140—141°.

V. *Condensation of Active 1-Methylcyclohexane-3-one with Ethyl α -Bromo-n-butyrate*.—[With MAHLON RENTSCHLER.]—The *hydroxy-ester*, $CH_2 \begin{smallmatrix} \diagup CHMe \cdot CH_2 \\ \diagdown CH_2-CH_2 \end{smallmatrix} C(OH) \cdot CHEt \cdot CO_2Et$, has b. p. 165—170°/15 mm. The unsaturated *ester*, b. p. 135—140°/13 mm. The unsaturated acid forms a *silver* salt, $C_{11}H_{17}O_2Ag$. 1-Methyl-3-propyridenecyclohexane, $C_{10}H_{18}$, b. p. 170—173°, D 0·814, n_D^{19} 1·4591, has $n_D - 32'3''$ to $34'28''$ (100 mm. tube). The *nitrolpiperidide*,

$C_{10}H_{17}(NOH) \cdot C_5H_{10}N$, m. p. 96°. When heated with dimethylaniline and distilled with sulphuric acid, the nitrosochloride yields a ketone, which is obtained in two fractions: the fraction b. p. 218—220° forms a *semicarbazone*, m. p. 174°, whilst that of b. p. 225—228° forms a *semicarbazone*, m. p. 180°. On treatment of the ketone with 1% permanganate solution, a residue equal to about 40% of the whole and consisting of *m-tolyl ethyl ketone* was obtained. This forms a *semicarbazone*, $C_{11}H_{15}ON_3$, m. p. 175—176°, and an *oxime*, $C_{10}H_{18}ON$, m. p. 68—69°, and on oxidation with hypobromite solution yields *m-toluic acid*.

When heated with sodium acetate and glacial acetic acid, the nitrosochloride yields 3-propionyl-1-methyl- Δ^2 -cyclohexene,



b. p. 220—222°, D 0·9345, n_D^{20} 1·4807, which forms a *semicarbazone*, $C_{11}H_{19}ON_3$, m. p. 193—194°.

VI. *Condensation of 1-Methylcyclohexane-4-one with Ethyl α -Bromo-n-butyrate*.—[With MAHLON RENTSCHLER.]—The condensation product, b. p. 138—140°/10 mm., consisted of a mixture of the *hydroxy-ester*, $CHMe \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix} C(OH) \cdot CHEt \cdot CO_2Et$, and the unsaturated *ester*, b. p. 121—125°/10 mm., into which it is converted completely by the

action of potassium hydrogen sulphate. The *hydroxy-acid*,

$C_{10}H_{18}(OH) \cdot CO_2H$,
m. p. 100—101°. The unsaturated acid, b. p. 154—158°/10 mm., forms a *silver salt*, $C_{11}H_{17}O_2Ag$.

The product, b. p. 175—177°, $D^{19} 0.8135$, $n_D 1.4516$, obtained on distilling the unsaturated acid, is a mixture consisting chiefly of 1-methyl-4-propylidenecyclohexane, $C_6H_9Me \cdot CHEt$, since on careful oxidation with permanganate it yields 1-methylcyclohexane-4-one and only traces of a keto-acid. The *nitrosochloride* was obtained in three fractions, m. p. 132—137°, 135—140°, and 138—141°, and the *nitrolpiperidine* in four fractions, m. p. 116—135°, 138—145°, 143—150°, and 150—152°. When treated with sodium acetate, the nitrosochloride forms an *oxime*, m. p. 105—106°, which yields an unsaturated ketone, m. p. 230—231°, $D^{20} 0.952$, $n_D^{20} 1.4947$; the *semicarbazone*, m. p. 183—184°. Reduction of the ketone leads to the formation of a saturated ketone, which forms a *semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 178—179°, and on oxidation with hypobromite solution yields an acid. The *silver salt*, $C_8H_{13}O_2Ag$, was analysed.

After being boiled with alcoholic sulphuric acid, the methylpropylidenecyclohexane, b. p. 175—177°, had b. p. 177—178°.

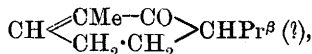
VII. *Condensation of cycloHexanone with Ethyl α-Bromoisobutyrate*.—[With HEINRICH MALLISON.]—The *hydroxy-ester*, b. p. 125—135°, on treatment with potassium hydrogen sulphate, yields the acid, $C_6H_9 \cdot CMe_2 \cdot CO_2Et$, which crystallises in rhombic prisms, m. p. 71—72°, b. p. 146—152°/13 mm., and on distillation forms *isopropylidenecyclohexane*, $C_6H_{10} \cdot CMe_2$. This solidifies in liquid air, has b. p. 160—161°, $D^{20} 0.836$, $n_D^{20} 1.4723$, and, on oxidation with permanganate, yields cyclohexanone and a *glycol*, m. p. 82°. With nitrosyl chloride, *isopropylidenecyclohexane* forms a blue oil, which solidifies to colourless crystals, m. p. 83°. *isoPropyl-Δ¹-hexene*,

$CH_2 < \begin{smallmatrix} CH_2-CH \\ CH_2-CH_2 \end{smallmatrix} > CPr^{\beta}$ (Sabatier and Mailhe, *loc. cit.*), prepared by boiling the propylidene compound with alcoholic sulphuric acid, has b. p. 155—157°, $D^{20} 0.829$, $n_D 1.4606$. This hydrocarbon was obtained on one occasion by distillation of a crude specimen of the unsaturated acid. The *nitrosochloride* crystallises in white prisms, m. p. 129—130°, and when heated with alcoholic piperidine does not form a nitrolpiperidine, but yields an *oxime*, m. p. 72°, which is formed also by heating the nitrosochloride with sodium acetate and glacial acetic acid, and is hydrolysed by sulphuric acid to 1-isopropylhexane-2-one. This forms a *semicarbazone*, m. p. 165—166°.

VIII. *Condensation of 1-Methylcyclohexane-4-one with Ethyl α-Bromoisobutyrate*.—[With J. B. CHURCHILL.]—The *hydroxy-ester*, $OH \cdot C_6H_9Me \cdot CMe_2 \cdot CO_2Et$, has b. p. 148—150°/16 mm. The unsaturated ester, $CHMe < \begin{smallmatrix} CH_2-CH \\ CH_2-CH_2 \end{smallmatrix} > C \cdot CMe_2 \cdot CO_2Et$, b. p. 125—126°/13 mm., on hydrolysis yields 1-methyl-Δ³-cyclohexene-4-α-isobutyric acid, m. p. 95—96°, together with small amounts of a crystalline substance, m. p. 194—195°. The unsaturated acid forms a *hydrobromide*, $C_{11}H_{19}O_2Br$, m. p. 112—117° if slowly, or 120—122° if quickly, heated. On distillation under the ordinary pressure, the

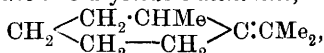
unsaturated acid yields $\Delta^{4(8)}$ -menthene (Abstr., 1906, i, 682), which on oxidation with permanganate at 0° yields acetone and 1-methylcyclohexane-4-one, together with β -adipic acid. *i*- Δ^3 -Menthene, formed by boiling the semicyclic menthene with alcoholic sulphuric acid, can be converted by way of menthone into *i*-menthol, which is thus synthesised from 1-methylcyclohexane-4-one.

IX. *Condensation of 1-Methylcyclohexane-3-one with Ethyl Bromoisobutyrate*.—[With J. B. CHURCHILL.]—1-Methylcyclohexene-3-isobutyric acid, b. p. $165\text{--}168^\circ/14$ mm., prepared by hydrolysis of its ester (Braun, Abstr., 1901, i, 157), forms a *hydrobromide*, $\text{C}_{11}\text{H}_{19}\text{O}_2\text{Br}$, m. p. $115\text{--}117^\circ$. The product obtained on distilling the unsaturated acid contains tetramethylsuccinic acid; hence Braun's ester must have contained ethyl tetramethylsuccinate, formed by the action of zinc on ethyl bromoisobutyrate. The chief product of the distillation is $\Delta^{3(8)}$ -*m*-menthene, $\text{CH}_2 \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > \text{C} : \text{CMe}_2$, which has b. p. $173\text{--}175^\circ$, $D_{20} 0.8250$, $n_D^{20} 1.4670$, when oxidised with permanganate yields 1-methylcyclohexane-3-one, and with nitrosyl chloride forms a blue oil volatile with steam. The semicyclic hydrocarbon is stable towards dilute aqueous sulphuric acid, but when boiled with alcoholic sulphuric acid is converted into a *hydrocarbon*, b. p. $164\text{--}168^\circ$, $D_{20} 0.82$, $n_D 1.4561$, which forms a solid *nitrosochloride*. Sodium methoxide converts this into an *oxime*; the corresponding *semicarbazone*, $\text{C}_{11}\text{H}_{19}\text{ON}_3$, m. p. $150\text{--}151^\circ$. Hydrolysis of the semicarbazone leads to the formation of *menthenone*,



b. p. $208\text{--}209^\circ$, $D_{20} 0.9202$, $n_D^{20} 1.4749$, which when reduced with sodium and alcohol yields a *m*-menthol, $\text{C}_{10}\text{H}_{20}\text{O}_2$, b. p. about 215° , which has an odour of peppermint and is stable towards permanganate.

X. *Condensation of 1-Methylcyclohexane-2-one with Ethyl Bromoisobutyrate*.—[With J. B. CHURCHILL.]—1-Methylcyclohexene-2-isobutyric acid, prepared by the usual series of reactions, has b. p. $162\text{--}164^\circ/16$ mm. The *silver salt*, $\text{C}_{11}\text{H}_{17}\text{O}_2\text{Ag}$, was analysed. When distilled, the unsaturated acid yields *o*-menthene,



which has b. p. $160\text{--}162^\circ$, $D_{20} 0.8345$, $n_D^{20} 1.4670$, forms a blue *nitrosochloride*, and on oxidation with permanganate is converted into 1-methylcyclohexane-2-ol. When boiled with alcoholic sulphuric acid, the semicyclic *o*-menthene is transformed to only a small extent, as the product forms only traces of a solid *nitrosochloride*. G. Y.

Electrolysis of the Compounds of Aluminium Bromide with Toluene and Benzene. W. W. NEMINSKY and WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 391—396).—When the compounds, $\text{AlBr}_3 \cdot 3\text{C}_6\text{H}_6$ and $\text{AlBr}_3 \cdot 3\text{C}_7\text{H}_8$, described by Gustavson (Abstr., 1883, 577) are electrolysed with a platinised platinum cathode and a platinum or aluminium anode, benzene and toluene are liberated in amounts corresponding with three gram-mols. per 96.54 coulombs. The hydrocarbon collects mainly in the cathode

compartment. The conductivity of the freshly-prepared complexes varies to some extent with the method of preparation and purification employed, and undergoes a gradual diminution. T. H. P.

Three Lecture Experiments on the Preparation of Iodochlorides and Iodoxy- and Iodonium Compounds. CONRAD WILLGERODT (*Ber.*, 1908, 41, 1097—1098).—The formation of phenyl-iodochloride is strikingly shown by wetting the walls of a cylinder containing chlorine with a solution of iodobenzene in chloroform, when crystals of the compound are at once produced.

When the iodochloride is boiled with a freshly prepared solution of bleaching powder, iodoxybenzene separates after a short time in white crystals.

Diphenyliodonium chloride and iodide are readily prepared by adding hydrochloric acid or potassium iodide respectively to the corresponding iodonium hydroxide solution, itself prepared by rubbing sodium hydroxide and the iodochloride together until the solid disappears. W. R.

Studies in Nitration. II. Melting-Point Curves of Binary Mixtures of *o*-, *m*-, and *p*-Nitroanilines. A New Method for Determining the Composition of such Mixtures. J. BISHOP TINGLE and H. F. ROELKER (*J. Amer. Chem. Soc.*, 1908, 30, 822—828).—In an earlier paper (Tingle and Blanck, *Abstr.*, 1907, i, 120), an account was given of the nitration of some *N*-substituted aniline derivatives. In the course of this investigation, a simple method was required for the determination of the composition of mixtures of the isomeric nitroanilines, and a study has therefore been made of the curves produced by plotting the melting points of binary mixtures of these substances against their composition.

In the case of the mixtures of *o*- and *m*-, and of *m*- and *p*-nitroanilines, these curves are comparatively regular; they fall to the eutectic point and then rise to the melting point of the pure compound. The curve for mixtures of *o*- and *p*-nitroanilines, however, is very irregular, and no explanation for this can at present be offered. The curves for the *o*- and *m*-, and *m*- and *p*-compounds can be employed for determining the composition of such mixtures by a simple and rapid method which requires very little material. The results are usually accurate within 2%. E. G.

Action of Sodium Hyposulphite on Nitro-derivatives. II. ALPHONSE SEYEWETZ and NOEL (*Bull. Soc. chim.*, 1908, [iv], 3, 497—500. Compare Seyewetz and Bloch, *Abstr.*, 1906, i, 490).—It has been shown previously (*loc. cit.*) that, when nitro-derivatives of hydrocarbons are heated with sodium hyposulphite solution in presence of trisodium phosphate, there is a partial reduction of the nitro-group with the formation of sulphonamates of the type $R \cdot NH \cdot SO_3Na$. This reaction has now been extended to the dinitro-derivatives of aromatic hydrocarbons.

o-Dinitrobenzene is not readily attacked by the reagent, but yields a little *o*-phenylenediamine, and a small quantity of a product which appears to be sodium *o*-aminophenylsulphonamate. *m*-Dinitrobenzene

furnishes in this reaction only *m*-phenylenediamine. 1-Chloro-2:4-dinitrobenzene furnishes 1% of *sodium chloroaminophenylsulphonamate*, m. p. 80—85°, which crystallises in colourless leaflets, is readily soluble in alcohol or water, but insoluble in ether or light petroleum. Sodium hyposulphite has no action under these conditions on dinitrotoluene or dinitronaphthalene.

T. A. H.

Electrolytic Production of Nitrosobenzene. O. DIEFFENBACH (D.R.-P. 192519).—Although nitrosobenzene is the first product of the electrolytic reduction of nitrobenzene, it is not isolated in the ordinary method of effecting this reaction because of its conversion into azoxybenzene. It has now been found that when nitrobenzene is reduced in neutral electrolytes, nitrosobenzene is obtained in good yield. Two litres of 10% sodium sulphate and 150 grams of nitrobenzene were thoroughly stirred and electrolysed with 5 amperes for eight hours, the cathode being of nickel gauze, whilst the anode was of lead. On distillation, 35—40 grams of nitrosobenzene were obtained.

Other sulphates, such as those of magnesium or aluminium, may be used. An electrolytic cell with a diaphragm may be employed, and in this case the anode and cathode solutions are repeatedly changed during electrolysis, and care is taken that both solutions remain neutral.

G. T. M.

Amides of *p*-Aminobenzenesulphonic Acid. P. GELMO (*J. pr. Chem.*, 1908, [ii], 77, 369—382).—The action of acetylaniline-*p*-sulphonyl chloride on ammonia and aromatic amines and the behaviour of the resulting acetylaniline-*p*-sulphonamides towards hydrolysing agents have been studied in extension of Schroeter's investigation of the acylanilinesulphonic acids and the action of acylaniline-sulphonyl chlorides on diazo-salts (Abstr., 1906, i, 415).

Acetylaniline-*p*-sulphonyl chloride reacts with aqueous ammonia, aniline, and the toluidines, with development of heat, or with the naphthylamines in hot alcoholic solution, forming acetylaniline-*p*-sulphonamides, which crystallise in glistening leaflets, and are stable towards dilute ammonia, acids, or alkalis at the ordinary temperature, but are hydrolysed on prolonged boiling with dilute acids or alkalis, yielding the anilinesulphonamides, or by hot concentrated acids or alkalis, forming acetic and *p*-sulphanilic acids and the corresponding amines. The hydrolysis takes place most easily with acetylaniline-*p*-sulphonamide, least so with the acetylaniline-*p*-sulphon-naphthylamides. The aniline-*p*-sulphonamides crystallise in needles, yield crystalline *hydrochlorides* and, if derived from aromatic amines, nitroso-derivatives; they also form diazo-salts, from which azo-dyes are obtained resembling those, such as Orange II, prepared from sulphanilic acid.

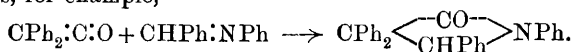
The following acetylaniline-*p*-sulphonamides, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NHR}$, and aniline-*p*-sulphonamides, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NHR}'$, are described; the temperatures are melting points:

$\text{R} = \text{H}$, 219°; $\text{R}' = \text{H}$, 163°; $\text{R} = \text{Ph}$, 214°; $\text{R}' = \text{Ph}$, 200°; $\text{R} = o\text{-C}_7\text{H}_7$, 236°; $\text{R}' = o\text{-C}_7\text{H}_7$, 132°; $\text{R} = m\text{-C}_7\text{H}_7$, 205°; $\text{R}' = m\text{-C}_7\text{H}_7$, 135°; $\text{R} = p\text{-C}_7\text{H}_7$, 209°; $\text{R}' = p\text{-C}_7\text{H}_7$, 109°; $\text{R} = \alpha\text{-C}_{10}\text{H}_7$, 215°; $\text{R}' = \alpha\text{-C}_{10}\text{H}_7$, 196°; $\text{R} = \beta\text{-C}_{10}\text{H}_7$, 212°; $\text{R}' = \beta\text{-C}_{10}\text{H}_7$, 203°. G. Y.

Some Derivatives of 2:6-Dinitro-1:3-dimethylbenzene-4-sulphonic Acid. WILLIAM J. KARSLAKE and W. J. MORGAN (*J. Amer. Chem. Soc.*, 1908, 30, 828—831).—2:6-Dinitro-1:3-dimethylbenzene-4-sulphonyl chloride, m. p. 123°, was prepared by the action of phosphorus pentachloride on the potassium salt (Claus and Schmidt, *Abstr.*, 1886, 708). The *anilide*, m. p. 154°, prepared by the action of the sulphonyl chloride on aniline, forms yellow needles. The *o-toluidide*, m. p. 135°, crystallises in white needles. By the action of the sulphonyl chloride on benzene in presence of aluminium chloride, 2:6-dinitro-1:3-dimethylphenyl phenyl sulphone, m. p. 178°, is produced, and forms large, lustrous plates. On oxidising potassium 2:6-dinitro-1:3-dimethylbenzene-4-sulphonate with potassium permanganate and treating the product with phosphorus pentachloride, a *substance*, m. p. 127—128°, was obtained, which was probably an impure acid chloride. By the action of ammonia on this compound, a substance was produced which crystallises in yellow plates, chars at about 290°, and is probably 2:4-dinitro-6-sulpho-m-toluic acid; its *barium*, *strontium*, and *barium hydrogen* salts are described. E. G.

Preparation of Pure Indene. JOHANNES BOES (*Chem. Zentr.*, 1908, i, 469; from *Apoth. Zeit.*, 1907, 22, 1137).—The isolation of indene from the nitrosite by treatment with water, dilute acids, dilute alkalis, or by dry distillation was unsuccessful. Reduction by means of zinc and hydrochloric acid yielded, instead of indene, a base apparently without aromatic character, which was volatile in steam, and gave a crystalline platinichloride and zincichloride. From the product obtained by heating a benzene solution of indene with metallic potassium or potassium hydroxide, only polymerised indene could be obtained. J. V. E.

Ketens. VIII. Preparation of Quinonoid Hydrocarbons from Diphenylketen. HERMANN STAUDINGER (*Ber.*, 1908, 41, 1355—1363. Compare this vol., i, 318).—Ketoketens are readily added on to some compounds containing the :C:N- group, yielding β -lactams, for example,



Addition to a carbonyl group also occurs when an olefine double linking is adjacent to the carbonyl group, as, for instance, with quinone and dibenzylideneacetone. The β -lactones thus formed, such as $\text{O}:\text{C}_6\text{H}_4 \begin{array}{c} \text{CPh}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CO}$, are readily decomposed when heated, yielding compounds of the type of diphenylquinomethane and tetraphenylquinodimethane. The reaction appears to afford a fairly general method for transforming a reactive :CO group into a :C:CPh₂ group.

Phenylcarbimide and phenylthiocarbimide do not form additive compounds with quinone in the same manner as diphenylketen.

The β -lactone, $\text{O}:\text{C}_6\text{H}_4 \begin{array}{c} \text{CPh}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CO}$, separates when a suspension of quinone in dry ether is added to a solution of diphenylketen in light petroleum, and may be crystallised from hot benzene, ethyl acetate, or

acetone. When heated it decomposes at 143° , carbon dioxide and quinone are evolved, and a reddish-brown mass is left. Diphenylquinomethane (Abstr., 1903, i, 639) is readily formed when the β -lactone is heated under reduced pressure, first at 100° and afterwards at 110° . Tetraphenylquinodimethane, $\text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2$ (Abstr., 1904, i, 491), is formed when the β -lactone is heated with xylene, but a better yield is obtained when a xylene solution of diphenylketen (2 mols.) (or diphenylketenquinoline) and quinone (1 mol.) is boiled.

Tetraphenylxyloquinodimethane, $\text{CPh}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CPh}_2$, is obtained from *p*-xyloquinone and diphenylketen. It crystallises from xylene in red needles with a purple lustre, and has m. p. 200° (decomp.).

Tetraphenyl- α -naphthaquinodimethane, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{CPh}_2) \cdot \text{CH} \\ \text{C}(\text{CPh}_2) \cdot \text{CH} \end{smallmatrix}$, separates from benzene as a light yellow powder, m. p. $262\text{--}263^{\circ}$, but orange-coloured at about 200° .

When diphenylketenquinoline and anthraquinone are heated together at $190\text{--}200^{\circ}$, carbon dioxide is evolved, and a colourless product $\text{C}_{40}\text{H}_{28}$, m. p. $302\text{--}303^{\circ}$, is obtained. J. J. S.

New Method for Preparation of Homologues of Naphthalene. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1908, 146, 933—934).—Naphthyl alkyl ketones (Rosset, Abstr., 1897, i, 75; 1898, i, 593), like the phenyl alkyl ketones (Abstr., 1905, i, 66), are converted quantitatively into the corresponding hydrocarbon by direct hydrogenation at 180° in the presence of nickel, obtained by reducing the oxide at 250° . The following alkylnaphthalenes were thus prepared: α - and β -ethylnaphthalenes from α - and β -acetylnaphthalenes respectively; α -isobutylnaphthalene, b. p. $136\text{--}138^{\circ}/11\text{ mm.}$, from α -isobutyrylnaphthalene, is a mobile liquid with an odour of petroleum; β -isobutylnaphthalene, b. p. $112\text{--}113^{\circ}/6\text{ mm.}$, from β -isobutyrylnaphthalene, is a mobile liquid with a slight odour. M. A. W.

Ketens. IX. Coloured Hydrocarbons from Diphenylketen. HERMANN STAUDINGER (*Ber.*, 1908, 41, 1493—1500)—It has been shown in the previous communication on this subject (this vol., i, 318) that only those carbonyl compounds which have a double linking in the neighbouring position react readily with ketoketens. In agreement with this, dibenzylideneacetone forms an *additive* compound with diphenylketen slowly at the ordinary temperature, but rapidly in boiling toluene solution. The β -lactone, $\text{CO} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CPh}_2 \end{smallmatrix} \text{C}(\text{CH}:\text{CHPh})_2$, formed as the primary product cannot be isolated, as it decomposes even in the cold more rapidly than it is formed, yielding carbon dioxide and $\alpha\epsilon$ -diphenyl- γ -diphenylmethylene- $\Delta^{a\delta}$ -pentadiene, $\text{CPh}_2 \cdot \text{C}(\text{CH}:\text{CHPh})_2$.

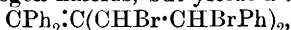
In their structure, the derivatives of γ -methylene- $\Delta^{a\delta}$ -pentadiene, $\text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH}:\text{CH}_2 \\ \text{CH}:\text{CH}_2 \end{smallmatrix}$, formed in this manner, resemble the fulvenes, $\text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix}$, and may be termed "acyclic fulvenes." Only one acyclic fulvene has been previously prepared (Fellenberg, Abstr.,

1904, i, 961). It is a colourless substance, as is probably also the parent γ -methylene- Δ^{ab} -pentadiene, colour appearing in this group only when the hydrogen atoms are substituted by phenyl groups; the acyclic fulvenes derived from diphenylketen are coloured, but less strongly than the fulvenes, which is in analogy to the fact that diphenylfulvene is much more strongly coloured than fulvene.

The acyclic fulvenes undergo auto-oxidation, but to a less degree than the fulvenes, whilst, in agreement with Thiele and Bühner's observation (Abstr., 1906, i, 569) that only hydrocarbons with a cyclopentadiene grouping can be reduced by aluminium amalgam, the acyclic fulvenes are stable towards this reagent.

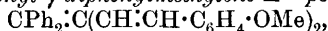
Di-*p*-chlorobenzylidene-, dianisylidene-, and dicinnamylidene-acetones react with diphenylketen in the same manner and under the same conditions as does dibenzylideneacetone; phorone and methyl and ethyl ketopentadienedicarboxylates, on the other hand, react with diphenylketen only at high temperatures and to a small extent. Those ketones which react readily with diphenylketen also form coloured *additive* compounds with hydrogen haloids (Baeyer and Villiger, Abstr., 1902, i, 1189; Baeyer, Abstr., 1905, i, 281), the capacities for the two reactions disappearing simultaneously. These facts are opposed to Vorländer and Mumme's view that the capacity of an ethylene linking for adding on hydrogen haloids is diminished by the proximity of a carbonyl group (Abstr., 1903, i, 495).

$\alpha\epsilon$ -Diphenyl- γ -diphenylmethylene- Δ^{ab} -pentadiene, $C_{30}H_{24}$, prepared by boiling dibenzylideneacetone with diphenylketen in toluene solution, or by fusing dibenzylideneacetone with diphenylketenquinoline, crystallises from ethyl acetate in sulphur-yellow needles, m. p. 173—174°, or from benzene in yellow needles containing C_6H_6 , which is lost at 130°. It is converted into resinous products when boiled in benzene in presence of air, and does not form *additive* compounds with hydrogen haloids, but yields a *tetrabromide*,



which crystallises in colourless plates, m. p. 168.5—169°, and is stable to dry bromine in chloroform solution or to permanganate in acetone-benzene solution, but reacts readily with moist bromine, forming hydrogen bromide and benzaldehyde.

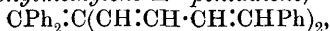
$\alpha\epsilon$ -Di-*p*-methoxyphenyl- γ -diphenylmethylene- Δ^{ab} -pentadiene,



prepared from dianisylideneacetone and diphenylketen or its quinoline *additive* compound, crystallises in yellow needles with green fluorescence, which become yellow at 130°, m. p. 176.5—177.5°.

$\alpha\epsilon$ -Di-*p*-chlorophenyl- γ -diphenylmethylene- Δ^{ab} -pentadiene, $C_{30}H_{22}Cl_2$, m. p. 195.5—196.5°, crystallises from benzene.

$\alpha\epsilon$ -Distyryl- γ -diphenylmethylene- Δ^{ab} -pentadiene,



crystallises from benzene in yellow prisms ($\frac{1}{2}C_6H_6$), or from glacial acetic acid or ethyl acetate in yellow needles, m. p. 150—151°.

Diphenylketenquinoline reacts with methyl ketopentadienedicarboxylate at 140—150°, with the ethyl ester at 150—160°, and with phorone at 180—190°, yielding carbon dioxide; a crystalline product could not be obtained.

G. Y.

Crystallography of some Cyclic Organic Compounds.

FRANZ M. JAEGER (*Zeitsch. Kryst. Min.*, 1908, **44**, 561—575).—Crystallographic determinations are given of the following compounds: *o*-Nitrosoacetanilide, monoclinic [$a:b:c=0.8940:1:0.7295$; $\beta=97^{\circ}54'$]. *o*-Nitroacetanilide, monoclinic [$a:b:c=0.8935:1:1.9198$; $\beta=96^{\circ}9'$]. 2:4:6-Trichlorobenzamide, rhombic

$$[a:b:c=0.5380:1:1.5180].$$

Lupeone, rhombic [$a:b:c=0.8071:1:1.2248$]. Cholestenone, monoclinic [$a:b:c=0.8463:1:1.3538$; $\beta=104^{\circ}44'$]. β -Phytosteryl acetate tetrabromide, monoclinic [$a:b:c=2.4832:1:3.7797$; $\beta=113^{\circ}33\frac{1}{2}'$]. 6-Hydroxy-2:4-dimethylpyrimidine (+2H₂O), monoclinic [$a:b:c=0.6815:1:1.0142$; $\beta=101^{\circ}9'$]; its nitrate is triclinic [$a:b:c=0.9323:1:0.9951$; $a=112^{\circ}45\frac{1}{3}'$; $\beta=95^{\circ}42'$; $\gamma=78^{\circ}5'$]. *o*-Nitrobenzoylpiperidide, triclinic [$a:b:c=1.3444:1:0.9672$; $a=101^{\circ}34'$; $\beta=95^{\circ}59\frac{1}{3}'$; $\gamma=70^{\circ}36'$]. *p*-Nitrobenzoylpiperidide, rhombic [$a:b:c=1.1128:1:0.9620$]. Piperine, monoclinic [$a:b=0.9837:1$; $\beta=109^{\circ}37\frac{3}{4}'$]. 1:3-Dichloro-4:5-dinitrobenzene, tetragonal

$$[a:c=1:2.0306].$$

L. J. S.

Bromination. JULIUS B. COHEN and W. E. CROSS (*Amer. Chem. J.*, 1908, **39**, 431—432). SOLOMON F. ACREE, J. M. JOHNSON, and SIDNEY NIRDLINGER (*ibid.*, 544—554).—Polemical. A question of priority (see *Proc.*, 1907, **23**, 148; this vol., ii, 29).

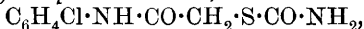
Action of Sodium Hydroxide on Derivatives of Dithiodiglycollic Acid and Diselenodiglycollic Acid. GUSTAV FRERICHS and EDWIN WILDT (*Annalen*, 1908, **360**, 105—127).—As is well known, the action of sodium hydroxide on phenyl disulphide leads to the formation of thiophenol and benzenesulphonic acid. A similar, simultaneous reduction and oxidation is now found to take place with the arylamides of dithiodiglycollic acid; these yield the corresponding thioglycollamides and derivatives of thionoxalic acid, which appear instead of the sulphonic acid. Diselenodithioglycollamides, on the other hand, under the same conditions, yield derivatives of selenoxalic acid, but together with selenodiglycollamides instead of selenoglycollamides. Dithiodiglycollarylamides are prepared by the action of hydrogen peroxide on carbaminethioglycollarylamides in ammoniacal solution (Beckurts and Frerichs, *Abstr.*, 1902, i, 763). The preparation of diselenodiglycollarylamides is described by Frerichs (*Abstr.*, 1903, i, 609).

When moistened with alcohol and boiled for two to three minutes with 20% sodium hydroxide solution, dithiodiglycollanilide yields thioglycollanilide and thionoxanilide (Reissert, *Abstr.*, 1904, i, 999), together with small amounts of hydrogen sulphide, phenylcarbimide, thionoxanilic acid, and aniline thionoxanilate (Reissert, *loc. cit.*), which are formed by decomposition of the thionoxanilide. When treated with hydrogen peroxide in sodium hydroxide solution, thionoxanilide yields oxanilide.

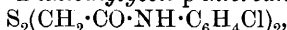
Thionoxal-p-toluidide, C₆H₄Me.NH.CS.CO.NH.C₆H₄Me, formed together with thioglycoll-*p*-toluidide from dithiodiglycoll-*p*-toluidide, crystallises in yellow needles, m. p. 153—154°, and is oxidised to

oxal-*p*-toluidide by the action of hydrogen peroxide in sodium hydroxide solution. *Thionoxal-o-toluidide*, crystallising in yellow leaflets or needles, m. p. 126°, and *thionoxal-m-toluidide*, crystallising in yellow needles or leaflets, m. p. 88—89°, were obtained in the same manner.

Carbaminethioglycoll-p-chloroanilide,

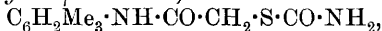


prepared by successive treatment of *p*-chloroaniline with chloroacetic acid and potassium thiocyanate, separates from alcohol in crystals, m. p. 174° (decomp.). *Dithiodiglycoll-p-chloroanilide*,



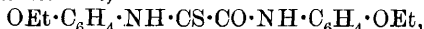
crystallises from alcohol in colourless needles, m. p. 194—195°. *Thionoxal-p-chloroanilide*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CS}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, forms long, yellow needles, m. p. 157—158°.

Carbaminethioglycoll-ψ-cumidide,



prepared from ψ-cumidine, chloroacetic acid, and potassium thiocyanate, separates from alcohol in crystals, m. p. 171—172° (decomp.). *Dithiodiglycoll-ψ-cumidide*, $\text{S}_2(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Me}_3)_2$, separates from glacial acetic acid in crystals, m. p. 194—195°. *Thionoxal-ψ-cumidide*, $\text{C}_6\text{H}_5\text{Me}_3\cdot\text{NH}\cdot\text{CS}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{Me}_3$, crystallises from alcohol in yellow needles, m. p. 179—180°.

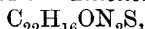
Thionoxal-p-phenetidide,



is obtained in crystals, m. p. 156—157°.

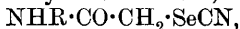
The following naphthyl derivatives were prepared in the same manner:

Carbaminethioglycoll-α-naphthylamide, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$, colourless needles, m. p. 165—166° (decomp.). *Dithiodiglycoll-α-naphthylamide*, $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2\text{S}_2$, m. p. 210—211°. *Thionoxal-α-naphthylamide*,

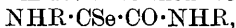


yellow needles, m. p. 184—185°. *Carbaminethioglycoll-β-naphthylamide*, white needles, m. p. 185—186° (decomp.). *Dithiodiglycoll-β-naphthylamide*, white needles, m. p. 204—205°. *Thionoxal-β-naphthylamide*, yellow needles, m. p. 184—185°.

The following new selenocynoacetamides,



diselenodiglycollamides, $\text{Se}_2(\text{CH}_2\cdot\text{CO}\cdot\text{NHR})_2$, selenodiglycollamides, $\text{Se}(\text{CH}_2\cdot\text{CO}\cdot\text{NHR})_2$, and amides of selenoxalic acid,



are described.

R = Ph: *selenodiglycollanilide*, white needles, m. p. 198°; *selenoxanilide*, red needles, m. p. 139·5—140·5°. R = $\text{C}_6\text{H}_4\text{Me}$: *selenodiglycoll-p-toluidide*, m. p. 217—218°; *selenoxal-p-toluidide*, red needles, m. p. 165—166°; *selenodiglycoll-m-toluidide*, white needles, m. p. 170—171°; *selenoxal-m-toluidide*, m. p. 73—74°; *selenoxal-o-toluidide*, red needles and leaflets, m. p. 131·5—132·5°. R = $\text{C}_6\text{H}_4\text{Cl}$: *diselenodiglycoll-p-chloroanilide*, yellow needles, m. p. 172—173°; *selenodiglycoll-p-chloroanilide*, m. p. 190—191°; *selenoxal-p-chloroanilide*, yellowish-red needles, m. p. 166°. R = $\text{C}_6\text{H}_4\cdot\text{OMe}$: *selenocynoacet-p-phenetidide*, yellow needles, m. p. 162—163° (decomp.);

diselenodiglycoll-p-phenetidine, yellow needles, m. p. 161—162°; *selenodiglycoll-p-phenetidine*, m. p. 199—200°; *selenoxal-p-phenetidine*, red needles, m. p. 160—161°.

Selenodiglycollanilide, prepared by the action of chloroacetanilide on potassium selenide, is identical with that obtained by treating diselenodiglycollanilide with sodium hydroxide. G. Y.

9-Aminofluorene. JULIUS SCHMIDT and HERMANN STÜTZEL (*Ber.*, 1908, 41, 1243—1252).—Schmidt and Mezger (*Abstr.*, 1907, i, 43) have shown that the acetyl derivative of 9-hydroxyfluorene exists in two stereoisomeric modifications. 9-Aminofluorene studied from the same point of view is found to exist as an α -isomeride, m. p. 53—55°, and as a β -isomeride, m. p. about 123°; these form identical derivatives, excepting in the case of the compound formed with phenylcarbimide.

9-Aminofluorene has previously been described by Wegerhoff as having m. p. 50—60° (*Annalen*, 1889, 252, 37), and by Kerp (*Abstr.*, 1896, i, 239) as m. p. 161°.

On reducing fluorenoneoxime with zinc and acetic acid, a mixture of the two modifications is produced, m. p. 50—80°, which is separated by fractional crystallisation from light petroleum (b. p. 50—70°). The low melting α -9-aminofluorene separates first in splendid colourless needles, m. p. 53—55°, and dissolves in concentrated sulphuric acid with a green coloration. β -9-Aminofluorene crystallises in flocculent aggregates of minute needles, m. p. 123°, and on heating with solvents is slowly converted into the α -modification.

The following derivatives may be prepared from either isomeride. The *hydrochloride* forms colourless needles, sparingly soluble in water; the *nitrate* crystallises in needles, m. p. 180° (decomp.); the *picrate* forms yellow needles, which become brown at 180°, m. p. 240°; the *picrolonate*, $C_{13}H_{11}N \cdot C_{10}H_8O_5N_4$, separates in orange-yellow needles, which become green at 210°, m. p. 265° (decomp.). The *acetate* gives colourless needles, m. p. 260—261°; the *benzoate* forms colourless, silky, glistening needles, also m. p. 260—261°; indeed, these two compounds are remarkably alike. The *benzylidene* derivative forms yellow prisms, m. p. 141°.

9-*Fluorylcarbamide*, $C_{13}H_9 \cdot NH \cdot CO \cdot NH_2$, yields colourless crystals, which do not melt at 300°.

sym-*Di-9-fluorylthiocarbamide*,
 $CS(NH \cdot C_{13}H_9)_2$,

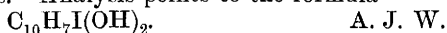
prepared by heating aminofluorene with alcohol and carbon disulphide, forms colourless crystals, m. p. 243°, with possibly also an indication of a lower melting isomeride. sym-9-*Fluorylphenylcarbamide*, obtained from α -9-aminofluorene, has m. p. 310° (decomp.); prepared from the β -form, it has m. p. 340° (decomp.). E. F. A.

Formation of Carbodiphenylimide from Phenylcarbimide. ROBERT STOLLÉ (*Ber.*, 1908, 41, 1125—1126. Compare Hofmann, *Abstr.*, 1885, 774).—Phenylcarbimide is converted into carbodiphenylimide with the liberation of carbon dioxide when heated in sealed tubes at 180°. The same product is obtained when triphenylisocyanurate is heated at 300°. During the preparation of the latter compound from phenylcarbimide and potassium acetate, the formation

of an *acid*, m. p. 220° , was observed, the investigation of which is in progress. W. H. G.

The Iodine Value of the Phenols. ERNEST WAKE and HARRY INGLE (*J. Soc. Chem. Ind.*, 1908, 27, 315—316).—The iodine values of certain phenols have been examined. *o*- and *p*-Polyphenols liberate iodine from Wys's solution, but not meta-derivatives, the reaction affording a test for the position of the hydroxyl group, and also for impurities in meta-compounds. α -Naphthol liberates iodine from Wys's solution, but β -naphthol does not. Free phenols absorb iodine in the ring, but phenolic esters (benzoates) do not.

The *product* of the action of Wys's solution on β -naphthol forms feathery, silky needles, m. p. 87° , which dissolve readily in alcohol, ether, and alkaline solutions. Analysis points to the formula



Preparation of Arylsulphonyl Derivatives of 1:2- and 2:1-Aminonaphtholsulphonic Acids. ACTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 193099).—The sulphonic acids of the 1:2- and 2:1-aminonaphthols, when treated with *p*-toluenesulphonyl chloride in alkaline solution, give a good yield (90—95%) of diazotisable *p*-toluenesulphonyl derivatives, which can be employed in the production of *o*-hydroxyazo-dyes.

The *p*-toluenesulphonyl derivative of 1-amino- β -naphthol-4-sulphonic acid is precipitated from alkaline solutions by acids, and melts indefinitely at 150 — 160° . G. T. M.

Condensation Products of Aliphatic Aldehydes with Phenol. A. I. LUNJAK (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 466—470. Compare Abstr., 1904, i, 495).—The following further condensation products have been prepared.

Di-p-hydroxydiphenylpropane, $\text{C}_2\text{H}_5\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, prepared from phenol and propaldehyde, crystallises from water in aggregates of needles, m. p. 130° . Its *dibenzoyl* derivative, $\text{C}_2\text{H}_5\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OBz})_2$, is deposited from alcohol in crystals, m. p. 146° . Its *dimethyl ether*, $\text{C}_2\text{H}_5\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, crystallises from a mixture of ether and alcohol in rhombic plates, m. p. 44° , b. p. 362.5 — $364.5^{\circ}/743.6$ mm.; when oxidised with chromic acid, it yields di-*p*-methoxybenzophenone and anisic acid.

Di-p-hydroxydiphenylbutane, $\text{C}_4\text{H}_8(\text{C}_6\text{H}_4\cdot\text{OH})_2$, prepared from phenol and *n*-butaldehyde, crystallises from water in long, silky needles, m. p. 136° . Its *dibenzoyl* derivative, $\text{C}_4\text{H}_8(\text{C}_6\text{H}_4\cdot\text{OBz})_2$, separates from alcohol in crystals, m. p. 124° . Its *dimethyl ether*, $\text{C}_4\text{H}_8(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, has b. p. 228.8 — $229.3^{\circ}/7$ mm., D_0^0 1.0690, D_0^{20} 1.0563, D_{20}^{20} 1.0572, and yields di-*p*-methoxybenzophenone and anisic acid on oxidation with chromic acid. T. H. P.

[1:2'-Dihydroxy-1':4'-dimethyldiphenylamine and its *Indo-phenol* Derivative.] LEOPOLD CASSELLA & Co. (D.R.-P., 191863).—An alkaline solution of *p*-xylenol and *p*-aminophenol, when oxidised with sodium hypochlorite, furnishes the sodium salt of *indophenol*,

which, when liberated with acid dissolved in hot dilute alcohol, separates on cooling in red crystals, m. p. 154° . 1:2'-*Dihydroxy-1':4'-dimethyldiphenylamine*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{OH}$, colourless, m. p. 158° , is obtained from the indophenol by reduction with zinc dust or sodium sulphide. A crystalline sulphur dye is obtained by heating in aqueous or alcoholic solution either 1:2-dihydroxy-1':4'-dimethyldiphenylamine or its indophenol with sodium sulphide and sulphur. The sodium salt of the dye separates in sparingly soluble, brown, metallic crystals; the free acid is a reddish-violet precipitate; it dyes unmordanted wool in the presence of sodium sulphide to a fast, deep violet shade. G. T. M.

Di- α -naphthyl Selenide and Telluride. ROBERT E. LYONS and G. C. BUSH (*J. Amer. Chem. Soc.*, 1908, 30, 831—836).—The work described in this paper was undertaken in connexion with a study of the periodic relationship in the oxygen group of elements.

Di- α -naphthyl selenide, $\text{Se}(\text{C}_{10}\text{H}_7)_2$, m. p. 114° , obtained by heating selenium with mercury di- α -naphthyl (compare Krafft and Lyons, *Abstr.*, 1894, i, 448), forms lustrous, pale yellow leaflets and decomposes rapidly on exposure to air and light. It is converted by bromine into the *dibromide*, $\text{Se}(\text{C}_{10}\text{H}_7)_2\text{Br}_2$, m. p. 183° (decomp.), which crystallises in white needles. The *dichloride*, $\text{Se}(\text{C}_{10}\text{H}_7)_2\text{Cl}_2$, m. p. 130° , forms colourless prisms.

Di- α -naphthyl telluride, $\text{Te}(\text{C}_{10}\text{H}_7)_2$, m. p. $126\cdot5^{\circ}$, crystallises in lustrous, brownish-yellow leaflets. The *dibromide*, m. p. 244° (decomp.), crystallises in lemon-yellow granules, and the *dichloride*, m. p. 265° , in colourless granules.

Diphenyl telluride *dichloride*, $\text{Te}(\text{C}_6\text{H}_5)_2\text{Cl}_2$, m. p. 160° , forms long, white prisms. Di- β -naphthyl selenide *dichloride*, m. p. 146° , crystallises in almost colourless leaflets.

A list of aromatic sulphides, selenides, and tellurides, and their halogen additive compounds, is given together with their m. p's. or b. p's., and shows that the change in b. p. or m. p. generally, but not always, varies directly with the atomic weight. With *o*-tolyl sulphide, selenide, and telluride, the reverse is the case, these substances having m. p's. 64° , 62° , and 38° respectively. The m. p's. of the halogen additive compounds are very irregular. E. G.

Preparation of Benzyl Alcohol from Benzaldehyde and Potassium Hydroxide. JAKOB MEISENHEIMER (*Ber.*, 1908, 41, 1420—1422).—For the purification of benzyl alcohol obtained by the Cannizzaro method, Fischer recommends shaking of the ethereal extract with a solution of sodium hydrogen sulphite before drying and distillation. This leads to an extensive conversion of the alcohol into benzyl ether during the distillation; this is due to the presence of small quantities of sulphuric acid. The defect is easily remedied by washing the ethereal solution with an alkali hydroxide after the treatment with sodium hydrogen sulphite. C. S.

"Unsaponifiable Matter" of Laurel Oil. HERMANN MATTHES and HEINRICH SANDER (*Arch. Pharm.*, 1908, 246, 165—177).—The

chief object of this investigation was to determine the nature of the resinous unsaponifiable matter, which various investigators have recorded as a constituent of the oil. The expressed oil used, after being freed from 2.43% of volatile oil, had the following constants: acid number, 9.4; saponification number, 200.9; Reichert-Meissl number, 3.2; Polenske number, 2.8; Hefner number, 85.8 (corrected for unsaponifiable matter); Hübl number, 82.2—82.4; "real" acetyl number, 5.108; "apparent" acetyl number, 15.33, and n_D^{20} 1.4643.

Eighty grams of unsaponifiable matter were obtained from 8 kilos. of oil, and this was found to consist of a mixture of myricyl alcohol with the following substances: (1) a *phytosterol*, $C_{27}H_{44}O$, H_2O , m. p. 132—133°, which crystallises in colourless needles and furnishes a crystalline *acetyl* derivative, m. p. 125°, which yields an amorphous *dibromide*, m. p. 130°; (2) *laurane*, $C_{20}H_{42}$, m. p. 69°, which crystallises from alcohol in slender needles and is readily soluble in light petroleum, benzene, or boiling alcohol, and (3) an aromatic, unsaturated oily substance. Laurane may be identical with the bryonane found by Etart in the leaves of *Bryonia alba* (Ber., 1892, 25, 287). The colour reactions given by the phytosterol are tabulated in the original in comparison with those given by phytosterols from other sources.

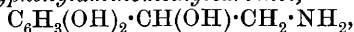
T. A. H.

Spongosterol, the Cholesterol from Suberites domuncula. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1908, 55, 427—432. Compare Abstr., 1904, i, 410).—Spongosterol forms an acetate, m. p. 124.5°, which on treatment in ethereal solution with bromine dissolved in glacial acetic acid yields a *monobromo*-derivative; this, after recrystallisation from glacial acetic acid and alcohol, melts at 157°. On reduction of this substance with zinc dust and glacial acetic acid, spongosteryl acetate is regenerated. Spongosterol appears to be a saturated compound of the formula $C_{27}H_{48}O$. The other derivatives prepared were *bromoacetylspongosterol*, m. p. 171° (by the action of bromoacetyl chloride), *spongosteryl chloride*, m. p. 91° (by the action of phosphorus pentachloride), and *spongostene*, a hydrocarbon obtained from spongosteryl chloride by the action of sodium and amyl chloride.

S. B. S.

Preparation of Aromatic Ethanolamines. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 193634).—The cyanohydrins of the aromatic aldehydes and ketones can be reduced with sodium amalgam (4% Na) to the corresponding ethanol bases. During the reduction, the solution is maintained as far as possible in the neutral condition by the addition of dilute acetic acid. In this way, *anilino-methylcarbinol* was produced from benzaldehyde cyanohydrin, and obtained as a colourless oil which slowly solidified; *hydrochloride*, soluble crystals, m. p. 176—177°, and *picrate*, m. p. 153—154°.

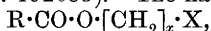
Protocatechualdehyde cyanohydrin, $C_6H_4(OH)_2 \cdot CH(OH) \cdot CN$, reddish-brown crystals, m. p. 100—105°, on reduction in the foregoing manner furnishes *dihydroxyphenylaminomethylcarbinol*,



white crystals, m. p. 191°.

G. T. M.

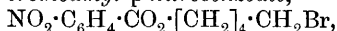
Preparation of Halogen Derivatives of Alkyl Carboxylates. EMANUEL MERCK (D.R.-P. 192035).—The halogen derivatives,



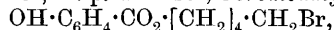
of the alkyl carboxylates (where X is a halogen and R a hydrocarbon residue) are produced by condensing the monoalkyl carboxylates, $R \cdot CO_2$, with excess of the dihalide ethers, $X \cdot [CH_2]_x \cdot X$.

γ-Bromopropyl benzoate, $Ph \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot CH_2Br$, colourless oil, b. p. 147—149°/6 mm., is obtained by condensing trimethylene bromide and dry sodium benzoate at 170—180°.

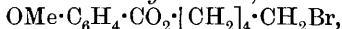
ε-Bromoamyl benzoate, $Ph \cdot CO_2 \cdot [CH_2]_4 \cdot CH_2Br$, pale yellow oil, b. p. 185—187°/5 mm., *ε-bromoamyl p-nitrobenzoate*,



greenish-yellow needles, m. p. 45—46°, *ε-bromoamyl salicylate*,



b. p. 193°/3 mm., and *3-bromoamyl anisate*,



oil, b. p. 215—217°/3 mm., are prepared from *αε*-dibromopentane and the sodium salt of the corresponding aromatic acid (benzoic, salicylic, &c.). G. T. M.

Catalysis. IV. Catalysis of Imino-esters. IRA H. DERBY (*Amer. Chem. J.*, 1908, 39, 437—473).—Stieglitz (this vol., ii, 167, 168) has given an account of the catalysis of imino-esters. The present paper deals with the experimental work on which his conclusions were based.

The imino-esters were prepared by a modification of Pinner's method. Ethyl iminobenzoate has b. p. 101—102°/11 mm., 115°/21.5 mm., and 219°/744.7 mm. (decomp.), n_D^{20} 1.5278, and is soluble in 100 c.c. of water to the extent of 0.396 gram; the partition coefficient between water and carbon tetrachloride has been determined at 23°. Methyl iminobenzoate has b. p. 91.8°/11 mm. and 106°/22 mm., n_D^{20} 1.5430, and is slightly more soluble in water than the ethyl ester. Propyl iminobenzoate has b. p. 121°/16 mm., n_D^{20} 1.5173, and is less soluble in water than either the ethyl or the methyl ester. *isoPropyl iminobenzoate* has b. p. 102°/10 mm. and 114°/20 mm., n_D^{20} 1.5144, and dissolves in water to the extent of 0.161 gram in 100 c.c. *Methyl m-nitroiminobenzoate*, m. p. 50.6°, is a pale yellow solid, which is very slightly soluble in water; the aqueous solution has a conductivity 4×10^{-6} at 25°.

The affinity constants of the esters, the velocity of decomposition of their hydrochlorides, the effect of temperature and of excess of hydrochloric acid on their velocity of decomposition, and the velocity of reaction of the free imino-esters in aqueous solution have been determined and the results are tabulated. E. G.

Resolution of Aminophenylacetic Acid into Optically Active Constituents. EMIL FISCHER and OSKAR WEICHOLD (*Ber.*, 1908, 41, 1286—1295).—The Walden rearrangement has been further studied in the case of optically active phenylacetic acid, in which the asymmetric group is between the electronegative phenyl and the carboxyl. Aminophenylacetic acid can be resolved by means of

the quinine and cinchonine salts of its formyl derivative; previously, only the *l*-form had been obtained by Ehrlich (this vol., i, 268) by partial fermentation of the racemic compound. The active acid in presence of either nitrous acid or nitrosyl bromide is so rapidly racemised that no pure optically active products could be isolated. The near position of the phenyl group apparently favours racemisation in this case, as with phenylalanine under like conditions there is comparatively little change.

dl-Formylaminophenylacetic acid, $\text{CHO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, crystallises in stellar aggregates of microscopic needles, which sinter at 176.5° , m. p. 180° (corr. decomp.). The *cinchonine* salt of the *l*-formyl compound crystallises out first in well-formed, colourless, often centimetre-long prisms. *l*-Formylaminophenylacetic acid crystallises in microscopic, thin plates from water, or in bunches of tiny needles from alcohol, m. p. 190° (corr. decomp.), and has $[\alpha]_D^{20} - 259.8^\circ$. To purify the *d*-compound, the *quinine* salt is first isolated in silky, glistening, colourless needles; the *d*-acid has $[\alpha]_D^{20} + 259.4^\circ$; the formyl compounds are hydrolysed by heating with 10% hydrobromic acid.

l-Aminophenylacetic acid (compare Ehrlich, *loc. cit.*) has m. p. $305\text{--}310^\circ$ (corr.), dissolves in 70 parts of hot water and 207 parts at 25° , and has $[\alpha]_D^{20} - 157.8^\circ$. The *hydrobromide* and *hydrochloride* form large, colourless needles, the latter have m. p. 246° (corr. decomp.). The *ethyl* ester is an oil, but forms a *hydrochloride*, m. p. 203° (corr.), $[\alpha]_D^{20} + 88.95^\circ$. *d*-Aminophenylacetic acid has similar properties; $[\alpha]_D^{20} + 157.9^\circ$.

By the action of nitrous acid, inactive mandelic acid was obtained equally from the racemic or the active acids. Similarly, in the case of the *ethyl* ester, only very feebly active products resulted; better results, however, are indicated by the use of the *amyl* ester.

E. F. A.

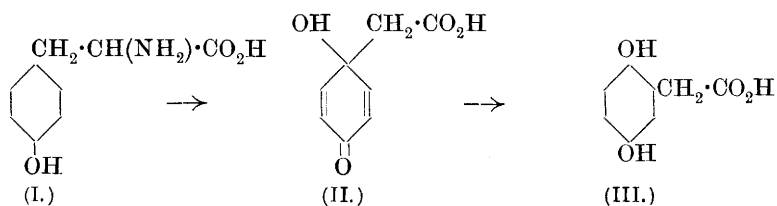
Synthesis of Polypeptides. XXIV. Derivatives of 2:5-Di-iodo-*l*-tyrosine. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Ber.*, 1908, 41, 1237—1243).—Polypeptides containing iodine substituted tyrosine are of considerable interest on account of their wide distribution in the organic skeleton of *Anthozoa*. Iodogorgonic acid, derived from coral, has been shown by Wheeler and Jamieson (*Abstr.*, 1905, i, 350) to be identical with 2:5-di-iodotyrosine.

2:5-Di-iodo-*l*-tyrosine, prepared by the action of iodine on *l*-tyrosine, derived from silk fibrin, by Wheeler and Jamieson's method, has m. p. 213° (corr.), and $[\alpha]_D + 2.27^\circ$ in dilute ammonia and $[\alpha]_D^{20} + 2.89^\circ$ in 4% hydrochloric acid. *Di-iodotyrosine methyl ester hydrochloride*, formed by the action of dry hydrogen chloride on a suspension of the acid in methyl alcohol, forms colourless needles, decomp. 210.9° (corr.); the corresponding *nitrate* crystallises in long needles. The free ester crystallises in glistening plates, decomp. 192° (corr.).

Coupled with chloroacetyl chloride in chloroform solution, it yields *chloroacetyldi-iodotyrosine methyl ester*; this forms tiny, prismatic needles, which sinter at 146° , m. p. 149° (corr.). *Chloroacetyldi-iodotyrosine*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{I}_2\cdot\text{OH}$, obtained on

hydrolysis of the ester with sodium hydroxide, crystallises in prismatic needles arranged in stellar aggregates, which become brown at 218° , decomp. 221° (corr.). *Glycyl-2:5-di-iodotyrosine*, prepared either by the action of aqueous ammonia on chloroacetyl-di-iodotyrosine or by that of iodine on glycyl-*L*-tyrosine, has decomp. 232° (corr.), and $[\alpha]_D^{20} + 51.20^{\circ}$ to $+52.69^{\circ}$. The *hydrochloride* of the *methyl ester* forms minute needles, decomp. 185° (corr.). *Glycyl-di-iodotyrosine methyl ester* sinters at 85.5° , decomp. 130° (corr.). E. F. A.

The Degradation of Carboxylic Acids in the Animal Body. VI. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 304—307).—The conversion of tyrosine into homogentisic acid in alcaptonuric individuals can only be explained by a change of position of the hydroxyl group in relation to the acid group in the benzene ring. Zincke, Auwers, and Bamberger have shown that such a change can take place in the case of the methyl group in certain quinol derivatives. It is suggested that quinol-like substances can be formed as intermediate products between tyrosine and homogentisic acid, and that a wandering of the acetic acid group can take place.



To test this hypothesis, ethyl *p*-hydroxylaminophenylacetate has been prepared. This substance should, by the Bamberger reactions, be convertible into substances of formulæ II and III. It was obtained by reducing the ethyl *p*-nitrophenylacetate in alcoholic solution with zinc dust and aqueous ammonium chloride. It melts at 64.5° , and gives, after treatment with sulphuric acid, the typical quinol reactions. S. B. S.

Preparation of Anthroxanic Acid. KALLE & Co. (D.R.-P. 191855).—*o*-Nitromandelic acid, when reduced with sufficient zinc dust and ammonium chloride to furnish the nitroso-derivative, gives rise to a moderately soluble acid, which melts at 130 — 135° , and at higher temperatures evolves carbon dioxide and furnishes a certain amount of isatin. This product is not identical with nitrosomandelic acid, for, unlike the latter, it is transformed by treatment with aqueous sodium hydroxide into sodium anthroxanate, this reaction being indicated by a change in the colour of the solution from violet to light yellow. On acidifying this liquid, the anthroxanic acid separates in white, sandy crystals. G. T. M.

Preparation of Methyleneцитryloxytoluic Acids. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193114. Compare Abstr., 1907, i, 1045).—The products of the action of methylene-citryl chloride on the hydroxytoluic acids have the same valuable therapeutic properties as methylenecitrylsalicylic acid. The conden-

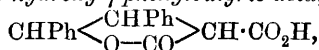
sation is effected in an anhydrous medium, for instance, benzene or chloroform in the presence of a tertiary base, such as quinoline or dimethylaniline, or the alkali salt of the acid may be condensed with the chloride. The following compounds were prepared: *methylenecitryloxy-p-toluic acid*, colourless crystals, soluble in alcohol, ethyl acetate, or ether, insoluble in water or petroleum, m. p. 175—178°; *methylene-citryloxy-m-toluic acid*, m. p. 179°; *methylenecitryloxy-o-toluic acid*, m. p. 170°; *methylenecitryloxy-o-toluic acid*, m. p. 170—175°. The last three melt indefinitely with decomposition. G. T. M.

Action of Magnesium Phenyl Bromide on the Second Methyl Ester of *p*-Dimethylamino-*o*-benzoylbenzoic Acid. J. PÉRARD (*Compt. rend.*, 1908, 146, 934—936).—Adopting the method employed by Meyer (Abstr., 1904, i, 747) for preparing the methyl ester of the tautomeric form of *o*-benzoylbenzoic acid (Haller and Guyot, Abstr., 1901, i, 146), the author has prepared a second methyl ester of *p*-dimethylamino-*o*-benzoylbenzoic acid. The new *methyl p*-dimethylamino-*o*-benzoylbenzoate, m. p. 116°, crystallises in large, silky leaves, readily soluble in benzene, sparingly so in ether; the isomeride prepared by Haller and Guyot (Abstr., 1894, i, 602) has m. p. 118° (those authors there gave 128°). The new methyl *p*-dimethylamino-*o*-benzoylbenzoate reacts with magnesium phenyl bromide to form the compound $\text{OH} \cdot \text{CPh} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} \right\rangle \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 194° (uncorr.), which is also similarly obtained from the isomeric methyl ester, m. p. 118° (Abstr., 1906, i, 755). M. A. W.

Fixation of Hydrogen Cyanide by Benzoylacrylic Acid. J. BOUGAULT (*Compt. rend.*, 1908, 146, 936—937).—Benzoylacrylic acid (this vol., i, 179, 269) combines with hydrogen cyanide to form α -cyano- β -benzoylpropionic acid, $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{H}$, identical with cyanophenacylacetic acid (Klobb, Abstr., 1894, i, 592; 1896, i, 126); the m. p's. of the hydrated and anhydrous acids are 70° and 103° respectively (Klobb gives 69° and 99—100°), and on reduction with sodium amalgam the acid yields the corresponding hydroxy-acid, *α -cyano- γ -hydroxy- γ -phenylbutyric acid*,
 $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{H}$,

which is readily converted into the lactone, $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CH}(\text{CN}) \cdot \text{CO} \\ \text{CHPh} \end{smallmatrix} \right\rangle \text{O}$, m. p. 132°.

When α -cyano- β -benzoylpropionic acid is hydrolysed, it is converted into the corresponding dibasic acid, α -carboxy- β -benzoylpropionic acid (β -benzoylisosuccinic acid), $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$ (Kues and Paal Abstr., 1886, 354); this acid has m. p. 174° (Kues and Paal give 178—179°), and on reduction with sodium amalgam furnishes the lactone of α -carboxy- γ -hydroxy- γ -phenylbutyric acid,



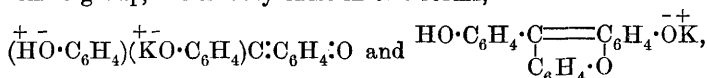
m. p. 106°.

M. A. W.

Santonin. JOSEPH KLEIN (*Ber.*, 1908, 41, 1094—1095).—Polemical. A reply to Wedekind (this vol., i, 183. Compare *Abstr.*, 1907, i, 421). W. R.

Theory of Indicators and the Reactions of Phthaleins and their Salts. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, 39, 528—544).—A continuation of the controversy with Stieglitz.

The theory of indicators proposed by Stieglitz (*Abstr.*, 1904, ii, 17) is criticised, and it is pointed out that the quinone hypothesis alone is inadequate. In the case of such compounds as the salts of phenolphthalein and aurin, the chief source of colour is not the quinone complex, but the phenol salt of a quinone compound, or a quinone-phenoxide group, which may exist in two forms,



in equilibrium, and the change from one to the other, or a corresponding movement of ions, is probably connected with the colour changes. Again, in the case of rosaniline and similar compounds, the principal cause of the colour is not the quinone group, but the double compound (or "quinaminone") formed by the inter- or intra-molecular union of the quinone complex with the free aniline (or phenylammonium hydroxide) groups of the dye. Evidence is brought forward in support of these views. In all cases, a small amount of colour is, of course, due to the quinone group, since all quinones are somewhat coloured. E. G.

Preparation of Aldehydes from Aromatic Compounds containing the Group C_3H_5 by Oxidation with Ozone. EDWARD CHARLES SPURGE (*D.R.-P.* 192565).—A stream of ozonised air is passed through a mixture of 75 parts of *isoeugenol*, 50 parts of sodium hydrogen sulphite solution, and fifty parts of water. Additional sulphite is added from time to time. The soluble vanillin bisulphite is produced. *isoSafrole* and *anethole* are similarly oxidised to piperonaldehyde and anisaldehyde. G. T. M.

Preparation of the Cyclic Carbonate of Protocatechuic Acid. HERMANN PAULY (*D.R.-P.* 190788).—Piperonaldehyde is converted into protocatechualdehyde by successive chlorination and hydrolysis with water. In the first step of the process, ω -dichloropiperonaldehyde is produced, which then reacts with 2 mols. of water. By treating this substance with only 1 mol. of water, the two chlorine atoms of the side-chain are replaced by one of oxygen, and the cyclic carbonate of protocatechualdehyde (*Abstr.*, 1907, i, 709) is produced: This product forms colourless triclinic crystals, m. p. 122° , and b. p. $160^\circ/13$ mm. and $289^\circ/760$ mm. The removal of chlorine is effected by heating dichloropiperonaldehyde with anhydrous oxalic acid at 120 — 130° , concentrated formic acid at 80 — 90° , or succinic acid at 160 — 170° . G. T. M.

Condensation Products of Cyclic Ketones with Aromatic Aldehydes. OTTO WALLACH, H. MALLISON, and K. MARTIUS (*Chem. Zentr.*, 1908, i, 637—639; from *Nachr. K. Ges. Wiss. Göttingen*, 1907, 399—405).—With the object of verifying some observations on the condensation of terpene ketones with benzaldehyde, the authors have investigated the behaviour of cyclic ketones on condensation with aromatic aldehydes. It is found that condensation does not take place with pure ortho substituted ketones; indeed, this is a method of purification from other ketones. The spacial configuration of the molecules appears to influence the possibility of condensation. Considerable difference is observed in the behaviour of the three nitrobenzaldehydes: *m*-nitrobenzaldehyde condensing very readily, the *p*-compound with some difficulty, whilst the *o*-compound does not condense at all, although *o*-chlorobenzaldehyde gives the reaction. The conditions under which condensation is carried out play an important part in determining the nature of the resulting product; thus benzaldehyde in very dilute aqueous solution in presence of excess of ketone gives in some cases the first product of condensation, the aldol. From benzaldehyde and *cyclohexanone*, the *monoaldol*, m. p. 101—102°, and the *dialdol*, m. p. 161—162°, have been prepared; also from inactive 1:3-methyl*cyclohexanone*, the *monoaldol*, m. p. 106—107°, and from 1:4-methyl*cyclohexanone*, the *monoaldol*, m. p. 127°. Active and inactive 1:3-methyl*cyclohexanone* behave differently, the latter only giving a well-defined aldol. In some cases, it is found that condensation takes place more readily in presence of excess of formic acid or acetic anhydride than with alkaline alcoholic solutions; dilute potassium cyanide solution may also be used instead of sodium hydroxide. Generally, the condensation products are yellow to orange in colour, and dissolve in concentrated sulphuric acid, exhibiting colour changes apparently dependent on the nature of the aldehyde employed. A table of the melting points of 65 condensation products is appended. J. V. E.

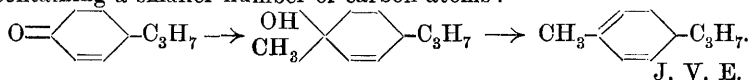
Mesitylenetrialddehyde (1:3:5-Trimethylalbenzene). JEAN BIELECKI (*Bull. Acad. Sci. Cracow*, 1908, 29—32).—The oxidation of mesitylene with chromic anhydride in presence of acetic anhydride and sulphuric acid (compare Thiele and Winter, *Abstr.*, 1900, i, 500) yields *mesitylenetrialddehyde hexa-acetate*, $C_6H_3[CH(OAc)_2]_3$, slender needles from methyl alcohol, m. p. 125—126° (corr.). When boiled with 4% hydrochloric acid, it yields *mesitylenetrialddehyde*, m. p. 94°. No analysis of this compound was made.

*Tetra- ω -chloro-*m*-xylene*, $C_6H_4(CHCl_2)_2$, was prepared by the action of chlorine on boiling *m*-xylene in presence of aluminium chloride, extracting with alcohol, and boiling with animal charcoal. It forms slender, silky needles, m. p. 223—223·5° (corr.). A. J. W.

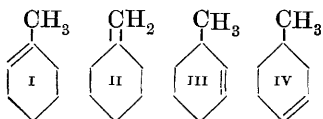
Terpenes and Ethereal Oils. XC. OTTO WALLACH (*Annalen*, 1908, 359, 2652—86).—*Transformation of Sabina ketone, and a Synthesis of α -Phellandrene*.—New methods of preparing sabina ketone are given: (1) from sabinene by oxidation, and (2) from sodium sabinenate by oxidation. Sabina ketone differs from nopinone by being more soluble

in water and solidifying more readily, forming prismatic crystals, m. p. 17°. Once solidified, it is a solid at the ordinary temperature, but readily remains liquid, having b. p. 218—219°, D^{20}_D 0.9555, $[\alpha]_D -24.41'$, n^{20}_D 1.4704. The *semicarbazone* is very readily soluble in alcohol, from which it separates in a gelatinous form, m. p. 135—137° (compare Semmler, Abstr., 1902, i, 550); from dilute methyl alcohol, it separates in hard crystals, m. p. 141—142°. Oxalic acid decomposes this semicarbazone, giving substantially unaltered sabina ketone; sulphuric acid yields *isopropylcyclohexenone*, only a trace of the hydrocarbon, C_9H_{14} , mentioned by Semmler (*loc. cit.*) being observed. When heated with dilute sulphuric acid, sabina ketone gives a yellow oily product, from which *isopropylcyclohexenone* is separated by distillation with steam. Sabina ketone isomerises under the influence of acids, chiefly forming 1-*isopropyl- Δ^1 -cyclohexen-4-one*, $O=\text{C}_6\text{H}_9\text{CHMe}_2$, *semicarbazone*, m. p. 170°, and this changes further to 1-*isopropyl- Δ^2 -cyclohexen-4-one*, $O=\text{C}_6\text{H}_9\text{CHMe}_2$, *semicarbazone*, m. p. 180°.

[With RICHARD HEYER]—When a solution of sabina ketone in a mixture of alcohol and ether is saturated with dry hydrogen chloride, the compound, $C_9H_{15}OCl$, is obtained, which separates from ether in clear, prismatic crystals, m. p. 77—78°. In glacial acetic acid solution, dry hydrogen chloride forms the compound, $C_{18}H_{29}OCl_3$, which crystallises from ethyl acetate, m. p. 124°. Hydrogen chloride may be removed from the monochloride, m. p. 77—78°, in both possible ways, giving *isopropyl- Δ^1 -cyclohexenone* and 4-*isopropylidenecyclohexenone* (Trans., 1907, 91, 1746), which were both identified by their semicarbazones. *isoPropyl- Δ^1 -cyclohexenone*, when warmed with mineral acids, undergoes a change to *isopropyl- Δ^2 -cyclohexenone*, b. p. 217—221°, $[\alpha]_D +2.15^\circ$, D^{19}_D 0.947, n^{19}_D 1.4807. Treated with magnesium methyl iodide, *isopropyl- Δ^2 -hexenone* yields α -phellandrene together with small quantities of an alcohol, b. p. 208—211°, D^{19}_D 0.9230, n^{19}_D 1.4760; this is the first synthesis of phellandrene from a substance containing a smaller number of carbon atoms:



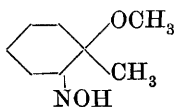
Terpenes and Ethereal Oils. XCI. OTTO WALLACH (*Annalen*, 1908, 359, 287—316. Compare Abstr., 1907, i, 1061).—*Isomeric Hexacyclic Hydrocarbons*, C_7H_{12} .—The author reviews the characteristic reactions of I and II of the following four isomeric substances, and gives further that I, by moderate oxidation with potassium permanganate, yields a *glycol*, m. p. 67°, which when warmed with acid is converted into 1-methyl-*cyclohexan-2-one*.



The nitrosochloride, m. p. 127°, from II readily loses hydrogen chloride, forming an *aldoxime*, crystallising from light petroleum, m. p. 97—99°, and this yields a *benzoyl* derivative, m. p. 101—102°. When warmed with acids, the oxime

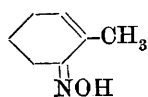
gives tetrahydrobenzaldehyde. Hydrogen chloride, passed into a glacial acetic acid solution of methylenecyclohexane, produces a *chloride*, b. p. 151—152°. When heated with a mixture of glacial acetic acid and sulphuric acid, the *acetate* is produced. Methyl- Δ^1 -cyclohexene has been prepared from 1-methyl-1-cyclohexanol by the action of anhydrous zinc chloride; it has b. p. 111—112°, D^{20}_D 0.811, n^{20}_D 1.4496. Further, to characterise this substance, it was oxidised with permanganate, whereby a volatile and a non-volatile product were obtained. The former readily gives a sparingly soluble semicarbazone, crystallises from methyl alcohol, m. p. 202—203°, and is probably identical with the compound, $C_7H_{10}O$, prepared by the oxidation of Δ^1 -cyclohexeneacetic acid (Abstr., 1906, i, 176). The non-volatile product contains 1-methyl-cyclohexan-1:2-diol, which separates from ether in small crystals, m. p. 67°, also δ -acetylvaleric acid, and probably adipic acid.

This new glycol, m. p. 67°, is decomposed by warming with concentrated oxalic acid solution or dilute sulphuric acid, giving 1-methyl-2-cyclohexanone, which is identified by converting to the semicarbazone. When the glycol (m. p. 67°) from methyl- Δ^1 -cyclohexene is ground together with the glycol (m. p. 76—77°) from methylenecyclohexane, the mixture becomes semi-fluid at the ordinary temperature. The nitrosochloride from 1-methyl- Δ^1 -cyclohexene was prepared and treated with sodium methoxide, whereby a solid and a liquid product were



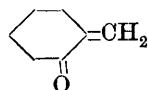
obtained. The solid portion is the *methoxyl-oxime* (annexed formula), which crystallises from light petroleum in small plates, m. p. 64—65°; it gives a *benzoyl* derivative, crystallising from dilute methyl alcohol in leaflets, m. p. 97—98°. The liquid portion yields

on extraction with ether a liquid which forms a solid sodium derivative, and this on benzoylation gives two products, one sparingly, the other easily, soluble in ether. The readily soluble substance is the *benzoyl-methoxyl-oxime*, m. p. 97—98°; the less soluble product is the benzoyl derivative of the normal unsaturated oxime (annexed



formula). This substance is slightly soluble in methyl alcohol, crystallising in needles, m. p. 142—143°. 1:4-Methylcyclohexanol, when heated with anhydrous zinc chloride, yields a substance, C_7H_{12} , b. p. 106—107°, D^{22}

0.7935, n^{22}_D 1.4384 which proves to be a mixture of methyl- Δ^1 -cyclohexene and methyl- Δ^3 -cyclohexene. 1-Methyl-2-cyclohexanol treated in a similar manner gives methyl- Δ^1 -cyclohexene. When Δ^1 -cyclohexeneacetic acid, m. p. 38°, is heated with potassium hydroxide, Δ^a -cyclohexeneacetic acid (Abstr., 1907, i, 616) is not obtained, but δ -acetylvaleric acid and a substance, $C_7H_{10}O$, shown to be neither tetrahydrobenzaldehyde nor methyl- Δ^1 -cyclohexenone (Abstr., 1906, i, 176), but probably the ketone (annexed formula). This substance, b. p. 172—174°, D^{17}_D 0.9445, n^{17}_D 1.4719, gives a *semicarbazone*, m. p. 202—204°, an *oxime*, m. p. 90—91°, and a *benzoyloxime*, m. p. 116—117°.



The behaviour of β -cyclohexylethylamine towards nitrous acid has been studied. *cyclo*Hexylacetoneitrile, b. p. 215°, D^{18}_D 0.913, n^{18}_D 1.4575, on reduction yields β -cyclohexylethylamine, b. p. 188—189°, D^{19}_D 0.8700, n^{19}_D 1.4647, which gives a hydrocarbon, b. p.

132—137°, and the primary and secondary *alcohols*, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot OH$ and $C_6H_{11} \cdot CHMe \cdot OH$, when treated with sodium nitrite in acid solution. These alcohols were identified by oxidising and converting to the *semicarbazones*, m. p. 132—134° and 172—173° respectively.

J. V. E.

Action of Phthalic Anhydride on Resacetophenone. HENRY A. TORREY and C. M. BREWSTER (*J. Amer. Chem. Soc.*, 1908, 30, 862—863).—Torrey and Kipper (this vol., i, 460) have stated that when diacetylquinol or diacetylresorcinol is treated with *m*-nitrobenzoyl chloride, the acetyl groups are replaced by *m*-nitrobenzoyl groups. An even more remarkable reaction has been observed, in which the acetyl group in resacetophenone, which, in this case, is directly attached to the ring, is replaced by a group of higher molecular weight. It has been found that when resacetophenone (2 mols.) is heated with phthalic anhydride (1 mol.) in presence of a dehydrating agent, acetic acid is produced and a large yield of fluorescein is obtained.

E. G.

An old Derivative of Benzanthrone. CARL LIEBERMANN and K. ROKA (*Ber.*, 1908, 41, 1423—1427).—A comparison of the physical properties and general behaviour of the substance, $C_{19}H_{14}O$, obtained by Liebermann by the action of concentrated sulphuric acid on amyloxanthranol (Abstr., 1882, 855), with those of benzanthrone (compare Bally, Abstr., 1905, i, 237) indicates that the substance must be a derivative of the latter. The analytical data correspond also with the formula $C_{18}H_{14}O$ or $C_{18}H_{12}O$, according to which the substance may be methyl-dihydrobenzanthrone or methylbenzanthrone. By oxidation with chromic and acetic and dilute sulphuric acids, it yields, like benzanthrone, anthroquinone- α -carboxylic acid, whilst reduction by hydriodic acid and phosphorus results in the formation probably of the methyl homologue of the *hydrocarbon*, $C_{17}H_{16}$ or $C_{17}H_{14}$, m. p. 80°, obtained by the reduction of benzanthrone in a similar manner. Both hydrocarbons yield colourless solutions in concentrated sulphuric acid which become red on warming.

C. S.

Some Derivatives of Tetrachloro-*o*-benzoquinone. C. LORING JACKSON and P. W. CARLETON (*Amer. Chem. J.*, 1908, 39, 493—505).—In an earlier paper (Jackson and MacLaurin, Abstr., 1907, i, 856), an account was given of the reactions of tetrachloro-*o*-benzoquinone with alcohols, toluene, glacial acetic acid, and other substances.

In continuation of this work, it has been found that when equal weights of tetrachloro-*o*-benzoquinone and tetrachlorocatechol are dissolved in the smallest possible quantities of hot chloroform, the solutions mixed, and the mixture rapidly cooled, octachloro-*o*-quinhydrone is produced, but that if the mixture is kept warm for some time, heptachloro-*o*-quinocatechol hemi-ether is formed.

*Octachloro-*o*-benzoquinhydrone*, $C_6Cl_4O_2 \cdot C_6H_2Cl_4O_2 \cdot \frac{1}{2}H_2O$, m. p. about 160°, forms lustrous, black needles, which readily effloresce, becoming dull and dark purple. The substance turns yellow at 70°, with formation of heptachloro-*o*-quinocatechol hemi-ether. When treated with

nitrobenzene, it yields tetrachlorocatechol, tetrachloro-*o*-benzoquinone, the red ether, $C_6Cl_4O_2 \cdot C_6Cl_2O_2$, and heptachloro-*o*-quinocatechol hemi-ether.

Heptachloro-o-quinocatechol hemi-ether, $C_6Cl_4(OH)O \cdot C_6Cl_3O_2$, m. p. about 214° (decomp.), crystallises in yellow scales.

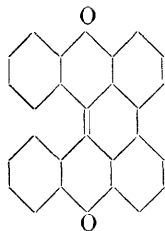
Improved methods are described for the preparation of hexachloro-*o*-quinomethylhemiacetalcatechol ether and hexachloro-*o*-quinodimethylhemiacetalcatechol ether (Jackson and MacLaurin, *loc. cit.*). The acetyl compound described by Jackson and MacLaurin (*loc. cit.*) as melting at 215° has the formula $C_6Cl_4O_2 \cdot C_6Cl_2O(OMe) \cdot OAc$, and m. p. 220° .

When tetrachloro-*o*-benzoquinone is treated with acetophenone, a compound, m. p. 281° , is produced. On oxidising tetrachloro-*o*-benzoquinone or tetrachlorocatechol with fuming nitric acid containing a little hydrochloric acid, a yellow substance, m. p. $146-147^\circ$, is formed, which is probably identical with the compound obtained by Jackson and MacLaurin (*Amer. Chem. J.*, 1907, 37, 19) by the prolonged action of chlorine on tetrachlorocatechol. E. G.

Preparation of Dimethyl Ether of *p*-Nitrochrysazin. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 193104. Compare Abstr., 1906, i, 677).—Hitherto the nitration of chrysazin and its ethers have led to the formation of di- and tetra-nitrochrysazins, but the following process furnishes the *dimethyl* ether of *p*-nitrochrysazin. The dimethyl ether of chrysazin was dissolved in cold concentrated sulphuric acid, and treated gradually with nitric acid (27% HNO_3). After twenty-four hours, the mixture was poured on to ice. The product, after crystallisation from chlorobenzene, separated in green needles, m. p. $232-233^\circ$.

p-Nitrochrysazin, obtained by hydrolysing the dimethyl ether with hot 10% sulphuric acid, separates from chlorobenzene in orange-yellow crystals, m. p. $232-234^\circ$. G. T. M.

Preparation of Anthracene Derivatives from α -Dianthraquinonyl.



ROLAND SCHOLL (D.R.-P. 190799).— α -Dianthraquinonyl and its derivatives, when treated with acidreducing agents, lose two oxygen atoms and become converted into complex diketo-derivatives, the simplest of which is regarded as having the annexed formula.

This compound, produced by reducing dianthraquinonyl with alcoholic stannous chloride or concentrated sulphuric acid and copper powder (or some other metal, such as nickel, iron, or zinc), is a sparingly soluble, brownish-yellow powder obtained crystalline from xylene or nitrobenzene. G. T. M.

New Borneol. OSSIAN ASCHAN (*Ber.*, 1908, 41, 1092—1094).—Camphene hydrochloride, when stirred with milk of lime at $50-60^\circ$ and finally at 80° during twelve to eighteen hours, then subjected to distillation with steam, extraction with ether, and fractionation in small portions after removal of the ether, gives a new borneol in good yield, *camphene hydrate*, $C_{10}H_{18}O$, which, on sublimation, crystallises

in strongly refractive tetrahedra, m. p. 150—151°. It has an odour resembling menthol, loses water very easily with dilute mineral acids, or on boiling with glacial acetic acid for a short time, or on distillation of large quantities at 180°, camphene being regenerated. Oxidation leads to the production of small quantities of camphor. The conclusion is drawn provisionally that it is a tertiary alcohol, formed by the replacement of tertiary chlorine by hydroxyl. W. R.

Preparation of Alkyloxyacetyl Derivatives of the Hydroaromatic Alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 191547).—The therapeutic application of the hydroaromatic alcohols, such as santalol, menthol, and borneol, is attended by the disadvantage that these substances have an intense odour and unpleasant secondary reactions. The alkyloxyacetyl derivatives of these alcohols are tasteless and odourless, and do not exhibit the secondary reactions.

Bornyl ethoxyacetate, $\text{OEt} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_{10}\text{H}_7$, colourless liquid, b. p. 175—178°/20 mm., was prepared by condensing borneol and ethoxyacetyl chloride in benzene solution in the presence of pyridine. *Santalyl ethoxyacetate* is a colourless liquid, b. p. 185—190°/20 mm.

Menthyl methoxyacetate, liquid, b. p. 140°/10 mm., was obtained from menthol, menthoxyacetic acid, and carbonyl chloride in benzene solution. G. T. M.

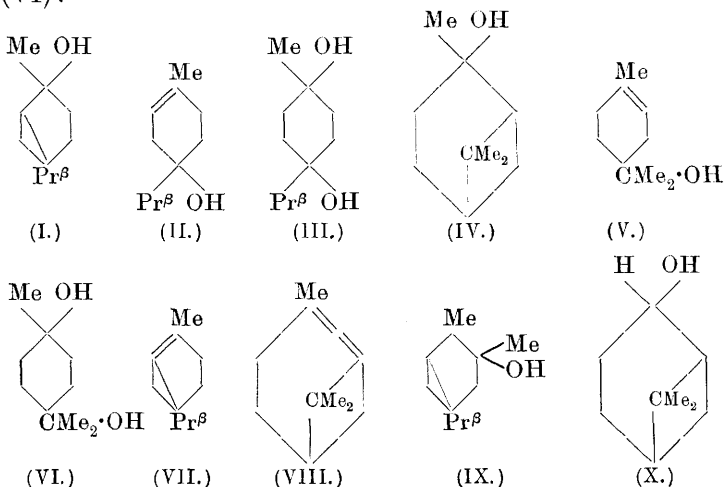
Preparation of *iso*Bornyl Oxalate. J. BASLER & Co. (D.R.-P. 193301).—It has been found that camphene (100 parts) and anhydrous oxalic acid (100 parts) in 300 parts of acetone containing 15 parts of sulphuric acid, when left at 15—25° for three days, furnish a mixture of the acid and normal *isobornyl* esters of oxalic acid. The unchanged oxalic acid is removed with hot water, and the *isobornyl* hydrogen oxalate extracted with aqueous sodium carbonate; the latter has not been obtained crystalline. *isoBornyl oxalate* crystallises from alcohol in colourless, odourless needles, m. p. 113—114°. The unaltered camphene was separated by distillation in steam; when the combination is carried out at 110—115°, this distillate contained both camphene and *isobornyl* formate. Both the esters are readily hydrolysed, yielding *isoborneol* and oxalic acid. G. T. M.

Terpenes and Ethereal Oils. XCIII. Resolution of Linkings by Addition of Water to Terpene Compounds. OTTO WALLACH (*Annalen*, 1908, 360, 82—104).—Although the addition of water to terpene molecules is well known to occur in specific cases, the course of such addition and the relative ease with which it takes place with terpene compounds of different structures have not previously been studied systematically. The investigation of these points has been undertaken, and the first results are now given.


In order that the results might be comparable, the hydration experiments have been carried out in each case, so far as possible, under the same conditions, the terpene compound being shaken with a large excess of 3% to 5% sulphuric acid at the ordinary temperature. The unavoidable differences in the experimental conditions lie in the varying solubilities of the compounds in dilute acid; solubility is, however, not of itself a decisive factor, since substances such as pinene and sabinene,

which are both sparingly soluble, behave very differently, whilst nopinol, in spite of its solubility, is regained unchanged from the dilute acid.

In many cases, the hydration is preceded by an intramolecular transformation. Thus sabinene hydrate (I) changes first into active terpinene-4-ol (II), terpineneterpin (III) being formed only as the product of a further reaction. In the same manner, *cis*-terpin (VI) is formed from pinene hydrate (IV), not directly, but by way of active α -terpinol (V). As the terpinene-4-ol and α -terpineol are optically active substances, they cannot have been formed from the glycols (III) and (VI):



It is considered that in such cases, the first stage is loss of water, sabinene hydrate and pinene hydrate forming the unsaturated hydrocarbons (VII) and (VIII), which then add on water, forming terpinene-4-ol and α -terpineol respectively. The ease with which the three-atom ring of (VII), or the four-atom ring of (VIII), is resolved, is ascribed to the influence of the quaternary carbon atom. In agreement with this, it is found that homothujyl alcohol (IX) is extremely stable towards acids; in this, the hydroxyl is differently placed towards the three-atom ring to that of sabinene hydrate, and loss of water cannot lead to the formation of a quaternary carbon atom. On the other hand, whilst methylnopinol (pinene hydrate) is easily attacked by dilute acids, nopinol (X) under the same conditions is stable. This is ascribed to the greater stability of the secondary alcohol grouping. These results agree with Perkin's view (Trans., 1907, 91, 817) that the stability of the cyclopropane and cyclobutane rings depends much more on the nature and position of the attached groups than on the number of carbon atoms in the ring.


I *Comparative Experiments on the Resolution of Four-Atom Rings by Addition of Water to Substances of the Type* .—Crystalline α - and

liquid β -nopinols remain unchanged on prolonged shaking with dilute sulphuric acid. Only in one experiment were indications of the formation of traces of a hydration product observed.

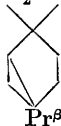
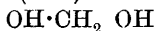
Methylnopinol (pinene hydrate), when shaken with dilute acid for two to three hours, is converted into terpin hydrate, but, if shaken only for one hour, yields *l*- α -terpineol, m. p. 37—38°, b. p. 218—219°, $[\alpha]_D -106^\circ$. This high rotatory power shows that previous specimens of active α -terpineol have contained more or less of the inactive substance. As methylnopinol is formed from nopinone by Grignard's reaction (Wallach and Blumann, Abstr., 1907, i, 936), its conversion into *l*- α -terpineol completes the first synthesis of an optically active α -terpineol from a substance containing a smaller number of carbon atoms. The synthetical *l*- α -terpineol forms a *nitrosochloride*, crystallising in needles, m. p. 107—108°, and a *nitrolpiperidide*, needles or prisms, m. p. 150°. When oxidised with permanganate, it yields a solid *glycerol*, which on further oxidation by means of chromic acid is converted into a *keto-lactone*, m. p. 46—47°; this forms a *semi-carbazone*, m. p. 199°.

Ethylnopinol (Abstr., 1907, i, 1059), when shaken with dilute acid, is first converted into a *homologue* of α -terpineol, b. p. 226—227°, which has the annexed constitution. Its behaviour is similar to that of α -terpineol, but it unites with water more slowly to form the corresponding terpin hydrate. *n*-Propylnopinol reacts with 3% sulphuric acid in the same manner as ethylnopinol.

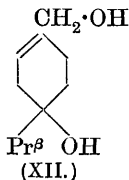
Nopic acid does not yield a saturated dihydroxy-acid when treated with cold dilute acid. Nopinone remains unchanged in the cold, but when heated with concentrated sulphuric acid is converted into isopropylhexenone, whereas pinocampnone is stable towards boiling acids.

II. *Comparative Experiments on the Resolution of Three-Atom Rings by Addition of Water to Compounds of the Type* .—Thujyl alcohol

and *homothujyl alcohol*, $C_{11}H_{20}O_2$, which is prepared from thujone and magnesium methyl iodide, and is obtained in a solid, m. p. 84°, and a liquid modification, remain unchanged when shaken with cold dilute sulphuric acid. Methylsabinaketol (sabinene hydrate), on the other hand, is converted successively into *d*-terpinene-4-ol and terpinene-terpin. The higher homologues of sabinene hydrate react in the same manner, but more slowly and less completely. Sabinene glycol (XI) yields an unsaturated glycol, m. p. 105°, which has probably the constitution (XII):



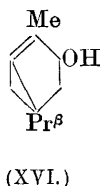
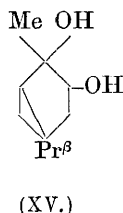
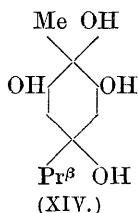
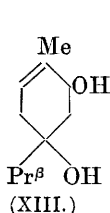
(XI.)



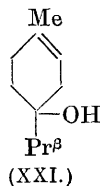
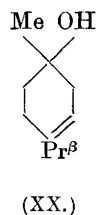
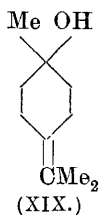
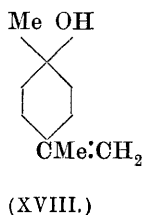
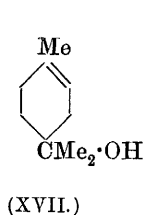
(XII.)

Sabinoglycerol is converted into an unsaturated *glycerol*, $C_{10}H_{15}O_3$, b. p. $200^\circ/10$ mm. Thujone remains unchanged in the cold, and is converted into *isothujone* by hot concentrated acid. Sabina ketone is much more stable than methylsabinaketol towards cold acid, but is converted into *isopropylhexenone* by hot alcoholic sulphuric acid.

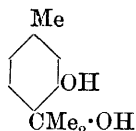
Thujene and sabinene yield terpinene-4-ol and terpineneterpin, the reaction taking place much the more rapidly in the case of sabinene. Sabinol is converted by 5% sulphuric acid in two days into a *glycol* (XIII), which on oxidation with permanganate yields a substance named by the author *erythrit* (XIV); this separates in crystals, m. p. 186° , and has a sweet flavour. The hypothetical intermediate products (XV) and (XVI) are assumed to be formed between sabinol and the glycol:



III. *Comparative Experiments on the Resolution of an Ethylene Linking by Addition of Water.*—Of the five isomeric menthenols, β - and γ -terpineols (XVIII) and (XIX) react more readily with dilute sulphuric acid than does α -terpineol (XVII), whilst terpinene-1-ol (XX) and terpinene-4-ol (XXI) react so much more slowly than the terpeneols that treatment with dilute acid may be used as a means of separation of these (Abstr., 1907, i, 943). Whilst α - and s -terpineols yield ordinary terpin hydrate, and the terpinenol forms terpineneterpin, m. p. 137° , the hydration product of γ -terpineol is a mixture of the two isomerides:



The resolution of an ethylene linking in a side-chain by addition of water is further illustrated by dihydrocarveol,



which forms a glycol, $OH \cdot C_6H_9Me \cdot CMe_2 \cdot OH$, and by *isopulegol*, $C_{10}H_{18}O$, which yields a *glycol*, m. p. 75° , having the annexed constitution.

The semicyclic ethylene linking of sabinene is readily resolved by water; the resulting hydrate is unstable, losing water and forming the first intermediate product of sabinene hydrate (VII), and therefore yields finally terpinene-4-ol.

Whilst pinene is slowly acted on by 5% sulphuric acid, limonene

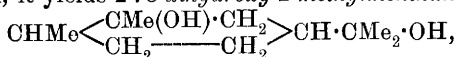
and methylenecyclohexane remain unchanged. It is the more remarkable that the hydrocarbon, obtained from water-fennel oil and consisting chiefly of β -phellandrene, yields *cis*-terpin together with small amounts of *trans*-terpin. G. Y.

Action of Magnesium Methyl Halides on Carvone and Dihydrocarvone. HANS RUPE and F. EMMERICH (*Ber.*, 1908, 41, 1393—1403. Compare Rupe and Liechtenhan, *Abstr.*, 1906, i, 374; Klages and Sommer, *ibid.*, 566; Klages, *Abstr.*, 1907, i, 597).—The authors have obtained a methylmenthatriene with $[\alpha]_D^{20} + 103.49^\circ$ by the action of acetic anhydride on 2-methylcarveol, a good yield of which is obtained when the additive compound of carvone and magnesium methyl iodide is gradually decomposed with dilute (10—20%) sulphuric acid. When kept for some months, the tertiary alcohol yields the unsaturated hydrocarbon. When distilled several times under reduced pressure, the rotatory power of the hydrocarbon is considerably diminished. When reduced with sodium and amyl alcohol, the hydrocarbon yields a *dihydro*-derivative, *methylmenthadiene*, $C_{11}H_{18}$, b. p. $72^\circ/9$ mm., $D_{20} 0.8576$, $n_D^{20} 1.46502$, $[\alpha]_D^{20} - 55.44^\circ$.

2-Methyldihydrocarveol, $CHMe \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CMe(OH)} \cdot \text{CH}_2 \end{smallmatrix} > CH \cdot CMe : CH_2$, obtained by the action of magnesium methyl iodide on dihydrocarvone, is a colourless liquid, b. p. $102\text{—}103^\circ/13.5$ mm., $D_{20} 0.9230$, $n_D^{20} 1.4779$. When heated with phthalic acid, it loses water and yields *2-methylhomolimonene* (*2-methyldihydrocarvene*), $C_{11}H_{18}$, b. p. $77\text{—}78^\circ/13.5$ mm. and $[\alpha]_D^{20} - 7.99^\circ$.

The same product is formed by the action of phosphoric oxide or zinc chloride on the alcohol, but the best yield is obtained by the elimination of hydrogen chloride from the *2-chloro-2-methyl- $\Delta^{3:9}$ -tetrahydrocymene*, $CHMe \begin{smallmatrix} \text{CMeCl} \cdot \text{CH}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} > CH \cdot CMe : CH_2$, which can be prepared by the action of phosphorus pentachloride on the alcohol. It is a colourless liquid of pungent odour, and has b. p. $105\text{—}108^\circ/10$ mm. When heated with quinoline at $200\text{—}210^\circ$, it yields *2-methylhomolimonene*, b. p. $72\text{—}74^\circ/10$ mm., $D_{20} 0.8598$, $n_D^{20} 1.48598$, $[\alpha]_D^{20} - 25.33^\circ$, and this yields white, crystalline compounds with hydroferro- and hydroferri-cyanic acids, an oily hydrobromide, $C_{11}H_{19}Br$, and does not yield crystalline compounds with nitrosyl chloride, nitrous acid, &c. It is not reduced when treated with sodium and amyl alcohol.

When methyldihydrocarveol is boiled with alcohol and 10% sulphuric acid, it yields *2:8-dihydroxy-2-methylmenthane*,



which crystallises from benzene in colourless, glistening needles, m. p. $135\text{—}136^\circ$.

The author accepts Klages' formula for methylmenthatriene.

J. J. S.

Components of Ethereal Oils. **Santalols**, $C_{15}H_{24}O$, and their **Derivatives.** FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 1488—1493. Compare *Abstr.*, 1907, i, 431, 433).—As *tricyclosantalol*, which has

one ethylene linking in the side-chain, is obtained mixed with *dicyclosantalol*, containing two ethylene linkings and probably other substances, the preparation of pure *tricyclosantalaldehyde* by oxidation of the *tricyclosantalol* has been attended with many difficulties. The pure aldehyde has now been obtained; its properties and those of its derivatives as now described should be compared with the description given previously (*loc. cit.*).

On oxidation with ozone, crude santalol yields an *oxide*, m. p. 157° , b. p. $114-116^{\circ}$, D^{15}_D 1.016, n_D 1.50513, *nortricyclosantalol*, and *tricyclosantalaldehyde*, $C_{11}H_{16}O$, which, after purification by conversion into the sodium hydrogen sulphite compound, has b. p. $110-111^{\circ}/10$ mm., D^{15}_D 0.9846, n_D 1.48905. Reduction of the aldehyde leads to the formation of *d-tricycloeksantalol*, $C_{11}H_{18}O$, b. p. $129-131^{\circ}/10$ mm., D^{18}_D 0.989, n_D 1.4962, $\alpha_D + 7^{\circ}$. The oxime of the aldehyde, $C_{11}H_{16}NOH$, b. p. $149-151^{\circ}/9$ mm., D^{15}_D 1.024, n_D 1.5097, $\alpha_D + 6^{\circ}30'$, is converted by acetic anhydride into *tricycloeksantaloxime*, b. p. $124-128^{\circ}/10$ mm., D^{15}_D 0.9904, n_D 1.48809, $\alpha_D + 14^{\circ}15'$ (100 mm. tube), which on reduction with sodium and alcohol yields the *tricycloeksantalyamine*, $C_{11}H_{17}NH_2$, b. p. $110-112^{\circ}/8$ mm., D^{15}_D 0.9409, n_D 1.4915.

tricycloEksantalic acid, $C_{11}H_{16}O_2$, b. p. $163-165^{\circ}/9.5$ mm., D^{15}_D 1.0482, n_D 1.49383, $\alpha_D + 7^{\circ}$ (100 mm. tube). The lactone, $C_{11}H_{16}O_2$, m. p. $98-100^{\circ}$, remains unchanged when treated with sodium and alcohol.

Methylhydrochlorodicycloeksantalate, b. p. $154-158^{\circ}/10$ mm., D^{15}_D 1.103, n_D 1.49668, $\alpha_D + 16^{\circ}$. *dicycloEksantalic acid* has b. p. $168-169^{\circ}/10.5$ mm., D^{15}_D 1.058, n_D 1.50327. Dihydroeksantalol, $C_{11}H_{20}O$, b. p. $134-136^{\circ}/10$ mm., D^{15}_D 0.9692, n_D 1.49192, is best prepared by reduction of methyl hydrochlorodicycloeksantalate with sodium and alcohol, and, on treatment with phosphorus pentachloride in light petroleum solution, yields *dihydroeksantalyl chloride*, $C_{10}H_{17}CH_2Cl$, b. p. $120-123^{\circ}/10$ mm., D^{15}_D 0.9949, n_D 1.48519, which is converted by sodium and alcohol into *dihydrodicycloeksantalane*, $C_{10}H_{17}Me$, b. p. $75-77^{\circ}/10$ mm. or $204^{\circ}/768$ mm., D^{15}_D 0.8705, n_D 1.47151. This may be identical with a hydrocarbon obtained by heating *tricycloeksantalic acid* with hydriodic acid and red phosphorus.

The molecular refractions of *tricyclosantalaldehyde* and its derivatives show a marked increment over the calculated refractions.

G. Y.

isoTerpenes of Flawitzky. EDWARD KREMERS (*Pharm. Rev.*, 1908, 26, 102-106).—From the *d*- and *l*-pinenes, obtained respectively from Russian and French oil of turpentine, Flawitzky (*Abstr.*, 1880, 264, 402; 1887, 968) prepared certain *isoterpenes*. The method employed involved the hydration of the pinene with dilute alcoholic sulphuric acid, and subsequent dehydration by means of acetic anhydride. Flawitzky was of opinion that these hydrocarbons were identical with the limonenes, and that their production was accompanied by the formation of considerable quantities of dipentene. These conclusions have now been confirmed.

E. G.

Optical Rotation of Spirits of Turpentine. CHARLES H. HERTY (*J. Amer. Chem. Soc.*, 1908, 30, 863-867).—The dextro-

rotatory character of American oil of turpentine has been shown by Long to be due to the fact that its chief constituent is the dextro-rotatory oil of *Pinus palustris*.

A study has been made of the oils of *Pinus palustris* (the "long leaf pine") and *P. heterophylla* (the "Cuban" or "slash pine"). Specimens of the oleo-resins were collected from trees of different ages and tapped to different depths. The rotatory power of the volatile oils distilled from these specimens showed a wide variation, even among those obtained from the same species, and sometimes among those obtained from the same tree at different ages. In general, the results confirm Long's observation that the volatile oil of *P. palustris* is dextro-, and that of *P. heterophylla* is lævo-, rotatory, but this is not invariably true. These oils consist largely of mixtures of *d*- and *l*-pinene, the preponderance of one or the other determining the character of the rotatory power. E. G.

Semicatalysis: Oxidation of Hydrocarbons by Air in the Presence of Phosphorus. ALBERT COLSON (*Compt. rend.*, 1908, 146, 817—818. Compare this vol., ii, 176).—Yellow phosphorus only dissolves in oil of turpentine in the absence of air, and on cooling the solution snow-white crystals are obtained. In the presence of air, the liquid becomes cloudy, and a white, odorous deposit, sometimes curdled and sometimes colloidal, is formed. Since this deposit is not decomposed by water and does not redden litmus, it cannot contain free phosphoric acid, and the fact that it is soluble in dilute ammonia shows the absence of free turpentine. Evaporation of its ethereal solution leaves a resin, m. p. 77—78°, having a camphor-like smell, and a composition corresponding with the formula $(C_{10}H_{16}O_3)_2H_3PO_4$. The degree of oxidation of the turpentine varies with the experimental conditions, but two molecules of the hydrocarbon seem always to react with one atom of phosphorus. The acetic acid solution of this compound is apparently unstable, since its m. p. rises on keeping. The turpentine is certainly oxidised, but, since the product is formed immediately, the phenomenon cannot be described as a slow oxidation, and it is not a case of real catalysis, since the phosphorus enters into the product. The author proposes to call the change, which is also characteristic of benzene, a *semicatalysis*.

E. H.

Volatile Oil of *Pinus serotina*. CHARLES H. HERTY and W. S. DICKSON (*J. Amer. Chem. Soc.*, 1908, 30, 872—874).—The volatile oil distilled from the oleo-resin of *Pinus serotina* (the Pond pine) gives the following fractions on re-distillation under the ordinary pressure: at 172—175°, 27.4%, with $[n]_D^{20}$ 1.4716 and α_D - 87°53' (100 mm. tube); at 175—180°, 57.0%, with $[n]_D^{20}$ 1.4724 and α_D - 92°21' (100 mm. tube); at 180—185°, 8.4%, with $[n]_D^{20}$ 1.4744 and α_D - 92°14' (100 mm. tube); above 185°, 7.2%, with $[n]_D^{20}$ 1.5045. The fraction of b. p. 175—176° contains a large proportion of limonene.

The resin left after distilling off the oil is pale yellow, and has an acid value 167. E. G.

Constituents of Tarragon Oil (*Oleum dracunculi*). MAURICE DAUFRESNE (*Chem. Zentr.*, 1908, i, 1057; from *Bul. Sci. Pharm.*, 1908, 15, 11—20).—A sample of French oil, D^{15} 0.949, $\alpha + 7.8'$, $n_D^{15.5}$ 1.51695, and a German oil, D^{15} 0.945, $\alpha + 7.24'$, n_D^{15} 1.51645, have been examined and found to contain 15—20% of a terpene, $C_{10}H_{16}$, b. p. 173—175° or 68—70°/13 mm., D^0 0.825, D^{15} 0.812, n_D^{15} 1.48636, with a strong smelling hydrocarbon similar to phellandrene, 60—75% of estragole absolutely free from anethole, 0.5—0.6% of *p*-methoxycinnamaldehyde, and 5—20% of higher boiling products. A sample of oil ten years old contained 4.5% of *p*-methoxycinnamaldehyde.

J. V. E.

Ozonides from African Caoutchouc. KURT OTTO GOTTLÖB (*Chem. Zentr.*, 1908, i, 467—468; from *Gummi Zeit.*, 1907, 22, 305—308. Compare Abstr., 1905, i, 364).—Harries' view (Abstr., 1906, i, 30) that the ozonide of gutta-percha is stereoisomeric with that of Para-caoutchouc is criticised. From studying the decomposition of the ozonides of various African caoutchoucs, the conclusion is drawn that African caoutchouc and gutta-percha are undoubtedly related substances; the behaviour of the ozonides allows of a discrimination between Para-caoutchouc and African caoutchouc.

J. V. E.

Manila and Pontianac Copals. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1908, [iv], 3, 453—459. Compare Abstr., 1907, i, 67).—Manila "hard" copal has D^{17} 1.065, m. p. 190°, acid number 72.8, and Köttstorfer number 87. Manila "friable" copal has D^{17} 1.060, m. p. 120°, acid number 145.2, and Köttstorfer number 185.1.

Pontianic copal has D^{16} 1.037, m. p. 135°, acid number 134.3, and Köttstorfer number 186.5.

The solubilities of these three copals in twelve common organic solvents are tabulated in the original.

T. A. H.

Burseracin and its Effects. WERNER VON BOLTON (*Zeitsch. Elektrochem.*, 1908, 14, 211—216).—Myrrh was used by the ancients for embalming and healing wounds. The active substance is isolated by extracting with alcohol, evaporating to dryness, and then extracting with water. The substance so obtained, *burseracin*, forms 1.5 to 2% of the original myrrh; after purification by solution in ether, it is a yellow, hygroscopic powder, m. p. 78.15°, readily soluble in hot water. It reduces Fehling's solution, and yields a hydrazone. An analysis and molecular weight determination point to the formula $C_{20}H_{28}O_8$. It is not a glucoside. Its odour and taste resemble those of burnt sugar, and it is also very bitter. It is oxidised by potassium permanganate. It leaves 2.69 to 3.06% of ash, consisting of calcium oxide. When evaporated over a flame with hydrogen peroxide, it explodes violently; by evaporation in a vacuum, a glassy, hygroscopic mass is obtained, which softens at 52°, fuses completely at 100°, and explodes on further heating. It liberates iodine from potassium iodide; titanous acid does not give the reaction of hydrogen peroxide. This substance is named *oxyburseracin*. It seems to give off β -rays and also γ -radiation.

tion, as indicated by the discharge of an electroscope. It appears therefore to be an artificial radioactive substance. Neither burseracin nor oxyburseracin is poisonous; the latter coagulates fresh blood; the coagulum, filtered off and dried, forms an elastic membrane; no coagulum is formed in absence of air; burseracin has these properties in a less degree.

T. E.

Japanese Lacquer. KISABURŌ MIYAMA (*J. Coll. Eng. Tokyo*, 1908, 4, 89—110).—The principal constituent does not contain nitrogen, as supposed by Tschirch and Stevens (Abstr., 1906, i, 31), and is a catechol derivative of the probable composition $C_{34}H_{50}O_4$; the name *urushiol* is now suggested. It is a liquid which cannot be distilled; in the presence of lead oxide, manganese dioxide, &c., it hardens, even when the oxydase (laccase) is absent; it also hardens in the absence of any oxidising agent when heated above 96° . Urushiol gives a green coloration with ferric chloride, and reduces ammoniacal silver solution, but not Fehling's solution. It yields a tetra-acetyl and a tetrabenzoyl derivative, and readily absorbs 8 atoms of bromine; with excess of bromine, a substitution product, $C_{34}H_{42}Br_{12}(OH)_4$, is formed. The best raw lacquer contains about 80—87% of urushiol, 9—12% of moisture, a few per cent. of gum, and rather more than 1% of nitrogenous substances, but inferior (Chinese and Indian) varieties may contain very much less urushiol. The (fermentative) drying at the ordinary temperature consists entirely in the absorption of oxygen, but by drying at a high temperature a partial decomposition takes place. Methods for the analysis of lacquer and for the estimation of urushiol (by precipitation as the barium compound) are described.

G. B.

Decomposition of Amygdalin by Emulsin. KARL FEIST (*Arch. Pharm.*, 1908, 246, 206—209. Compare Caldwell and Courtauld, *Trans.*, 1907, 91, 666, 671; Auld, *Proc.*, 1907, 23, 72; 1908, 24, 97).—The benzaldehydecyanohydrin, formed when amygdalin is decomposed by emulsin at the atmospheric temperature, is a mixture of the racemic and dextro-rotatory forms, and on steam distillation becomes entirely racemised, so that commercial bitter almond oil is always optically inactive. On hydrolysis, the mixture of the *r*- and *d*-forms of the cyanohydrin yields a mixture of *r*- and *l*-forms of mandelic acid. *d*-Benzaldehydecyanohydrin probably has $[\alpha]_D +112^\circ$. It is suggested that by the action of emulsin at low temperatures on prulaurasin, *r*-benzaldehydecyanohydrin could be obtained, and that the *l*ævo-form could be prepared in like manner from sambunigrin.

T. A. H.

Rhamnosides. ERNST SCHMIDT (*Arch. Pharm.*, 1908, 246, 214—224. Compare Abstr., 1904, i, 681).—The author, in conjunction with collaborators, has shown (*loc. cit.*) that sophorin and caper-rutin are identical, and globularia-citrin (Abstr., 1903, ii, 608) possibly identical with rutin. The present paper deals with viola-quercitrin (viola-quercitrin), fagopyrum-rutin, globularia-citrin, and caper-rutin, and shows that the first three are also identical with rutin. The

identity of caper-rutin with rutin is still undecided, since it has been found impossible so far to reconcile a slight difference in melting point between the two substances, but this may be due to traces of impurity in the caper-rutin used. It is shown that viola-rutin, on decomposition by acids, yields 1 mol. each of quercetin, rhamnose, and dextrose, and not, as A. G. Perkin supposed (*Trans.*, 1902, **81**, 478), 2 mols. of dextrose, whence it becomes probable that osyritrin and myrticolorin, which Perkin (*loc. cit.*) showed were identical with viola-rutin, are identical with rutin. Rutin crystallises with $3\text{H}_2\text{O}$, and loses 1 mol. of water slowly at temperatures above 20° and rapidly at 100° , and the remaining 2 mols. at 115° .

T. A. H.

Viola-rutin (Viola-quercitrin). AEMILIUS WUNDERLICH (*Arch. Pharm.*, 1908, **246**, 224—238. Compare preceding abstract).—A detailed account of the isolation of viola-quercitrin from the flowers of *Viola tricolor*, and of the comparison of this glucoside with rutin, is given, resulting in the proof that the two are identical. The flowers also contain salicylic acid, a trace of alkaloid, and a second colouring matter, which is soluble in water, and gives with hydrochloric acid violet, with dilute alkali solutions blue, and concentrated alkali solutions green, colorations.

T. A. H.

Euphorbone. OSKAR EMMERLING (*Ber.*, 1908, **41**, 1373—1378. Compare Paul, *Diss.*, *Berlin*, 1905).—Euphorbone, $\text{C}_{30}\text{H}_{48}\text{O}$, has m. p. $115\text{--}116^\circ$, $[\alpha]_D^{25} + 16.46^\circ$. With benzoic anhydride at 160° , it yields a benzoyl derivative, $\text{C}_{30}\text{H}_{47}\text{O}\cdot\text{COPh}$, m. p. $128\text{--}130^\circ$, which is also formed by the action of benzoyl chloride in the presence of pyridine. The *p*-nitrobenzoyl derivative has m. p. 140° .

The compound combines with bromine vapour, yielding the unstable compound $\text{C}_{30}\text{H}_{48}\text{OBr}_8$, which begins to decompose at 135° . When crystallised from alcohol, it yields the compound $\text{C}_{30}\text{H}_{48}\text{OBr}_4$, m. p. 83° . When boiled with concentrated nitric acid, euphorbone yields a small amount of β -dinitropropane. It is not oxidised by hypobromite.

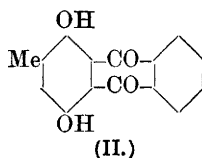
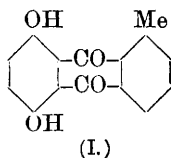
J. J. S.

Compounds from Rhubarb and Allied Substances. OSWALD HESSE (*J. pr. Chem.*, 1908, [ii], **77**, 383—390. Compare this vol., ii, 418).—A number of errors in the previous paper under the same title (*Abstr.*, 1900, i, 40) are now corrected.

Jowett and Potter's statement (*Trans.*, 1902, **81**, 1578) that chrysophanohydroanthrone, the reduction product of chrysophanic acid, is identical with chrysarobin is confirmed. The name chrysophananthranol is preferred for this substance, as it contains the grouping $\begin{array}{c} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{CH} \end{array}$.

Chrysophanic acid has probably the constitution (I), as it gives Bornträger's reaction, as do also emodin, alemodin (aloe-emodin), rhabarberone, physcione, chrysarone, and rhein, whilst methylquinizarin, which does not give this reaction, is considered to

have the constitution (II) (compare Liebermann, Abstr., 1900, i, 355; Tschirch and Christofetti, Abstr., 1905, ii, 851).



Emodin remains unchanged when treated with chromic acid in acetic acid solution, but on reduction with hydriodic acid yields *emodinanthranol*, $C_{15}H_{12}O_4$, which crystallises in light yellow leaflets, m. p. 236° , and gives a brownish-red coloration with alcoholic ferric chloride. The same anthranol is obtained from emodin from rhubarb and from that from *Rhamnus Frangula*.

Reduction of aloe-emodin, m. p. $223-224^\circ$, with hydriodic acid leads to the formation of a *product*, $C_{15}H_{12}O_3$, m. p. 182° , which gives an olive-green coloration with ferric chloride in alcoholic solution, and may be identical with Oesterle's substance obtained by reduction of aloe-emodin with tin and hydrochloric acid (Abstr., 1900, i, 304).

Rhein, $C_{15}H_{10}O_6$, has m. p. $312-316^\circ$ (sublimes); the m. p. $262-265^\circ$ (Abstr., 1900, i, 40) is that of the monoacetyl-derivative. The diacetyl derivative, m. p. 240° (compare Tschirch and Heuberger, Abstr., 1903, i, 107; Tschirch and Edner, Abstr., 1907, ii, 501), contains two free hydroxyls, as it dissolves in 2 mols. of potassium hydroxide in aqueous solution; it is rapidly hydrolysed by excess of alkali. The *sodium* and *potassium*, $C_{15}H_8O_6K_2$, derivatives of rhein are described. When boiled with hydriodic acid, D 1.7, rhein forms a dark mass, from which it is regained unchanged on treatment with boiling acetic acid or acetic anhydride. G. Y.

The Chlorophyll Group. Action of Acids on Chlorophyll. LAD. HILDT, LEON MARCHLEWSKI, and J. ROBEL (*Biochem. Zeitsch.*, 1908, 10, 131—166).—Under the name of chlorophyllan, Hoppe-Seyler described a product obtained by the concentration of an alcoholic extract of chlorophyll, the formation of which, as Tschirch subsequently showed, was due to the presence of plant acids. Schunck and Marchlewski, under the name of phyllogen, described a product obtained by treating an alcoholic extract of chlorophyll with gaseous hydrochloric acid. Later still, Willstätter and Hocheder, under the name of phaeophytin, described a product obtained from chlorophyll by treatment with oxalic acid.

The substances described under these names have been further examined, and the authors come to the conclusion that they are identical products with varying quantities of impurities. The chlorophyllan was purified by repeated solution in chloroform and precipitation by alcohol; the product was not entirely soluble in the first-named solvent, and in this way an impurity could be separated. Nor were the products obtained from different plants always identical, for in some cases the ethereal solution, on shaking

with 15% hydrochloric acid solution, yielded some colouring matter to the acid. As Schunck and Marchlewski have previously shown, phyllogen, on treatment with acids, yields phylloxanthin and phyllocyanin, of which the latter is soluble in 15% hydrochloric acid and the former only in 24% acid. Some of the preparations, which as originally obtained yielded no colouring matter to 15% hydrochloric acid when the ethereal solution was shaken with acid of this strength, could be made to do so after warming for three hours with $\frac{1}{2}$ % oxalic acid solution. Raw chlorophyllan also yields pigment to 5% hydrochloric acid, not, however, the product purified in the manner already described. The conclusions obtained by chemical methods were confirmed by examination of the optical behaviour (absorption spectra) both of the substances themselves and their zinc and copper salts. It is proposed to retain the name chlorophyllan, and to discard the names phyllogen and phaeophytin. S. B. S.

Is Phosphorus an Essential Constituent of Chlorophyllins? M. TSVETT (*Ber. deut. bot. Ges.*, 1908, 26a, 214—220).—The author agrees with Willstätter (Abstr., 1907, i, 71) that chlorophyll does not contain phosphorus, and attributes the presence of phosphorus in the preparations of Stoklasa, Brdlik, and Just (this vol., i, 279) to contamination with colourless lecithins. This is partly due to these authors having extracted their chlorophyll from the aqueous alcoholic solution with benzene, instead of with light petroleum. Experiments by the author's fractional adsorption method are quoted in support of his views. G. B.

Acid Derivatives of Chlorophyllin. M. TSVETT (*Ber.*, 1908, 41, 1352—1354. Compare Abstr., 1906, i, 973; ii, 144; 1907, i, 787, 948).—Willstätter and Hocheder's phaeophytin (Abstr., 1907, i, 784) appears to be a mixture of α - and β -chlorophyllans. J. J. S.

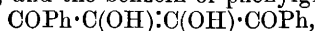
Theory of Mordant Dyes. ALFRED WERNER [with E. THOMANN] (*Ber.*, 1908, 41, 1062—1071).—Liebermann and Kostanecki's rule (Abstr., 1888, 274; 1889, 137, 868) that the oximino- and hydroxyl-groups in compounds which give mordant dyes with basic oxides are in the ortho- or peri-positions, was extended by Möhlau and Steimmig (*Zeitsch. Farb. Text. Chem.*, 1904, 3, 358), who stated that a hydroxyl in the ortho- or peri-position to a chromophore was requisite for such a dye. Tschugaeff (Abstr., 1907, i, 17, 392, 830), from a study of the α -oximino-ketones, drew the conclusion that the mordant properties are due to metallic derivatives having a cyclic complex structure. These conceptions have been extended, and a general theory arrived at. The internally complex salts of acetylacetone (Werner, Abstr., 1901, i, 682; compare Dilthey, 1906, i, 342) (the formula of the platinum salt is now given as $\text{CH} \begin{smallmatrix} \diagup \text{CMe} \cdot \text{O} \\ \diagdown \text{CMe} \cdot \text{O} \end{smallmatrix} \text{Pt} \begin{smallmatrix} \diagdown \text{O} \cdot \text{CMe} \\ \diagup \text{O} \cdot \text{CMe} \end{smallmatrix} \text{CH}$) and the complex salts investigated by Bruni (Abstr., 1904, i, 855) and Ley (Abstr., 1907, i, 301, 302, 730) are all characterised by great stability, sparing solubility in water, and unlikeness to ordinary metallic salts. The

varying colour of such salts is held to be due to the nature of the supplementary valencies of the group united to the metal.

The following additional evidence is adduced. The three $\alpha\gamma$ -diketones, benzoylacetone, dibenzoylmethane, and anisoylbenzoylmethane give with ferric oxide orange-yellow shades, and the conclusion is drawn that they have the complex $\text{CH} \begin{smallmatrix} \text{CR} \cdot \text{O} \\ \text{CR} \cdot \text{O} \end{smallmatrix} \text{M}$ derived from the enolic form, a view supported by the examination of hydroxymethylenecamphor, which gives violet tones.

α -Benzilmonoxime, moreover, has dyeing properties, whereas the γ -compound has not, a result in agreement with the stereochemical hypothesis, and also pointing to the cyclic complexes being six-membered rings. *iso*Nitrosocamphor has no dyeing property. In addition to β -benzildioxime, dimethylglyoxime and methylethylglyoxime give red and orange-red shades with nickel.

Amino-oximes, such as benzenylamino-oxime and *o*- and *p*-tolenyl-amino-oximes, give the same tint with a copper salt, whilst oxalenediamino-oxime gives a much more intense colour; their constitution is given as $\text{CR} \begin{smallmatrix} \text{NH}-\text{O} \\ \text{NH} \cdots \text{M} \end{smallmatrix}$ or $\text{CR} \begin{smallmatrix} \text{N} \cdots \text{O} \\ \text{NH}_2 \cdots \text{M} \end{smallmatrix}$. The hydroxamic acids show analogous behaviour, and the benzoin of phenylglyoxal,



has marked dyeing properties with mordants.

The conclusion drawn from the above facts is that the mordant dyeing properties of chemical compounds depend on the capacity of forming these co-ordinated cyclic complex salts. Compounds which would not be expected to form these complex salts, such as *o*-hydroxybenzylideneacetophenone, which would form an eight-membered ring, have no dyeing function whatever.

W. R.

Theory of Mordant Dyes. CARL LIEBERMANN (*Ber.*, 1908, 41, 1436—1444).—Polemical. A disputation of Tschugaeff's (*Abstr.*, 1907, i, 392, 830) and of Werner's (preceding abstract) criticisms of the author's metallocyclic theory of the constitution of lakes.

C. S.

The Japanese Dyewood "Doss." E. ITO (*J. Coll. Eng. Tokyo*, 1908, 4, 57—62).—*Ilex Mertensii* or "Doss" contains a yellow colouring matter, *dossetin*, $\text{C}_{15}\text{H}_9\text{O}_5$, yellow needles from methyl alcohol, m. p. 271—272°; it can be used with a mordant, but has no great tinctorial value.

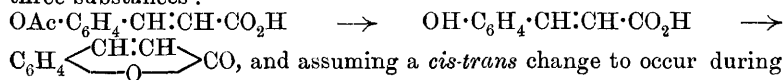
G. B.

Coumarin Derivatives. ALBERT REYCHLER (*Bull. Soc. chim.*, 1908, [iv], 3, 551—556 *).—Ebert's process (*Abstr.*, 1885, 391) for the conversion of coumarin into coumaric acid gives good results when alcohol free from water is employed (compare von Miller and Kinkel, *ibid.*, 1889, 989). Methylcoumaric acid was obtained by the action of methyl iodide on coumarin in presence of sodium ethoxide, and saponification of the methyl methylcoumarate first formed. Using

* and *Bull. Soc. chim. Belg.*, 1908, 22, 177—180.

methyl sulphate in place of methyl iodide, the reaction proceeds more rapidly, but the yield of acid is smaller. If sufficient water is added to the alcohol used, the isomeride of methylcoumaric acid, methylcoumarinic acid, is obtained (Perkin, *Trans.*, 1881, **39**, 409). The methyl methylcoumarinate, formed as an intermediate product in this reaction, on distillation must be partly converted into methyl methylcoumarate, since the distillate on saponification yields some methylcoumaric acid, although the latter is not formed by the action of alcoholic sodium hydroxide on methylcoumarinic acid.

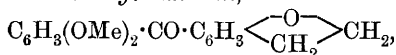
Since salicylic acid boils at 196° and its ethyl ether at 238°, it seems probable that the former has the ketonic-aldehyde structure, whilst the latter is a true phenol ether. Tiemann and Herzfeld's conversion of salicylaldehyde into acetylcoumaric acid (*Abstr.*, 1877, **i**, 708), which may be transformed into coumaric acid and eventually coumarin, is explained by assigning the following formulæ to the last three substances:



the transformation; a similar explanation accounts for Perkin's synthesis of coumarin and for von Miller's conversion of *o*-nitrosalicylaldehyde into the corresponding nitrocoumarin (*loc. cit.*). When the phenolic hydrogen of salicylaldehyde is replaced by an alkyl group, there is less tendency to dehydration, and consequently less tendency to form coumarin derivatives (von Miller, *loc. cit.*). T. A. H.

Elimination of the Methoxy-group. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, **41**, 1327—1329).—It was hoped to obtain by the reduction of leucotrimethylgalloylcoumaran (*Abstr.*, 1907, **i**, 951) an analogous product to that obtained on the reduction of catechin tetramethyl ether (*Abstr.*, 1907, **i**, 334). The coumaran ring is, however, very stable, a compound crystallising from dilute alcohol in long leaflets, *m. p.* 84—85°, and insoluble in alkali, being obtained instead, which is a dimethoxybenzylcoumaran. By the following synthesis of this compound, it has been proved that the methoxy-group in the para-position to the secondary carbinol group has been eliminated during the reduction.

4-Benzoyl-3' : 5'-dimethoxycoumaran,



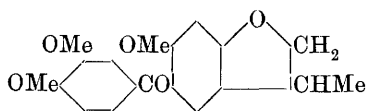
obtained from 3 : 5-dimethoxybenzoyl chloride and coumaran, crystallises from dilute alcohol in short needles, *m. p.* 94—95°, and on reduction with sodium and alcohol gives a *3' : 5'-dimethoxy-4-benzylcoumaran*, $\text{C}_7\text{H}_{15}\text{O}_3$, identical in all respects with the product obtained from leucotrimethoxygalloylcoumaran. W. R.

Studies in the Coumaran Group. I. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, **41**, 1330—1335).—*Ethyl 5-methoxy-2-methylcoumarilate*, $\text{OMe} \cdot \text{C}_6\text{H}_3 \cdot \left\langle \begin{array}{c} \text{O} \\ \text{CMe} \end{array} \right\rangle \text{C} \cdot \text{CO}_2\text{Et}$, is prepared by adding quickly hot methyl sulphate and potassium

hydroxide to a boiling solution of ethyl 5-hydroxy-2-methylcoumarilate (Hantzsch, Abstr., 1887, 282) in alcohol. It is found, in general, that the more energetically the methylation is carried out the better the yield of ether. It crystallises in short, stout needles, m. p. 74—75°. The alkaline filtrate, on acidification, gives 5-methoxy-2-methylcoumarilic acid, which is also easily obtained by hydrolysing the ester with potassium hydroxide; it separates from dilute alcohol in white needles, m. p. 190° (decomp.). Methyl 5-methoxy-2-methylcoumarilate, $C_{12}H_{12}O_4$, crystallises in needle aggregates, m. p. 78°.

When the methoxymethylcoumarilic acid is heated in a retort, carbon dioxide is evolved, and a mixture of unchanged acid and 5-methoxy-2-methylcoumarone, $OMe \cdot C_6H_3 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown CMe \diagup \end{smallmatrix} CH$, distils over, and

are separated by distillation with steam, in which the latter is volatile. The coumarone crystallises in white leaflets, m. p. 58°, b. p. 246°/705 mm., and has an odour resembling that of absinthe. On its repeated reduction in alcoholic solution with sodium, 5-methoxy-2-methylcoumaran, $OMe \cdot C_6H_3 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown CHMe \diagup \end{smallmatrix} CH_2$, is obtained as a colour-

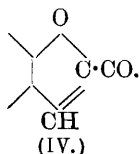
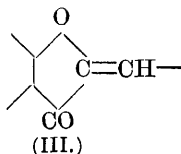
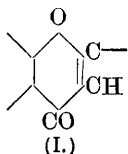


less oil, b. p. 245°/705 mm., and this, on treatment with veratroyl chloride and aluminium chloride in carbon disulphide, leads to the formation of 4-veratroyl-5-methoxy-

2-methylcoumaran, annexed formula, which separates from dilute alcohol in needle aggregates, m. p. 119—120°. The leuco-compound has only as yet been obtained as a viscid, colourless oil. W. R.

Function of the Double Chromophore $CO \cdot C:C$. FELICIA ZWAYER and STANISLAUS VON KOSTANECKI (*Ber.*, 1908, 41, 1335—1341). —Dyes with the double chromophore $CO \cdot C:C$ may be divided in four classes, according to the position of the chromophores, thus: (1) the two chromophores “cyclostatic,” as in hydroxyflavone, I; (2) the two chromophores “streptostatic,” as in hydroxychalkone,

$\begin{smallmatrix} \diagup \diagdown \\ \diagdown CO \cdot CH:CH \diagup \end{smallmatrix}$; (3) “CO cyclostatic,” “C:C streptostatic,” as in oxindogenide, III; (4) “CO streptostatic,” “C:C cyclostatic,” as in hydroxy-1-benzoylcoumarone, IV.



The first class are characterised by their yellow colour and colourless alkyl and acyl derivatives, the second are reddish-yellow, and their alkyl and acyl derivatives are yellow. The colours of the third class are closely related to those of the second class (Klobski and Kostanecki,

Abstr., 1898, i, 371), and both contain "C:C streptostatic." Representatives of the fourth class had not hitherto been prepared, and, as it was of importance from the standpoint of colour that they should be obtained, the investigation was undertaken.

2-Hydroxy-4'-methoxychalkone, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, prepared by condensing salicylaldehyde and *p*-methoxyacetophenone in the presence of 50% sodium hydroxide, crystallises in yellow leaflets, m. p. 148° (decomp.). The sodium salt is orange-red and easily soluble, the acetate, $\text{C}_{18}\text{H}_{16}\text{O}_4$, crystallises in pale yellow leaflets, m. p. 129—130°. When the acetate is treated with 1 mol. of bromine, 2-acetoxy-4'-methoxychalkone dibromide, $\text{C}_{15}\text{H}_{16}\text{O}_4\text{Br}_2$, is formed, which separates from alcohol in white needles, m. p. 123°. This, on treatment with alcoholic potassium hydroxide, leads to the formation of 1-*p*-methoxybenzoylcoumarone, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, which crystallises in white needles, m. p. 103—104°. The same compound is obtained from coumarilic chloride, anisole, and aluminium chloride.

1-*p*-Hydroxybenzoylcoumarone, $\text{C}_{15}\text{H}_{10}\text{O}_3$, prepared from coumarilic chloride, phenol, and aluminium chloride, and hydrolysis of the resulting coumarilic ester by alkali, crystallises from dilute alcohol in short, stout, light yellow needles, m. p. 179—180°. It is therefore more similar in colour to 4-hydroxychalkone (Bablich and Kostanecki, Abstr., 1896, i, 239) and to 4'-hydroxychalkone (Abstr., 1899, i, 704) than to 4'-hydroxyflavone (Abstr., 1900, i, 669). The acetate, $\text{C}_{17}\text{H}_{12}\text{O}_4$, forms white needles, m. p. 116—117°.

[With FRL. M. SZWEJKOWSKA.]—2-Hydroxy-3':4'-dimethoxychalkone, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$, obtained by the condensation of salicylaldehyde with acetoveratrone, forms stout, yellow prisms, m. p. 148°. Its sodium salt is red. 2-Acetoxy-3':4'-dimethoxychalkone dibromide, $\text{C}_{19}\text{H}_{18}\text{O}_5\text{Br}_2$, forms white needles, m. p. 174—175° (decomp.), and is converted by alcoholic potassium hydroxide into 3':4'-dimethoxy-1-benzoylcoumarone, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$, which may also be obtained from veratrole and coumarilic chloride. It forms colourless, well-defined rhombohedra, m. p. 90—91°.

All the compounds described give characteristic colorations with sulphuric acid.

As benzoylphenylacetylene is colourless, the conclusion that all chromophores contain double linkings is strengthened. W. R.

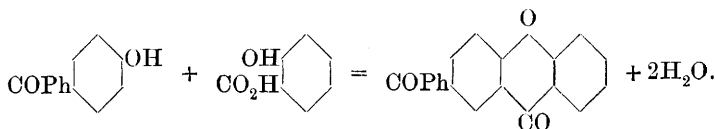
Coumaroneglycol. JOHANNES BOES (*Chem. Zentr.*, 1908, i, 1185; from *Apoth. Zeit.*, 1908, 23, 153).—The action of hypochlorous acid on coumarone gives rise probably to a mixture of isomeric coumarone chlorohydrins; the product, however, when purified from benzene yields a coumarone chlorohydrin, which crystallises in needles, m. p. 123°. This substance, when decomposed in alcoholic solution by means of potassium hydroxide, neutralised with acetic acid, and steam distilled, gives a small quantity of coumaroneglycol, m. p. 151°, which crystallises from benzene. No glycol could be obtained by the oxidation of coumarone by means of potassium permanganate or bleaching powder. J. V. E.

Action of Benzoyl Chloride on Xanthen. J. HELLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1908, 41, 1324—1327).—The conclusion previously drawn that the benzoylcoumaran and benzoylchroman, prepared by the action of the acyl chloride on the cyclic phenol ether in the presence of aluminium chloride, are para-derivatives was not directly proved, because the rupture of the oxygen ring did not take place (*Abstr.*, 1907, i, 950). In order to support this conclusion, the action of the acyl chloride on xanthen has been studied, and, as it is proved directly that substitution occurs in the para-position in this case, the conclusion with regard to the coumaran and chroman derivatives is regarded as resting on a solid basis.

2-Benzoylxanthen, annexed formula, prepared by shaking xanthen, benzoyl chloride, and aluminium chloride in carbon disulphide solution and afterwards leaving it for forty-eight hours, crystallises from a mixture of pyridine and alcohol in white leaflets, m. p. 148°. By reduction of an alcoholic solution with zinc dust and potassium

hydroxide, *leuco-2-benzoylxanthen*, $\text{OH} \cdot \text{CHPh} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained, which crystallises in stout prisms, m. p. 136—137°. Reduction, however, of the benzoyl compound or its leuco-derivative with sodium and alcohol leads to the formation of *2-benzoylxanthen*, $\text{CH}_2\text{Ph} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{C}_6\text{H}_4$, which separates from alcohol in white crystals, m. p. 93—94°.

Oxidation of 2-benzoylxanthen with boiling nitric acid leads to the formation of *2-benzoylxanthenone*, $\text{C}_{20}\text{H}_{12}\text{O}_3$, which crystallises from alcohol in glistening plates, m. p. 146—147°. The constitution of this compound is proved by its preparation from *p*-hydroxybenzophenone and salicylic acid in the presence of acetic anhydride:



W. R.

Tritan Series. HANS VON LIEBIG (*Annalen*, 1908, 360, 128—264).—*Fluorescence and Colour of Organic Substances*.—Whilst many organic substances are coloured and fluorescent, the phenomenon of pleochroism is less common, and all three properties have been observed previously in only one substance, chlorophyll, which in solution has a red fluorescence, and appears green in thin layers, but in thicker layers is green by reflected, red by transmitted, light. The vegetable dyes belong to the aromatic series, and contain commonly two hydroxyls in the meta-position to each other. The frequency with which such dyes occur suggests that they are related to chlorophyll, the more that *m*-dihydroxy-compounds are especially suited for the assimilation of carbon dioxide and oxygen. The simplest

m-dihydroxy-compound, resorcinol, forms fluorescent dyes when heated with dehydrating agents, but the properties of these dyes render them unsuited for the study of the phenomena of colour and fluorescence. On the other hand, many of the dyes formed by condensation of resorcinol with other substances contain a pyrone ring which is itself a chromophore, and therefore disguises the colour and fluorescent properties of the resorcinol grouping. Resorcinol and benzil, however, condense, forming a series of coloured and colourless compounds, the "tritan" (triphenylmethane) derivatives (for the constitution and nomenclature, see Abstr., 1905, i, 781; 1907, i, 45, 930, 1045), which cannot contain a pyrone grouping, and which in consequence of the accumulation of benzene nuclei in the molecule crystallise readily and have convenient solubilities. As the phenyl groups are not chromophoric, the colour and fluorescence of the tritan compounds must be ascribed to the resorcinol portion of the molecule.

Whilst 2:4-dihydroxytritanolactone is colourless and not fluorescent, *m*-tetra-2:4-dihydrotritanol diether and its diacetyl derivative are colourless, but fluoresce blue, and a tetra-acetyl derivative of the triether is blue, but is not fluorescent. Two of the tritanone ethers are red or brown, and have a weak green fluorescence; the monoacetyl derivative of the diether and the penta-acetyl derivative of the triether are yellow and have a strong green fluorescence. *m*-Di-2:4-dihydroxytritanol ether is brown and fluoresces blue in alkaline aqueous, but green in alkaline alcoholic, solution. The solutions of the tritanone-acid-ether derivatives are pleochroic, being blue by reflected, and red by transmitted, light when concentrated, but red only when dilute. Finally, the penta- and hepta-acetyl derivatives of *m*-tetra-2:4-dihydroxytritanol ether (EL, p. 447) exhibit not only colour, pleochroism, and fluorescence as does chlorophyll, but also varying fluorescence. Of the tritan compounds, those with one resorcinol group are colourless and not fluorescent, colour and fluorescence appearing when the molecule contains two resorcinol groups, whilst compounds with four resorcinol groups are pleochroic. It is remarkable that these variations in colour properties depend on the building up of arrangements of carbon, oxygen, and hydrogen atoms without the assistance of nitrogen.

These observations are made the basis of a long discussion of the theory of colour and fluorescence of organic compounds, which leads to the following conclusions:

1. The ultraviolet fluorescence of benzene and its most simple derivative arises from oscillations, probably of electrons, caused by the circular shifting of the double linkings of Kekulé's benzene ring.

2. Persistent fluorescence in the visible spectrum is caused by retardation of the oscillation in two ways. Firstly,

3. by union of the benzene ring with other rings, as in naphthalene and anthracene, which causes usually blue, more seldom yellowish-green, fluorescence; and secondly,

4. by the coupling of the benzene ring with other rings by means of oxygen, sulphur, or nitrogen bridge-atoms, which increases the

intensity and diminishes the rate of the oscillations and causes red, yellow, or green fluorescence.

5. Transient fluorescence may arise from the change of non-benzenoid into benzenoid structures.

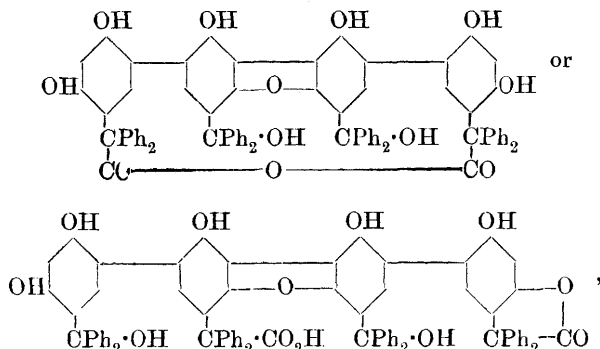
6. True quinones fluoresce in the ultra-violet, and not in the visible spectrum unless benzenoid nuclei are present.

7. There exists only one organic chromophore, the system $\begin{matrix} R & R & R \\ || & || & \\ A_1 & -A_2 & -A_3 \end{matrix}$, in which three singly-linked atoms are each united to another atom by a double bond.

8. This system (7) does not alone suffice to produce colour; there must be present some influence, the nature of the atoms or a cyclic grouping, which causes the three double linkings to assume a given relation to one another.

Derivatives of Tetra-2 : 4-dihydroxytritanol.—The product obtained on fusing benzil with resorcinol contains resorcylic acid, benzoic acid, 2 : 4-dihydroxytritanic acid, resorcinolbenzein, and five coloured substances, which for convenience are termed EU, EL, EK, EN, and EB. Tetraphenyldifuran, previously stated to be a product of the reaction, has now been found to have been formed from resorcinol and a small amount of benzoin. Of the five coloured substances, EU (2^I-acetoxy-*m*-tetra-2 : 6-dihydroxytritanol-6^I2^{II}, 6^{III}2^{IV}-diether-7^{II}7^{III}-anhydride) has been already described (Abstr., 1907, i, 45). The present paper contains an account of the method employed in separating the fusion products and of the remaining four coloured substances. When distilled, these decompose, forming diphenylmethane.

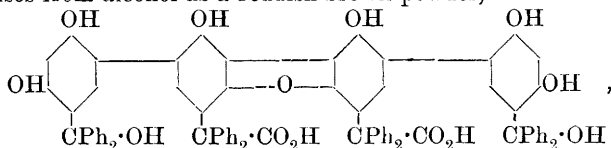
EL (*m*-tetra-2 : 4-dihydroxytritan-1,1,1,1-ol-I,IV-anhydride-6^{II}2^{III}-ether or *m*-tetra-2 : 4-dihydroxytritan-1,1,1,1-ol-II-acid-IV-lactone-6^{II}2^{III}-ether) :



crystallises from toluene as a brownish-red, granular powder, m. p. 250—260°, forms red solutions with green fluorescence, and dissolves in aqueous alkalis, separating immediately as the alkaline salts; these form dark bluish-red aqueous solutions with strong green fluorescence. When boiled with alcoholic potassium hydroxide, EL forms *m*-tetra-2 : 4-dihydroxytritan-1,IV-ol-II,III-acid, $C_{78}H_{56}O_{12}$, which is obtained as a brownish-red powder, soluble in aqueous alkali carbonates. The *hydrochloride*, $C_{78}H_{54}O_{12} \cdot HCl$, formed by heating

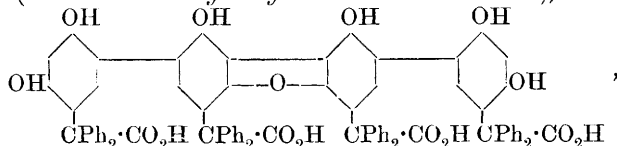
EL with alcoholic hydrogen chloride, is obtained as a brownish-black powder. When heated at 300° , EL loses carbon dioxide and forms a red powder, $C_{76}H_{54}O_8$ or $C_{97}H_{52}O_9$, which is insoluble in alkalis. El-*diacetyl* derivative, $C_{82}H_{58}O_{14}$, m. p. about 140° . The *penta-acetyl* derivative, $C_{88}H_{64}O_{17}$, forms a bluish-red, granular powder, sinters at 170 – 180° , melts slowly, and decomp. about 200° ; the solutions are red with red, or in the presence of ammonia green, fluorescence; by transmitted light, the concentrated solution containing ammonia is green, becoming brown on dilution. The *hepta-acetyl* derivative, $C_{92}H_{70}O_{20}$, a dark red, granular powder, m. p. above 300° , forms similar fluorescent solutions. The *triacetyl* derivative, $C_{84}H_{60}O_{15}$, yellowish-brown powder, m. p. about 210° , is not fluorescent. The colourless *tetra-acetyl*, m. p. about 190° , and *hexa-acetyl*, $C_{90}H_{62}O_{16}$, m. p. about 240° , derivatives are described.

EK (m-*Tetra-2 : 4-dihydroxytritan-III,III-ol-I,IV-acid-6^{II2III}-ether*) crystallises from alcohol as a reddish-brown powder,



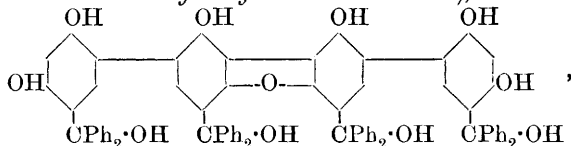
forms red solutions with green fluorescence, and is soluble in alkalis. The *diacetyl*, $C_{82}H_{60}O_{15}$, m. p. 180° , and *penta-acetyl*, $C_{88}H_{64}O_{17}$, m. p. 180 – 190° , derivatives are not fluorescent.

EN (m-*Tetra-2 : 4-dihydroxytritanic acid-6^{II2III}-ether*),



crystallises from alcohol as a black powder with green lustre, forms red solutions with green fluorescence, and dissolves readily in cold alkalis. The *triacetyl* derivative, $C_{86}H_{60}O_{17}$, is a brownish-red powder, and forms red solutions, which are not fluorescent. The *tetra-acetyl* derivative, $C_{88}H_{60}O_{17} \cdot 2C_2H_6O$, is a yellow, granular powder, m. p. 118 – 125° . The *penta-acetyl* derivative, $C_{90}H_{66}O_{20} \cdot 2H_2O$, m. p. about 210° , forms solutions with red fluorescence.

EB (m-*Tetra-2 : 4-dihydroxytritanol-6^{II2III}-ether*),



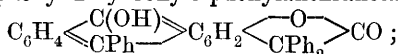
crystallises from alcohol or acetone-glacial acetic acid as a red powder, sinters about 140° , and dissolves in hot aqueous alkalis to a red solution with slight green fluorescence. The *diacetyl* derivative, $C_{80}H_{58}O_{12}$, white powder, sinters at 130° . The *tetra-acetyl* derivative, $C_{84}H_{64}O_{15}$, white powder, m. p. about 125° . The *penta-acetyl* derivative, $C_{86}H_{64}O_{15}$, reddish-brown powder, m. p. about 220° , forms red solutions

which are not fluorescent. When heated at 200—220°, EB loses water, forming a *product*, $C_{70}H_{50}O_8$, which is obtained as a red powder, m. p. 180—190°. Reduction of EB with zinc dust and glacial acetic acid leads to the formation of a *product*, $C_{76}H_{54}O_8$, which is obtained as a white powder, m. p. 164—165°.

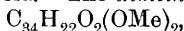
Combination of Benzil with Phenol.—[With PAUL KEIM.]—Bistrzycki's method of forming tritan derivatives by condensation of benzil with phenols in presence of stannic chloride is not applicable to the formation of resorcinol derivatives, but benzil and resorcinol condense readily when heated alone or with sodium sulphate, or when brought together in cold concentrated sulphuric acid, forming 2:4-dihydroxytritanolactone. Whilst 2:4-dihydroxydiphenylacetic acid closely resembles triphenylacetic acid, 2:4-dihydroxytritanic acid differs markedly in its behaviour, and hence it was thought possible that the condensation product of resorcinol and benzil is 3:5-dihydroxytritanolactone. It is now found, however, that 2-hydroxytritanolactone (Abstr., 1907, i, 930, 1045), formed from benzil and phenol, behaves in the same manner as the dihydroxylactone, the constitution of which as 2:4-dihydroxytritanolactone is therefore confirmed. *p*-Hydroxytritanolactone is not formed even in traces by the condensation of benzil with phenol. The following details are new.

On hydrolysis with alcoholic potassium hydroxide, methyl *o*-methoxytritanate yields *o*-methoxytritanic acid and a *substance*, $C_{42}H_{38}O_5$, m. p. 106°, which is considered to be a molecular compound of *o*-methoxytritanic acid and *o*-methoxytritanol. A similar molecular compound was previously obtained by hydrolysis of methyl 2:4-dimethoxytritanate (Abstr., 1905, i, 781).

The substance, m. p. 239°, formed together with *o*-hydroxytritanolactone by condensation of benzil with phenol (Abstr., 1907, i, 931), is the lactone of diphenyl-2-hydroxy-9-phenylanthranolacetic acid,



the *dipotassium*, $C_{34}H_{22}O_4K_2 \cdot H_2O$, and *potassium*, $C_{34}H_{23}O_4K \cdot 6H_2O$, salts are described. The lactone is not reduced by zinc dust and glacial acetic acid, but on treatment with chromic acid in glacial acetic acid solution yields a *product*, $C_{34}H_{24}O_5$, which separates from alcohol in colourless crystals, m. p. 148—149°, and gives a greenish-yellow coloration with sulphuric acid. The *dimethyl* derivative,

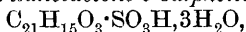


formed by the action of methyl sulphate on the dipotassium salt, crystallises in white needles, m. p. 187°, and remains unchanged when boiled with alcoholic potassium hydroxide. The *trinitro*-compound, $C_{34}H_{19}O_3(NO_2)_3$, forms a yellow powder, m. p. 120—130°.

2:4-Dihydroxytritanolactonesulphonic Acid.—[With OTTO HERR.]—*o*-Hydroxytritanolactone, *p*-hydroxytritanic acid, and 2:4-dihydroxytritanolactone ether do not form sulphonic acids. On the other hand, 2:4-dihydroxytritanolactone and its methyl ether, methyl 4-hydroxy-2-methoxytritanate-4-ether, $O[C_6H_3(OMe) \cdot CPh_2 \cdot CO_2Me]_2$, 2:4-dimethoxytritanic acid and its methyl ester, and *o*-methoxytritanic acid readily form sulphonic acids when shaken with cold concentrated sulphuric acid. The ethoxy-derivatives react even more easily than do

the methoxy-compounds. The carbmethoxy-group, $\cdot\text{CO}_2\text{Me}$, is split off in the sulphonation of the methyl esters. The 2:4-dimethoxytritanol-sulphonic acid, formed in this manner from methyl 2:4-dimethoxytritanate, is isomeric with that prepared directly from 2:4-dimethoxytritanol. 2-Hydroxy-4-acetoxytritanolactone is also readily sulphonated; the reaction takes place most easily with the tetramethyl ether of 2:4-dihydroxytritanolactone ether, which forms a tetrasulphonic acid, whereas the other compounds form monosulphonic acids only.

2-Hydroxy-4-methoxytritanolactone-5-sulphonic acid,



crystallises in needles, m. p. $160-161^\circ$; the ammonium salt crystallises in leaflets. The corresponding 4-ethoxysulphonic acid ($3\text{H}_2\text{O}$) forms needles, m. p. $140-141^\circ$, and yields a colourless ferric salt which gradually becomes red. 2:4-Dimethoxytritanol-5-sulphonic acid, $\text{C}_{21}\text{H}_{19}\text{O}_3 \cdot \text{SO}_3\text{H}$, crystallises in needles, m. p. $207-208^\circ$, becoming red, decomp. about 330° . The isomeric 6-sulphonic acid, leaflets, m. p. 221° , gives a violet coloration with ferric chloride. 2:4-Dimethoxytritanolether-tetrasulphonic acid, $\text{O}[\text{C}_6\text{H}(\text{OMe})(\text{SO}_3\text{H})_2 \cdot \text{CPh}_2 \cdot \text{OH}]_2$, gives a green fluorescence with an excess of alkali, but not a coloration with ferric chloride; the ammonium salt, needles. Ammonium o-methoxytritanol-3-sulphonate, m. p. 180° (decomp.). o-Ethoxytritanol-6-sulphonic anhydride, $\text{OEt} \cdot \text{C}_6\text{H}_3 \cdot \text{SO}_2 \cdot \text{CPh}_2 \cdot \text{O}$, forms colourless needles, m. p. 100° (decomp.).

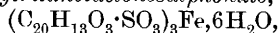
2:4-Dihydroxytritanolactonesulphonic acid, $\text{C}_{20}\text{H}_{13}\text{O}_3 \cdot \text{SO}_3\text{H} \cdot 2\text{H}_2\text{O}$, crystallises from benzene in rectangular prisms, m. p. 132° , decomp. about 180° , gives a reddish-violet coloration with ferric chloride, and liberates mineral acids, including sulphuric acid, from their salts. Eighteen salts of this acid are described. The acid remains unchanged when fused with potassium hydroxide or boiled with alcoholic potassium hydroxide in a reflux apparatus. On treatment with acetyl chloride, the monoammonium salt yields ammonium 2-hydroxy-4-acetoxytritanolactonesulphonate, $\text{C}_{22}\text{H}_{15}\text{O}_4 \cdot \text{SO}_3\text{NH}_4$, needles, m. p. $235-236^\circ$, and ammonium 2-hydroxy-4-acetoxysulphotritanate, leaflets, m. p. 233° if slowly, or $200-230^\circ$ if quickly, heated. The product, $\text{C}_{22}\text{H}_{17}\text{O}_5 \cdot \text{SO}_3\text{NH}_4$, obtained on successive treatment of 2-hydroxy-4-acetoxytritanolactone with sulphuric acid and ammonium sulphate, crystallises in leaflets, m. p. $235-236^\circ$. Sodium 2-hydroxy-4-acetoxytritanolactonesulphonate, $\text{C}_{22}\text{H}_{15}\text{O}_4 \cdot \text{SO}_3\text{Na}$, m. p. $124-125^\circ$.

2:4-Dihydroxytritanol-5-sulphonic acid, $\text{C}_{19}\text{H}_{15}\text{O}_3 \cdot \text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, formed by oxidation of the lactonesulphonic acid, separates from ether in colourless crystals, m. p. 186° .

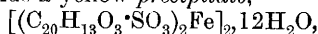
The sulphonic acid group is split off from 2:4-dihydroxytritanolactonesulphonic acid by the action of acetyl chloride on the monoammonium salt or of methyl sulphate on the potassium salt, 2:4-dihydroxytritanolactone being formed. In presence of potassium hydroxide, the action of methyl sulphate leads to the formation of methyl 2:4-dimethoxytritanate, 2:4-dimethoxytritanic acid, and 2-hydroxy-4-methoxytritanolactone. When treated with bromine in glacial acetic acid solution, the sodium sulphonate is converted into Kohlhaas's bromo-compound, m. p. 184° (*Diss.*, Marburg, 1905).

The action of nitric acid on the potassium sulphonate in glacial acetic acid solution leads to the formation of *nitro-2:4-dihydroxytritanolactone*, m. p. 183°, which forms an *acetyl* derivative, m. p. 159°. *Dinitro-2:4-dihydroxytritanol*, yellow crystals, m. p. 175—176°, is formed by the action of concentrated nitric acid on 2:4-dihydroxytritanolactone or its potassium sulphonate. On reduction with tin and hydrochloric acid in glacial acetic acid solution, it yields the *diamino*-compound, crystallising in blue leaflets, m. p. 200°.

Ferric 2:4-dihydroxytritanolactonesulphonate,



forms colourless leaflets, which become blue, but retain the same composition on treatment with oxygen in cold ethereal solution. When heated, the blue crystals commence to decompose at 180°, evolving carbon monoxide. When treated with oxygen in aqueous solution, the ferric sulphonate yields a yellow *precipitate*,



and a free sulphonic acid.

G. Y.

[Preparation of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid.] KALLE & Co. (D.R.P. 192075).—*Carbomethoxy-o-thio-benzoic acid*, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, yellowish-white crystals, m. p. 213°, is produced by condensing chloroacetic and thiosalicylic acids or their esters in alkaline solutions. 3-Hydroxy-(1)-thionaphthen-

2-carboxylic acid (*thioindoxylcarboxylic acid*), $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$

or $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$, is produced together with 3-hydroxy-(1)-

thionaphthen by heating the preceding acid with sodium hydroxide and water at 170—200° and acidifying the fusion with dilute mineral acid. When distilled in steam, the carboxylic acid loses carbon dioxide

and furnishes 3-hydroxy-(1)-thionaphthen, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CH}$ or

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CH}_2$.

G. T. M.

Quinine Salts of Anhydromethylenecitrylsalicylic Acid.

LUIGI SANTI (*Boll. chim. farm.*, 1908, 47, 219—224).—The author has prepared the two following quinine salts of anhydromethylenecitrylsalicylic acid, $\text{CH}_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{smallmatrix} \text{C}(\text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$ (compare

Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1907, i, 1045):

(1) the *normal* salt, $\text{C}_{20}\text{H}_{24}\text{O}_9\text{N}_2$, $\text{C}_{21}\text{H}_{16}\text{O}_{11}$, and (2) the *basic* salt, $2\text{C}_{20}\text{H}_{24}\text{O}_9\text{N}_2$, $\text{C}_{21}\text{H}_{16}\text{O}_{11}$. The first of these salts is of therapeutical interest, as it contains a greater proportion of salicylic acid than any of the ordinary pharmaceutical preparations containing both salicylic acid and quinine.

T. H. P.

Solubilities of True and False Tannates of Quinine. F.

MURARO (*Gazzetta*, 1908, 38, i, 427—430; *Boll. chim. farm.*, 1908, 47, 255—258).—The author has determined the solubilities in water and dilute hydrochloric acid at 37° of the two true tannates of quinine

having the composition (1) $C_{20}H_{24}O_2N_2 \cdot C_{14}H_{10}O_9 \cdot 4H_2O$ and (2) $2C_{20}H_{24}O_2N_2 \cdot 3C_{14}H_{10}O_9 \cdot 8H_2O$, and of the false tannate (3) $2(C_{20}H_{24}O_2N_2 \cdot H_2SO_4) \cdot 5C_{14}H_{10}O_9 \cdot 14H_2O$. These solubilities are as follows: In water, (1) 0%, (2) 0%, (3) 0.313%. In 0.1% hydrochloric acid, (1) 0.984%, (2) 1.210%, (3) 0.847%, corresponding respectively with 0.443%, 0.448%, and 0.195% of quinine. In 0.3% hydrochloric acid, (1) 3.656%, (2) 4.756%, and (3) 1.560%, corresponding respectively with 1.645%, 1.760%, and 0.359% of quinine.

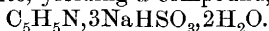
The two true tannates tend to liberate free tannic acid, and thus form more highly basic tannates, whilst the opposite is the case with the false tannate (3). Thus, when the last is washed for a long time with water, its composition becomes nearly that required by the formula $2(C_{20}H_{24}O_2N_2 \cdot H_2SO_4) \cdot 7C_{14}H_{10}O_9 \cdot 22H_2O$. T. H. P.

Ephedrine and ψ -Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1908, 246, 210—214. Compare Abstr., 1904, i, 769; 1906, i, 602).—It has been suggested previously (*loc. cit.*) that when ephedrine is heated with hydrochloric acid an equilibrium mixture of ephedrine and ψ -ephedrine is formed. In the present paper, the validity of this view is established by the observation that each of these two substances can be converted into the equilibrium mixture, whence it appears certain that ephedrine and ψ -ephedrine are geometrical, not structural, isomerides. An attempt to form ψ -ephedrine from ephedrine by heating the latter at 213° , resulted in the partial decomposition of the base into methylamine and the isomeride of cinnamyl alcohol already obtained by Miller from ephedrine by a less direct method (Abstr., 1903, i, 110). A small amount of ψ -ephedrine is also formed in this reaction. T. A. H.

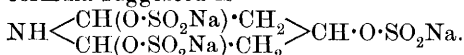
Preparation of Morphine Alkyl Bromides. J. D. RIEDEL (D.R.-P. 191088. Compare Abstr., 1906, i, 530).—The morphine alkyl bromides may be conveniently prepared by the interaction of the corresponding alkyl chlorides and hydrobromic acid or a soluble bromide. This double decomposition may be effected in aqueous alcoholic or acetone solutions. Morphine ethyl bromide and the corresponding methyl bromides were obtained in this manner.

G. T. M.

Pyridine. HANS TH. BUCHERER and JULIUS SCHENKEL (*Ber.*, 1908, 41, 1346—1352).—Körner's formula for pyridine represents this compound as containing the grouping $X \cdot N \cdot CH \cdot X$, characteristic of Schiff's bases. According to Miller, the latter unite with sodium hydrogen sulphite. It is shown that pyridine also combines with sodium hydrogen sulphite, yielding a compound,



Substituted pyridines appear to react in a similar manner. The constitutional formula suggested is



The compound is prepared by boiling pyridine for twenty-four to thirty hours with a 40% sodium hydrogen sulphite solution, neutralising care-

fully with sodium carbonate, adding the requisite amount of barium iodide solution, filtering, evaporating the filtrate under reduced pressure, and precipitating with 96% alcohol. When rapidly heated, it decomposes at 235°, but when slowly heated it begins to decompose at 115°. It is readily decomposed by alkalis, yielding ammonia and a product with a characteristic odour. After warming for half an hour with alkali, the whole of the sulphur is present in the form of sulphite.

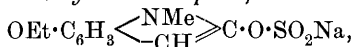
J. J. S.

Glycine and Indole Derivatives. OSCAR HINSBERG (*Ber.*, 1908, 41, 1367—1373).—The reaction between aromatic amines and glyoxal sodium hydrogen sulphite (Abstr., 1888, 372; 1892, 1458; 1895, i, 144; 1898, i, 275; Pschorr and Kultz, Abstr., 1905, i, 236; Pschorr and Karo, Abstr., 1906, i, 887) has been extended by the inclusion of the more complex amines: *p*-aminophenol, *p*-phenylenedimethyldiamine, 6-aminoquinoline, and methyl-*p*-phenetidine. Of these, only the last named yields an indolesulphonic acid; aminophenol and *p*-phenylenedimethyldiamine yield glycine derivatives, and aminoquinoline yields the compound $C_2H_2(O\cdot SO_2Na)_2(NH\cdot C_9H_6N)_2$.

The formation of this compound indicates that in the reaction between an amine and the sodium bisulphite derivative of glyoxal, the first stage consists in the replacement of one or both of the hydroxyl groups by a substituted amino-group. If the resulting product is sparingly soluble, it can be isolated, but if readily soluble it loses sodium hydrogen sulphite, and by a process of molecular rearrangement yields a glycine derivative, or ring formation occurs and an indole derivative is formed. The compounds described previously as indolesulphonic acids are now regarded as esters derived from sulphurous acid and hydroxyindoles, for example, $X\begin{smallmatrix} <NH \\ >CH \end{smallmatrix}C\cdot O\cdot SO_2H$.

Phenylglycine is formed together with anilinoacetanilide by the action of aniline on glyoxal sodium bisulphite. *p*-Aminophenol and the bisulphite compound yield *p*-hydroxyanilinoaceto-*p*-hydroxyanilide, $OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot OH$, and *p*-hydroxyphenylglycine (Vater, Abstr., 1884, 1144). The former compound crystallises from dilute alcohol in colourless needles, m. p. 190°. The hydrochloride crystallises from water in colourless needles. Tetramethyldiaminodiphenylglycineamide, $NMe_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot NMe_2$, obtained from *p*-aminodimethylaniline and glyoxal sodium bisulphite, crystallises from dilute alcohol in glistening plates, m. p. 173°. It yields a soluble hydrochloride and a reddish-yellow nitrosoamine.

Sodium 5-ethoxy-1-methylindole sulphite,



forms colourless crystals, and on hydrolysis yields 5-ethoxy-1-methylindole, $OEt\cdot C_6H_3\begin{smallmatrix} <NMe \\ >CH_2 \end{smallmatrix}CO$, which crystallises from water in stout prisms, m. p. 94°. The nitrosoamine, $C_{11}H_{13}O_2N$, has m. p. 254° (decomp.).

Aminoquinoline glyoxaline bisulphite, $C_{20}H_{18}O_6N_4S_2$, forms an

intensely yellow, crystalline powder with acidic properties, and is readily hydrolysed to sulphurous acid, glyoxal, and aminoquinoline.

J. J. S.

Action of Ethylamine on Isatin. C. HASLINGER (*Ber.*, 1908, 41, 1444—1453. Compare *Abstr.*, 1907, i, 975).—The author has prepared other derivatives of the compounds obtained by the action of ethylamine on isatin. In addition to the three classes of compounds described previously, a fourth has been obtained by treating 5:7-dibromoisatin in chloroform and alcohol with 33% aqueous ethylamine, whereby 5:7-dibromoisatin ethylamine, $C_6H_2Br_2 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \cdot ONH_3Et$, is precipitated, which separates from chloroform in violet-brown needles, readily changes to 5:7-dibromo-3-ethyliminoisatin by loss of water, and loses ethylamine by keeping or by treatment with dilute acids or alkalis.

By passing sulphur dioxide into an alcoholic suspension of 3-ethyliminoisatin, a white, crystalline substance is obtained, $C_{10}H_{12}O_4N_2S$, which readily loses sulphurous acid, regenerating 3-ethyliminoisatin, to which is ascribed the constitution $N \begin{smallmatrix} \text{C} \cdot OH \\ \diagup \quad \diagdown \\ C_6H_4 \end{smallmatrix} > C(O \cdot SO_2H) \cdot NH_3Et$, or of the corresponding internal salt. 5-Bromo- and 5:7-dibromo-3-ethyliminoisatins yield analogous compounds. In addition to the preceding, compounds have been obtained containing one molecule of water more; they yield isatin under the influence of acids or alkalis, and consequently have constitutions such as $N \begin{smallmatrix} \text{C} \cdot OH \\ \diagup \quad \diagdown \\ C_6H_4 \end{smallmatrix} > C(OH) \cdot O \cdot SO_2 \cdot NH_3Et$. Members of both of these classes of sulphurous acid derivatives become brown and then violet on heating, resembling 3-ethyliminoisatin in this respect.

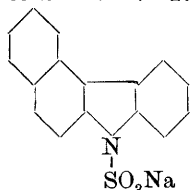
By prolonged treatment with alcoholic potassium hydroxide, the red crystals of the potassium salt of 3-ethyliminoisatin are changed to colourless crystals of a potassium salt, from which hydrochloric acid liberates a substance, $C_8H_8O_2N_2$, m. p. 343° , which is identical with benzoylenecarbamide (2:4-dioxy-1:3-quinazoline) (compare *Abt.*, *Abstr.*, 1889, 609; Gabriel and Colman, *Abstr.*, 1905, i, 944). By distillation with lime, it yields *o*-aminobenzonitrile. In a similar manner, 5-bromo-3-ethyliminoisatin is converted into 6-bromo-2:4-dioxy-1:3-quinazoline, $C_8H_5Br \begin{smallmatrix} CO \cdot NH \\ \diagup \quad \diagdown \\ NH \cdot CO \end{smallmatrix}$, m. p. 354° . C. S.

[A Double Salt from 8-Hydroxy-7-iodoquinoline-5-sulphonic Acid.] RICHARD GRIESE (D.R.-P. 190956).—The double ammonium salt, $C_9NH_4I(OH) \cdot SO_3 \cdot NH_4 \cdot NH_4I$, obtained in orange-yellow leaflets by concentrating an aqueous solution containing molecular proportions of ammonium 7-iodo-8-hydroxyquinoline-5-sulphonate and ammonium iodide, is very soluble in water or alcohol and decomposes at 225° . This compound has the germicidal properties of its components; dilute hydrochloric acid decomposes it, liberating iodine. These properties render it valuable in therapeutics. G. T. M.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. V. HANS TH. BUCHERER and FRANZ SEYDE (*J. pr. Chem.*, 1908, [ii], 77, 403—413. Compare *Abstr.*, 1903, i, 627; 1904, i, 309, 395; 1905, i, 48, 585; 1907, i, 509).—In analogy to the formation of aryl-substituted β -naphthylamines by the sulphite method, the immediate product of the action of phenylhydrazine on β -hydroxynaphthoic acid is *s*-phenyl- β -naphthylhydrazine,



The reaction, however, does not stop here; the product undergoes a further series of changes, leading to the formation of a sodium sulphamate of 1:2-phenonaphthacarbazole, which has the annexed constitution. It is considered that the *s*-hydrazine undergoes oxidation



to the azo-compound, which combines with sodium hydrogen sulphite, forming the intermediate substance, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NPh}\cdot\text{SO}_3\text{Na}$, the last stage in the reaction being an intramolecular condensation of this, resembling Fischer's indole synthesis. A small amount of the sodium sulphamate undergoes intramolecular change into a sodium sulphonate,

whilst by a side-reaction small quantities of the *s*-hydrazine form 2-amino-1-o-aminophenylnaphthalene by the benzidine change. When heated above its m. p., the dihydrochloride of the diamino-compound decomposes, forming hydrogen chloride, ammonium chloride, and 1:2-phenonaphthacarbazole, thus confirming the ortho-position of the two amino-groups. The same products are obtained, but in smaller yields, from phenylhydrazine and β -naphthol. The interaction of *p*-tolylhydrazine and β -hydroxynaphthoic acid takes place in the same manner.

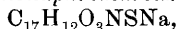
Sodium 1:2-phenonaphthacarbazole-N-sulphonate, $\text{C}_{16}\text{H}_{10}\text{O}_3\text{NSNa}$, is obtained in a 70% yield from β -hydroxynaphthoic acid, but only a 45% yield from β -naphthol; it crystallises from alcohol in white needles, is soluble in water, and when heated with mineral acid yields 1:2-phenonaphthacarbazole, m. p. 135° (Japp and Maitland, *Proc.*, 1901, 186). The *barium* salt, $(\text{C}_{16}\text{H}_{10}\text{O}_3\text{NS})_2\text{Ba}$, is crystalline.

On recrystallisation of the preceding sodium salt from alcohol, a small amount of an insoluble salt is obtained, which on acidification yields a *sulphonic acid*, $\text{C}_{16}\text{H}_{11}\text{O}_3\text{NS}$, crystallising in needles; it forms an aqueous solution with blue fluorescence, and couples with *p*-nitrodiazobenzene chloride, forming a weak violet *dye*.

2-Amino-1-o-aminophenylnaphthalene, $\text{C}_{16}\text{H}_{14}\text{N}_2$, crystallises from alcohol in glistening prisms, m. p. 154° , decomp. $160\text{--}200^\circ$, forming 1:2-phenonaphthacarbazole, is insoluble in water, forms a blue fluorescent solution in alcohol, and when diazotised and coupled with R-salt in alkaline solution forms a red *dye*, which dyes wool red, or un mordanted cotton a weak red.

On prolonged heating with dilute sodium hydrogen sulphite on the water-bath, hydrazobenzene is converted into benzidine.

Sodium 2'-methyl-1:2-phenonaphthacarbazole-N-sulphonate,

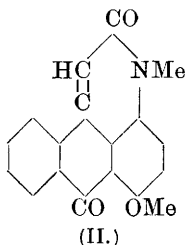
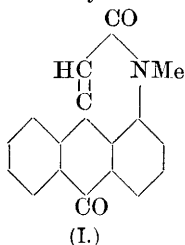


prepared from *p*-tolylhydrazine and β -hydroxynaphthoic acid, crystallises in needles, and when heated with hydrochloric acid yields 2'-methyl-

1:2-phenonaphthacarbazole, m. p. 181° (Ullmann, Abstr., 1904, i, 776). G. Y.

Preparation of Anthraquinone Derivatives Containing Nitrogen. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 192201)—The acyl derivatives of the secondary aminoanthraquinones undergo condensation, forming cyclic compounds containing a new nitrogen ring.

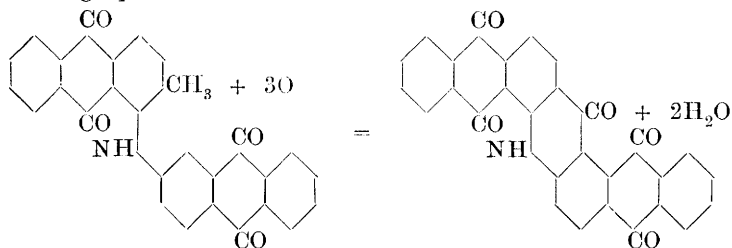
1-Acetylmethylaminoanthraquinone, when heated with aqueous sodium hydroxide, furnishes a condensation product (I) crystallising from pyridine in yellow needles :



4-Nitro-1-acetylmethylaminoanthraquinone, when boiled for three hours with sodium and methyl alcohol, furnishes the compound (II). The patent contains references to thirteen other condensation products of this type, derived from derivatives of methylaminoanthraquinone.

G. T. M.

[Oxidation of 2-Methyl-1:2'-dianthraquinonylamine.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 192436. Compare Abstr., 1907, i, 226).—A mixture of 2-methyl-1:2'-dianthraquinonylamine and litharge was added to fused potassium hydroxide at 170° , when an orange-red oxidation product was obtained in accordance with the following equation :



The compound crystallises from nitrobenzene, and in the hyposulphite vat it furnishes a violet colouring matter which dyes cotton in this shade, the dyed fabric slowly acquiring by oxidation of the violet vat dye a very fast, orange-red colour.

G. T. M.

New Synthesis of *iso*Oxazoles. JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1908, 41, 1252—1260).—*iso*Oxazoles are formed by the action of red fuming nitric acid on γ -diketones. The reaction has been studied in the case of ethyl β -diacetylsuccinate, which, as

Knorr's investigations have shown, reacts both as a γ -diketone and a β -ketonic acid ester. By the action of red fuming nitric acid at a temperature of 0° to 5° , *ethyl 5-methylisooxazole-3:4-dicarboxylate* is formed, crystallising in large, colourless plates, m. p. $56-57^{\circ}$. On hydrolysis in the cold with the calculated quantity of normal alkali,

5-methylisooxazole-3:4-dicarboxylic acid, $O < \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \text{N} = \text{C} \cdot \text{CO}_2\text{H} \end{array}$, is formed,

and crystallises in colourless needles, m. p. 183° . The *silver* salt is a colourless powder, which decomposes explosively when heated; the *copper* salt forms a green powder. When heated under special precautions at 185° , carbon dioxide is eliminated from the dicarboxylic acid, forming *5-methylisooxazole*, $O < \begin{array}{c} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{CH} \end{array}$, b. p. $103-105^{\circ}/20 \text{ mm.}$ E. F. A.

Preparation of *p*-Nitrodiphenylamine and its Derivatives. FRITZ ULLMANN (D.R.-P. 193448).—4-Nitrodiphenylamine-2-sulphonic acid and its substitution products readily lose their sulphonic group on heating with mineral acid at temperatures not exceeding 100° .

4-Nitro-3'-amino-4'-methylidiphenylamine-2-sulphonic acid, when warmed with 5 parts of 80% sulphuric acid at $80-90^{\circ}$ for ten to twenty minutes, dissolves completely, and 4-nitro-3'-amino-4'-methylidiphenylamine, yellowish-red needles from toluene, m. p. 168° , is precipitated on the addition of alkali.

4-Nitrophenyl-4'-tolylamine, yellow needles from benzene, m. p. 139° , is similarly obtained from the sulphonic acid produced by condensing *p*-nitrochlorobenzene-*o*-sulphonic acid and *p*-toluidine.

3'-Chloro-4-nitrodiphenylamine, yellow leaflets, m. p. 129° , is prepared from 3-chloro-4-nitrodiphenylamine-2-sulphonic acid, and 4-nitro-4-hydroxydiphenylamine, reddish-brown needles with steel-blue reflex, is obtained from the corresponding sulphonic acid. G. T. M.

Preparation of *p*-Aminodiphenylamine and its Derivatives. FRITZ ULLMANN (D.R.-P. 193351).—4-Aminodiphenylamine-2-sulphonic acid and its derivatives have now been found to undergo hydrolysis when heated with mineral acids at temperatures not exceeding 100° .

4-Amino-2-sulphodiphenylamine-2'-carboxylic acid, produced by heating anthranilic and *p*-chloronitrobenzene-*o*-sulphonic acids in aqueous sodium acetate and then reducing the nitro-compound obtained, is a colourless compound, forming soluble alkali salts and yielding 4-amino-diphenylamine-2-carboxylic acid on heating at 100° with 60% sulphuric acid. The final product forms yellow needles, m. p. 200° , rapidly turning blue on exposure to air. G. T. M.

[2-Amino-4:6-diacetyldiaminophenol.] LEOPOLD CASSELLA & Co. (D.R.-P. 191862).—2-Amino-4:6-diacetyldiaminophenol is prepared by reducing the nitro-compound obtained by treating 2:4'-diacetyldiaminophenol with excess of nitrous acid; it gives rise to a *diazo*-derivative, which readily couples to form azo-dyes with the sulphonic acids of the naphthols, aminonaphthols, dihydroxynaphthalenes, and naphthylenediamines. G. T. M.

Preparation of 6-Amino-2:4-diacetyldiaminophenol. LEOPOLD CASSELLA & Co. (D.R.-P. 191549).—6-Nitro-2:4-diacetyldiaminophenol, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{NHAc})_2 \cdot \text{OH}$, yellow needles, m. p. 215° , is prepared by adding sodium nitrite solution to a thin paste of 2:4-diacetyldiaminophenol in dilute hydrochloric acid. On reduction with zinc dust and dilute sulphuric acid, this nitro-compound yields the *sulphate* of 2:4-diacetyl-2:4:6-triaminophenol; the free base forms colourless needles, m. p. 205° , which are readily soluble in water or alcohol and furnish a sparingly soluble diazo-derivative. G. T. M.

β -Phenylbenzylhydrazine. GIACOMO PONZIO and E. VALENTE (*Atti R. Accad. Sci. Torino*, 1908, 43, 378—386 *).—Schlömman (Abstr., 1893, i, 452) described β -phenylbenzylhydrazine as a solid, m. p. 155° , but, on repeating his experiments, the authors were only able to obtain α -phenylbenzylhydrazine and benzaldehydephenylbenzylhydrazone, $\text{CH}_2\text{Ph} \cdot \text{NPh} \cdot \text{N} \cdot \text{CHPh}$ (compare Minunni, Abstr., 1893, i, 97). Attempts to prepare β -phenylbenzylhydrazine by the interaction of benzyl bromide and phenylhydrazine (compare Fischer and Knoevenagel, Abstr., 1887, 932) in cold ethereal solution resulted in the formation of phenyldibenzylazonium bromide, $\text{NH}_2 \cdot \text{NBrPh}(\text{CH}_2\text{Ph})_2$, and benzaldehydephenylbenzylhydrazone. When, however, phenylbenzylpiperazone is hydrolysed by means of 20% hydrochloric acid (compare Michaelis and Hermens, Abstr., 1892, 1494; 1893, i, 370), it yields succinic acid and β -phenylbenzylhydrazine hydrochloride. The authors' results show that the compound obtained by Paal and Bowedig (Abstr., 1892, 1455), and described as phenyldi-*o*-nitro-dibenzylhydrazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, is really *o*-nitrobenzaldehyde-*o*-nitrophenylbenzylhydrazone,

$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2.$$

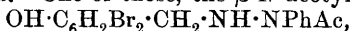
Phenyldibenzylazonium bromide, $\text{NH}_2 \cdot \text{NBrPh}(\text{CH}_2\text{Ph})_2$, crystallises from alcohol in shining, white prisms, m. p. 143° .

β -Phenylbenzylhydrazine, $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{NHPh}$, is obtained as a light, colourless oil, which oxidises rapidly in the air to benzylazobenzene, $\text{CH}_2\text{Ph} \cdot \text{N} \cdot \text{NPh}$. Its *hydrochloride*, $\text{C}_{13}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$, forms white laminæ, m. p. 193 — 195° . T. H. P.

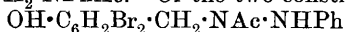
Capacity of Acyl Groups for Migration in the Molecules of Organic Compounds. KARL AUWERS and H. DANNEHL (*Annalen*, 1908, 360, 1—10. Compare Abstr., 1904, i, 736, 1051, 1053, 1054; 1907, i, 928).—This work was undertaken with the object of determining the capacity of acyl groups for intramolecular migration, and the conditions by which such migration is influenced. The present paper deals with the action of phenylhydrazine and its acyl derivatives on the acetate and benzoate of dibromo-*o*-hydroxybenzyl bromide, which leads to the formation of acyl-derivatives of the disubstituted *s*-hydrazine, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \underset{\alpha}{\text{NH}} \cdot \underset{\beta}{\text{NHPh}}$. In the nomenclature of the acyl derivatives, the two nitrogen atoms are distinguished as α -N and β -N, as indicated in the above formula.

* and *Gazzetta*, 1908, 38, i, 519—526.

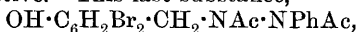
It is found that the product of the action of phenylhydrazine on dibromo-*o*-acetoxybenzyl bromide, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$, contains two *N*-acetyl compounds. One of these, the β -*N*-acetyl derivative,



is formed also from dibromo-*o*-hydroxybenzyl bromide and *as*-acetylphenylhydrazine, $\text{NH}_2\cdot\text{NPhAc}$. Of the two constitutions,



and $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{NHAc}$, the former is ascribed to the second product, which is therefore the α -*N*-acetyl derivative, as the two isomerides when boiled with acetic anhydride yield the same triacetyl derivative, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NAc}\cdot\text{NPhAc}$, formed also by the action of acetic anhydride on the parent *s*-hydrazine and the *NN*-diacetyl derivative. This last substance,



is formed by the action of acetyl chloride on the *s*-hydrazine or its β -*N*-acetyl, but not the α -*N*-acetyl, derivative in cold pyridine solution, or by heating dibromo-*o*-acetoxybenzyl bromide with *as*- or *s*-acetylphenylhydrazide at 120—130°.

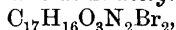
Somewhat different results are obtained with dibromo-*o*-benzoxybenzyl bromide. The action of phenylhydrazine on this leads to the formation of only one product, the α -*N*-benzoyl derivative,



The isomeride, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NPhBz}$, is prepared by the action of *as*-benzoylphenylhydrazide on dibromo-*o*-hydroxybenzyl bromide. Moreover, the product of the action of *as*-acetylphenylhydrazide on dibromo-*o*-benzoxybenzyl bromide is the α -*N*-acetyl-*o*-benzoyl derivative, $\text{OBz}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NAc}\cdot\text{NHPh}$. This substance is insoluble in alkalis, as is also the triacetyl derivative, whereas those compounds which contain a free hydroxyl are soluble.

It has been shown previously that an acetyl group attached to a phenolic oxygen atom may undergo transmigration to the first or second atom of a side-chain; the present results have extended this transmigration to the third atom. On what influences the differences observed in the behaviour of the acetyl and benzoyl groups depend remains for further investigation, as does also the question whether the transmigration of the benzoyl group is under all conditions limited to the second atom of the neighbouring side-chain.

s-Phenyldibromo-*o*-hydroxybenzylhydrazine, $\text{C}_{13}\text{H}_{12}\text{ON}_2\text{Br}_2$, prepared by heating 2 mols. of phenylhydrazine with 1 mol. of dibromo-*o*-hydroxybenzyl bromide in benzene solution, crystallises from alcohol in colourless needles, m. p. 163—164°. The α -*N*-acetyl derivative, $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2\text{Br}_2$, crystallises from alcohol in white plates, m. p. 183°, and is sparingly soluble in cold alcohol. The β -*N*-acetyl derivative forms white needles, m. p. 129—130°, and is readily soluble in alcohol. The two monoacetyl derivatives form mixed crystals, m. p. 134—136°. The *di*-*N*-acetyl derivative,



crystallises from alcohol in prismatic needles, m. p. 224°. The *triacetyl* derivative, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2\text{Br}_2$, forms glistening needles, m. p. 143—145°.

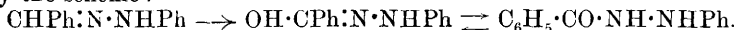
If the product obtained by heating phenylhydrazine and dibromo-

o-hydroxybenzyl bromide [sic] is treated with alkalis, there are obtained, in addition to the mixed crystals of the monoacetyl derivatives which form the chief product, small amounts of acetylphenylhydrazide, *s*-phenyldibromo-*o*-hydroxybenzylhydrazine, and a substance, $C_{22}H_{18}O_3N_2Br_4$, m. p. 240° , which must be formed by the introduction of an acetyl and two bromohydroxybenzyl groups into phenylhydrazine.

The α -*N*-benzoyl derivative, $C_{20}H_{16}O_2N_2Br_2$, crystallises in prismatic needles, m. p. 218 — 219° . The β -*N*-benzoyl derivative forms white prisms, m. p. 163 — 164° . The α -*N*-acetyl-*o*-benzoyl derivative,

$C_{22}H_{18}O_3N_2Br_2$, crystallises from alcohol in white needles, m. p. 190 — 191° , and remains unchanged on prolonged boiling with acetic acid. G. Y.

Action of Nitrobenzene on Aldehydephenylhydrazones in the Light. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 369—374).—The reaction occurring between benzaldehydephenylhydrazone and nitrobenzene under the influence of light is quite similar to that between aldehydes and nitrobenzene (compare Ciamician and Silber, *Abstr.*, 1906, i, 10), the hydrazone undergoing oxidation and the nitrobenzene reduction. Under these conditions, the oxidation products of benzaldehydephenylhydrazone are totally different from those obtained by the ordinary methods of oxidation; the main product is β -benzoylphenylhydrazine, and the change is represented by the scheme:



The reaction is complicated by the partial hydrolysis of the phenylhydrazone into aldehyde and phenylhydrazine, which react with the nitrobenzene and with its products of reduction. Other compounds isolated were benzaldehyde, benzoic acid, nitrosobenzene, benzylideneaniline, benzene, nitrogen, and a base giving a hydrochloride, m. p. 191° , which yields quinone when oxidised with chromic acid.

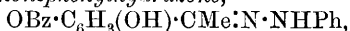
When heated together on a water-bath in the dark, benzaldehydephenylhydrazone and nitrobenzene react slowly, giving products different from those obtained under the action of light.

T. H. P.

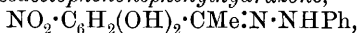
Hydrazones of Aromatic Hydroxyketones. Alkali-insoluble Phenols. II. HENRY A. TORREY and H. B. KIPPER (*J. Amer. Chem. Soc.*, 1908, 30, 836—861).—In an earlier paper (*Abstr.*, 1907, i, 325) attention has been drawn to the insolubility of certain phenolic compounds in aqueous alkali hydroxides, and suggestions have been put forward in explanation of this behaviour. The work has been continued, particularly with reference to the phenylhydrazones and similar derivatives of resacetophenone and resodiacetophenone. These compounds are arranged in two groups, according to their solubility in alkali hydroxides. The following substances are soluble: Resacetophenone-phenylhydrazone, semicarbazone, and monoazine derivative; resodiacetophenone monophenylhydrazone, and bisazine derivative; and nitroresacetophenonephenylhydrazone. The following are

insoluble: Phenylhydrazones of paeonol, 4-acetyl- and 4-benzoyl-resacetophenone, and 4-acetyl- and 4-benzoyl-resodiacetophenone; bisphenylhydrazones of resodiacetophenone and its 4-methyl ether, and of dibenzoylresorcinol, dibenzoylquinol, and bromoresodiacetophenone; bis-*p*-bromophenylhydrazone of resodiacetophenone, condensation product of benzidine and resodiacetophenone, and dianilinomonoazine derivative of resodiacetophenone. A discussion is given of the cause of the difference in solubility of these compounds, but no satisfactory explanation is at present available. In general, it may be said that the insolubility is due to the combined influence of a large group, such as $\cdot\text{CH}:\text{N}\cdot\text{NHPh}$ or $\cdot\text{CMe}:\text{N}\cdot\text{NHPh}$, in the ortho-position to the hydroxyl group and a carbon-containing group elsewhere in the ring, but whether it is due to an actual change in structure is not yet known. All the phenols which are insoluble in aqueous solutions of alkali hydroxide are readily soluble in alcoholic solutions, and can be reprecipitated by mineral acids.

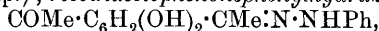
The following compounds are described: *Resacetophenonephenylhydrazone 4-methyl ether*, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CMe}:\text{N}\cdot\text{NHPh}$, m. p. 108°; *4-benzoylresacetophenonephenylhydrazone*,



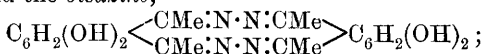
m. p. 181—182°; *4-acetylresacetophenonephenylhydrazone*, m. p. 127—128°; *nitroresacetophenonephenylhydrazone*,



m. p. 232—234° (decomp.); *resacetophenonesemicarbazone*, m. p. 214—220° (decomp.); *resodiacetophenonephenylhydrazone*,



m. p. 233° (decomp.); *bisphenylhydrazone of resodiacetophenone 4-methyl ether*, $\text{NHPh}:\text{N}:\text{CMe}\cdot\text{C}_6\text{H}_2(\text{OH})(\text{OMe})\cdot\text{CMe}:\text{N}\cdot\text{NHPh}$, m. p. 245—246° (decomp.); *2:4-diacetylresodiacetophenone*, m. p. 120°; *2:4-dibenzoylresodiacetophenone*, m. p. 118—119°; *4-acetylresodiacetophenonephenylhydrazone*, m. p. 214—215°; *resodiacetophenone bis-*p*-bromophenylhydrazone*, m. p. 270—271° (decomp.); *bromoresodiacetophenonebisphenylhydrazone*, which decomposes at 215—220°; *resodiacetophenonemonoazine*, $\text{N}_2[\cdot\text{CMe}\cdot\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{COMe}]_2$, its *dianilino*-derivative, and the *bisazine*,



and a condensation product of benzidine (2 mols.) with resodiacetophenone (2 mols.).

The supposed dibenzoylresacetophenonephenylhydrazone, m. p. 183°, described previously (*loc. cit.*), is really the phenylhydrazone of the monobenzoyl derivative.

Experiments were carried out on the action of *m*-nitrobenzoyl chloride on diacetylquinol and diacetylresorcinol in presence of condensing agents, but in no case did the nitrobenzoyl group enter the ring, it merely replaced one or both of the acetyl groups.

E. G.

Action of α -Benzoylphenylhydrazine on Halogen Derivatives of Quinones. WILLIAM MCPHERSON and WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1908, 30, 816—822).—It has been shown by

McPherson (Abstr., 1896, i, 127) that α -acylphenylhydrazines condense smoothly with benzoquinones and naphthaquinones to form hydrazones. The action of α -benzoyl- α -naphthylhydrazine on quinones has been studied by McPherson and Gore (Abstr., 1901, i, 572). A preliminary paper on the action of acylphenylhydrazines on the halogen derivatives of the quinones has already been published (McPherson and Fischer, Abstr., 1900, i, 411). This work has been continued, and it has been found that the reaction takes place in three different ways. (1) Condensation with the formation of hydrazones; the experiments which have been carried out indicate that this occurs only in the case of the monohalogen derivatives of the quinones. (2) One of the hydrogen atoms of the hydrazine molecule, together with one of the hydrogen atoms of the quinone, may be removed by the oxidising action of a second molecule of the quinone. Thus with trichloroquinone the following action takes place: $C_6H_5 \cdot NAc \cdot NH_2 + O = C_6Cl_3O_2 \cdot NH \cdot NAcPh + H_2O$. (3) One of the hydrogen atoms of the hydrazine may combine with a chlorine atom of the quinone with elimination of hydrogen chloride; thus with tetrachloroquinone the reaction is as follows: $C_6Cl_4O_2 + NPhAc \cdot NH_2 = C_6Cl_3O_2 \cdot NH \cdot NPhAc + HCl$.

Chlorobenzoquinonebenzoylphenylhydrazone, $C_6H_3ClO_2 \cdot N \cdot N BzPh$, m. p. 172.5° , forms yellow crystals, and on hydrolysis with sulphuric acid yields *benzeneazo-o-chlorophenol*, m. p. 86° , identical with the product of the action of diazobenzene chloride on *o*-chlorophenol.

Benzeneazo-o-chlorophenyl benzoate, $OBz \cdot C_6H_3Cl \cdot N \cdot N Ph$, obtained by the action of benzoyl chloride on *benzeneazo-o-chlorophenol*, m. p. 109° , forms reddish-yellow needles, and is also produced when an ethereal solution of chloroquinonebenzoylphenylhydrazone is heated with anhydrous potassium hydroxide. When *o*-chlorobenzoquinone is warmed with a solution of α -benzoylphenylhydrazine sulphate in glacial acetic acid, *benzeneazo-o-chlorophenol sulphate*, m. p. $188-190^\circ$ (decomp.), is produced, and forms dark red, silky needles. E. G.

Action of Diphenylhydroxyacetic Acid on Dimethylcarbamide. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 311—314).—The action of hydroxydiphenylacetic acid on *s*-dimethylcarbamide yields a compound identical with that obtained by Biltz (this vol., i, 218) by the interaction of benzil and *s*-dimethylcarbamide, and described by that author as 4:5-diphenyl-1:3-dimethylglyoxalone-4:5-oxide. This compound is hence a hydantoin derivative of the formula $CO \begin{smallmatrix} \nwarrow NMe \cdot CPh_2 \\ \nearrow NMe \cdot CO \end{smallmatrix}$, and owes its formation to the glycol formed initially undergoing the pinacol transformation, the group $-CPh(OH) \cdot CPh(OH)-$ passing first into $-CPh_2 \cdot C(OH)_2-$ and ultimately into $-CPh_2 \cdot CO-$. T. H. P.

The Constitution of the Products obtained by the Action of Substituted Carbamides on Benzil, and New Methods for the Preparation of 5:5-Diphenylhydantoins. HEINRICH BILTZ and CHAIM RIMPEL (*Ber.*, 1908, 41, 1379—1393. Compare this vol., i, 218).—The products obtained by the condensation of benzil and

s-dialkylcarbamides are now regarded as substituted hydantoin and not as glycol oxides, for example, the product from dimethylcarbamide as $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CPh}_2 \\ \text{NMe} \cdot \text{CO} \end{smallmatrix}$ and not as $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CPh} \\ \text{NMe} \cdot \text{CPh} \end{smallmatrix} \text{O}$. One reason for this change is that the same products are formed when benzoic acid is fused with dialkylcarbamides, and a second is the behaviour of the compounds towards alkalis. The condensation products from benzil and dialkylcarbamides are insoluble in alkalis, but condensation products in which there is the grouping $\text{CO} \cdot \text{NH} \cdot \text{CO}$ are readily soluble; the alkali salts thus formed react with methyl or ethyl sulphate, yielding *N*-alkylated derivatives. The hydrolysis of 5:5-dialkylhydantoins to the corresponding hydantoic acid has not been accomplished.

A third argument in favour of the new formulæ is found in their behaviour towards oxidising agents. Glyoxalones react readily with chromic acid, yielding diacylated carbamides; both 4:5-diphenylglyoxalone and its glycol yield dibenzoyldimethylcarbamide, whereas the anhydride of the glycol yields no trace of this oxidation product and hence presumably contains a different grouping, namely, the hydantoin. The hydantoin constitution is also supported by the behaviour of the acetyl derivatives.

A simple method of obtaining these hydantoins is by boiling alcoholic solutions of benzil, substituted benzils, or other α -diketones with carbamide or monoalkyl carbamides in the presence of sodium or potassium hydroxide. Quantitative yields of pure product are obtained when the solution is diluted with water, filtered, and saturated with carbon dioxide. Dialkylated carbamides under similar conditions yield diphenyldialkylglyoxalone glycols, whereas benzoic acid and carbamides do not react.

5:5-Diphenylhydantoin, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CPh}_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, prepared by the action of alcoholic potassium hydroxide on the diphenylglyoxalone glycol, crystallises from alcohol and has m. p. 286° . It is not affected by concentrated nitric acid or chromic anhydride. It yields a *monoacetyl* derivative, $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2$, which crystallises from dilute alcohol in rectangular plates, m. p. $215\text{--}217^\circ$. 5:5-Diphenyl-3-methylhydantoin, obtained by the action of methyl sulphate on a solution of the diphenylhydantoin in sodium hydroxide, is identical with the product obtained by condensing benzil with methylcarbamide (this vol., i, 218). The corresponding *ethyl* derivative, $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$, crystallises in compact, transparent rhombohedra, m. p. 155° .

5:5-Di-*p*-bromophenylhydantoin, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{C}_6\text{H}_4\text{Br})_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, is obtained as a by-product in the bromination of diphenylglyoxalone in acetic acid solution; it is also formed by the action of alcoholic potassium hydroxide on dibromodiphenylglyoxalone glycol or its ethers, or by condensing dibromobenzil and carbamide with alcoholic potash. It crystallises from alcohol in well-developed rhombohedra, m. p. 310° (corr.), and undergoes but slight decomposition when distilled under atmospheric pressure. It yields a *diacetyl* derivative, $\text{C}_{19}\text{H}_{14}\text{O}_4\text{N}_2\text{Br}_2$,
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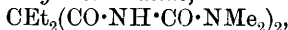
m. p. 187°, which is readily hydrolysed by water to the *monoacetyl* derivative, $C_{17}H_{19}O_3N_2Br_2$, m. p. 230°.

Dibenzoyldimethylcarbamide, $C_{17}H_{16}O_3N_2$, obtained by oxidising 4:5-diphenyl-1:3-dimethylglyoxalone or its glycol, crystallises from alcohol in plates, m. p. 162—163°.

When 5:5-diphenyl-1:3-dimethylhydantoin is boiled with an acetic acid solution of chromic anhydride, the chief product is 1-*formyl*-5:5-*diphenyl*-3-*methylhydantoin*, $C_{17}H_{14}O_3N_2$, m. p. 162—163°, together with 5:5-diphenyl-3-methylhydantoin. J. J. S.

Preparation of 5:5-Dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 193446).—The tetra-substituted diureides of the dialkyl malonic acids, $CX_2(CO \cdot NH \cdot CO \cdot NR_2)_2$, where R is an alkyl or acyl group, are converted into dialkylbarbituric acids by the action of acid condensing agents.

Diethylmalonyltetramethyldicarbamide,



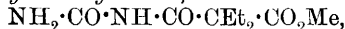
white crystals, m. p. 158°, and *diethylmalonyltetraethyldicarbamide*, needles, m. p. 123—126°, are obtained by condensing diethylmalonyl chloride with *as*-dimethyl- and *as*-diethyl-carbamide respectively; the corresponding diphenyldimethyldiureide melts at 172°. These diureides, when heated with acids or zinc chloride, furnish 5:5-diethylbarbituric acid. G. T. M.

[Preparation of Barbituric Acid and its 5-Mono- and Di-alkyl Derivatives.] C. F. BOEHRINGER and SÖHNE (D.R.-P. 193447).—The diureides of the half acid esters of malonic and alkylmalonic acids, having the general formula $CO \begin{smallmatrix} \diagup CR'R'' \cdot CO_2R''' \\ \diagdown NH \cdot CO \cdot NH_2 \end{smallmatrix}$, where R' and R'' are either hydrogen or an alkyl group, and R''' is an alkyl group, have the property of condensing with alkaline agents to form barbituric acid and its 5-alkyl derivatives.

Ethyl malonylureide, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot CO_2Et$, prisms, m. p. 128°, obtained by the interaction of carbamide (2 mols.) and ethyl malonyl chloride, furnishes sodium barbiturate and alcohol on treatment with cold dilute aqueous sodium hydroxide.

Ethyl ethylmalonylureide, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CHEt \cdot CO_2Et$, m. p. 133°, gives rise to 5-ethylbarbituric acid (m. p. 191°).

Ethyl diethylmalonylureide, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CEt_2 \cdot CO_2Et$, m. p. 85°, and *methyl diethylmalonylureide*,



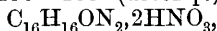
m. p. 115°, both serve for the production of 5:5-diethylbarbituric acid, and the formation of this substance is induced either by ammonia or trisodium phosphate in aqueous solution. G. T. M.

Transformations of Amino-ketones. SIEGMUND GABRIEL [with ALBERT LIECK] (*Ber.*, 1908, 41, 1127—1156. Compare this vol., i, 181, 274).—When α -aminoketones are liberated from their salts, they undergo oxidation and condensation, yielding disubstituted pyrazines, thus: $4X \cdot CO \cdot CH_2 \cdot NH_2 + O_2 \rightarrow 2N \begin{smallmatrix} \diagup CH \cdot CX \\ \diagdown CX \cdot CH \end{smallmatrix} N + 6H_2O$.

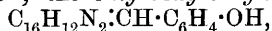
This change has been thoroughly investigated, but whether the reaction takes place in two phases, namely, first condensation and then oxidation, or in one phase, namely, condensation of the two molecules as a result of oxidation, is still uncertain. Braun and V. Meyer (Abstr., 1888, 1093) have studied previously the action of alkalis on α -aminoacetophenone hydrochloride, but repetition of their work has shown that several of their statements are incorrect. The highly reactive secondary base, diphenacylamine, $\text{NH}(\text{CH}_2\cdot\text{COPh})_2$, has been obtained by the action of ammonia on bromoacetophenone, and its chemical properties studied.

Diphenyldihydropyrazine, $\text{N} \begin{smallmatrix} \text{CH}_2\cdot\text{CPh} \\ \text{CPh}\cdot\text{CH}_2 \end{smallmatrix} \text{N}$, is formed when a solution of α -aminoacetophenone hydrochloride is neutralised with sodium hydroxide, sodium carbonate, or ammonia; it crystallises in orange-yellow, rhombic leaflets, m. p. $166-167^\circ$, and is converted, when boiled with hydrochloric acid, into α -aminoacetophenone. It undergoes oxidation when heated in the air at 100° , or when its alcoholic solution is boiled, yielding diphenylpyrazine, m. p. 194° (compare Harries and Gollnitz, Abstr., 1904, i, 427).

α -Aminoacetophenone hydrochloride yields, on treatment with an excess of alkali, a compound which is probably *anhydrobisphenacylamine*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{COPh}$; it crystallises in colourless, hexagonal leaflets, m. p. $130-133^\circ$ (decomp.); the *nitrate*,



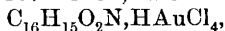
crystallises in microscopic prisms, m. p. about $112-113^\circ$ (decomp.); the *benzylidene* derivative, $\text{C}_{16}\text{H}_{14}\text{ON}_2\cdot\text{CHPh}$, crystallises in small, colourless prisms, m. p. $163-164^\circ$. The parent substance loses water when it is heated alone or in acid solution, being converted into *bisanhydrophenacylamine* (4-amino-3:5-diphenylpyrrole?), $\text{C}_{16}\text{H}_{14}\text{N}_2$, crystallising in flat, hexagonal plates or rhombohedra, m. p. $178-179^\circ$; the *platinichloride*, $(\text{C}_{16}\text{H}_{14}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in flat, orange-red needles, which do not melt below 230° ; the *hydriodide*, $\text{C}_{16}\text{H}_{14}\text{N}_2\cdot\text{HI}$, crystallises in white, pointed needles, sintering above 200° , m. p. 220° (decomp.); the *nitrate* forms glistening needles, decomposing at $182-183^\circ$; the *hydrochloride* crystallises in long, flat, colourless needles; the *benzoyl* derivative, $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Bz}$, crystallises in white prisms, m. p. $218-219^\circ$; the *o-hydroxybenzylidene* derivative,



crystallises in long, glistening, yellowish-green prisms, which sinter at 140° , m. p. 143° (decomp.); the *benzylidene* derivative, $\text{C}_{23}\text{H}_{18}\text{N}_2$, forms large, yellow, pointed prisms, which sinter at 140° , m. p. $144-145^\circ$ (decomp.); it readily oxidises in the presence of benzaldehyde, yielding a *substance*, $(\text{C}_{23}\text{H}_{17}\text{N}_2)_2$, which crystallises in long, flat, reddish-brown needles with a dark brown, metallic reflex, m. p. 310° , and forming a bluish-violet liquid. Bisanhydrophenacylamine, when heated with hydriodic acid and red phosphorus, is converted into the *hydriodide* of a *base*, $\text{C}_{16}\text{H}_{15}\text{ON}\cdot\text{HI}$; it melts and decomposes at 175° , forming an emerald-green liquid.

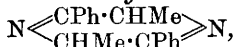
α -Bromoacetophenone is converted by aqueous ammonia into diphenyldihydropyrazine, diphenacylamine, and traces of diphenylpyrazine.

Diphenacylamine, $\text{NH}(\text{CH}_2\cdot\text{COPh})_2$, obtained by treating its hydrochloride with sodium acetate, forms small, red crystals, which sinter at about 60° , m. p. $74-75^\circ$; the *hydrochloride*, $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}\cdot\text{HCl}$, forms silvery leaflets, m. p. 235° (decomp.); the *platinichloride*, $(\text{C}_{16}\text{H}_{15}\text{O}_2\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in brown, rhombic leaflets or needles decomposing at $187-188^\circ$; the *aurichloride*,



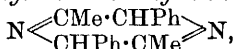
crystallises in flat needles and scales, m. p. $168-169^\circ$ (decomp.); the *picrate* forms long prisms, m. p. $170-171^\circ$ (decomp.); the *nitroso-derivative*, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}\cdot\text{NO}$, crystallises in glistening, yellow leaflets, m. p. 90° .

α -Aminopropiophenone hydrochloride, when treated with an equivalent amount of potassium hydroxide in aqueous solution, is converted into 3:6-diphenyl-2:5-dimethyl-2:5-dihydropyrazine,



crystallising in short, lemon-yellow prisms, which sinter at 94° , m. p. $99-100^\circ$; the *hydrochloride*, $\text{C}_{18}\text{H}_{18}\text{N}_2\cdot\text{HCl}$, forms brownish-red, hexagonal plates, m. p. $167-168^\circ$; the *oxalate*, $\text{C}_{18}\text{H}_{18}\text{N}_2\cdot\text{C}_2\text{H}_2\text{O}_4$, crystallises in brownish-red needles, m. p. 182° (decomp.). The free base readily oxidises in the air, forming 3:6-diphenyl-2:5-dimethylpyrazine (compare Kolb, Abstr., 1896, i, 576); the compound, m. p. $125-126^\circ$, incorrectly described by Behr-Bregowski (Abstr., 1897, i, 458) as having the composition $\text{C}_{18}\text{H}_{18}\text{ON}_2$, is undoubtedly diphenyldimethylpyrazine. 3:6-Diphenyl-2:5-dimethyl-2:5-dihydropyrazine is converted by boiling hydrochloric acid partly into α -aminoacetophenone, but principally into α -amino- α -phenylacetone; the *platinichloride* of the latter, $(\text{C}_9\text{H}_{11}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6$, forms brownish-yellow prisms, m. p. 192° (compare Kolb, *loc. cit.*).

α -Amino- α -phenylacetone hydrochloride is converted by aqueous ammonia into 3:6-diphenyl-2:5-dimethyl-3:6-dihydropyrazine,

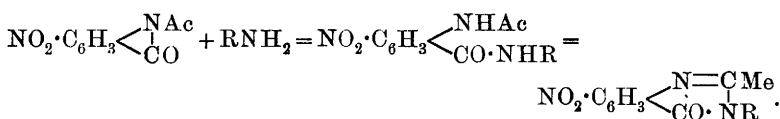


crystallising in small, pale yellow needles, sintering at 95° , m. p. about 140° (in an evacuated capillary tube); the *hydrochloride*, $\text{C}_{18}\text{H}_{18}\text{N}_2\cdot\text{HCl}$, crystallises in small, lemon-yellow, rhombic plates, m. p. 147° .

The free base rapidly oxidises in the air, forming 3:6-diphenyl-2:5-dimethylpyrazine. The compound described by Kolb (*loc. cit.*) as diphenyldimethyldihydropyrazine is probably slightly impure diphenyldimethylpyrazine.

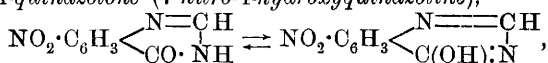
W. H. G.

Quinazolones. XX. Certain 7-Nitro-2-methyl-4-quinazolones from 4-Nitroacetantranil. MARSTON TAYLOR BOGERT and WILLIAM KLABER (*J. Amer. Chem. Soc.*, 1908, 30, 807-816).—An account of the synthesis of 7-nitro-2-methyl-4-quinazolones has been given by Bogert and Steiner (Abstr., 1905, i, 945) and Bogert and Seil (Abstr., 1906, i, 712). The present investigation is an extension of this work. The reaction between 4-nitroacetantranil and primary amines is expressed as follows:



In some cases the intermediate amide was isolated. The primary amines employed were ammonia, methylamine, *n*-propylamine, benzylamine, β -naphthylamine, aniline, and *p*-anisidine. All these substances condensed smoothly and gave good yields.

7-Nitro-4-quinazoline (7-nitro-4-hydroxyquinazoline),



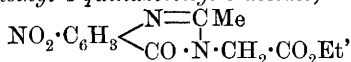
m. p. 276° (corr.), obtained from 4-nitro-2-aminobenzoic acid and formamide, crystallises in long, slender, yellow needles.

7-Nitro-2-methyl-4-quinazoline has m. p. 287—290° (corr.), and when oxidised with chromic acid yields a crystalline substance, m. p. about 327° (uncorr.). The potassium and silver salts of the quinazoline are described. 7-Nitro-2:3-dimethyl-4-quinazoline has m. p. 151—152° (corr.), and is nearly colourless. 7-Nitro-2-methyl-3-*n*-propyl-4-quinazoline, m. p. 140° (corr.), forms colourless needles. 7-Nitro-3-phenyl-2-methyl-4-quinazoline, m. p. 209° (corr.), crystallises in colourless, diamond-shaped plates. 7-Nitro-3-benzyl-2-methyl-4-quinazoline, m. p. 131—132° (corr.), forms yellow cubes; its hydrochloride has m. p. 229—230° (corr.). 7-Nitro-3-*p*-anisyl-2-methyl-4-quinazoline, m. p. 228° (corr.), crystallises in faintly yellow, lustrous scales. 7-Nitro-3- β -naphthyl-2-methyl-4-quinazoline, m. p. 218—219° (corr.), forms colourless needles.

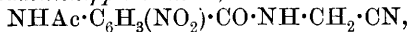
7-Amino-2-methyl-4-quinazoline (7-amino-4-hydroxy-2-methylquinazoline), m. p. 311° (corr.), obtained by reducing the corresponding nitro-compound, forms long, silky, colourless needles. 7-Nitro-3-amino-2-methyl-4-quinazoline, m. p. 223° (corr.), prepared by the action of hydrazine hydrate on 4-nitroacetanthranil, crystallises in pale yellow needles. By the action of phenylhydrazine on this compound, a substance, m. p. 230° (uncorr.), is produced, and forms colourless, feathery needles. 7-Nitro-3-acetyl-amino-2-methyl-4-quinazoline, m. p. 233° (corr.), crystallises in short, colourless prisms; its phenylhydrazone has m. p. 315° (corr.). The corresponding diacetyl derivative, m. p. 132° (corr.), forms pale yellow plates.

7:7'-Dinitro-2:2'-dimethyl-4:4'-diketotetrahydro-3:3'-diquinazoly], $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{N}=\text{C} \text{Me} \\ \diagup \text{CO} \cdot \text{N} \end{smallmatrix} \text{---} \begin{smallmatrix} \text{C} \text{Me} \cdot \text{N} \\ \diagup \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NO}_2$, m. p. 337.5° (corr.), obtained in small yield by heating 4-nitroacetanthranil with hydrazine hydrate, forms small, granular crystals; when treated with acetic anhydride, it yields a compound, m. p. 227° (uncorr.), which is probably an additive product.

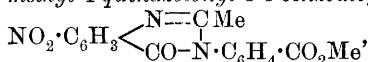
When 4-nitroacetylanthranil (1 mol.) is heated with guanidine (1 mol.), guanidine 4-nitroacetylanthranilate, m. p. 247° (corr.), is produced; in one case, in which 2 mols. of the anthranil were used to 1 mol. of guanidine, a small quantity of a yellow substance, m. p. 253°, was obtained.

Ethyl 7-nitro-2-methyl-4-quinazolonyl-3-acetate,

m. p. 139—140° (corr.), obtained by the action of ethyl aminoacetate on 4-nitroacetanthranil, forms colourless crystals. The corresponding *amide*, m. p. 275° (corr.), crystallises in silky needles, and the *nitrile*, m. p. 207—208° (corr.), in colourless, lustrous scales.

4-Nitro-2-acetylaminohippuronitrile,

m. p. 194° (decomp.), obtained as an intermediate product in the preparation of this quinazalone, forms colourless prisms, and is readily converted into the quinazolone by the action of hot dilute potassium hydroxide.

Methyl 7-nitro-2-methyl-4-quinazolonyl-3-o-benzoate,

m. p. 175° (corr.), obtained by heating 4-nitroacetylthranil with methyl anthranilate, forms yellow, granular crystals. The *amide*, m. p. 320—321° (corr.), crystallises in straw-coloured needles. The *nitrile*, m. p. 234° (corr.), forms yellow needles.

7-Nitro-2-methyl-4-quinazolonyl-3-(2 : 5-dimethyl-3 : 4-dicarbethoxy-pyrrole), $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{N} \end{array} \text{N} \begin{array}{l} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$ m. p. 171° (corr.),

obtained by the action of ethyl diacetylsuccinate on 7-nitro-3-amino-2-methylquinazolone, forms minute, colourless, lustrous scales. E. G.

Reaction of Indigotin with Potassium Permanganate. OSWALD MILLER and J. SMIRNOFF (*Ber.*, 1908, 41, 1363—1367*).—Pure indigotin has been obtained from natural and artificial indigo. The results of analysis agree well with the formula $\text{C}_{16}\text{H}_{10}\text{O}_5\text{N}_2$, and titrations with potassium permanganate in sulphuric acid solution indicate that 316.2 grams of permanganate oxidise 749.3 grams of indigotin, or 100 grams of indigotin require 42.26 grams of permanganate, numbers which confirm Mohr's results. The indigotin and permanganate solutions both contained 0.5 gram per litre, and preliminary experiments showed that concordant results are obtained when from 12.5 to 75 c.c. of indigotin solution are diluted with 600 c.c. of water purified by Hulett's method (*Abstr.*, 1897, ii, 94), and the solution titrated with the permanganate. J. J. S.

Preparation of Tri- and Tetra-bromoindigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193438).—The hitherto unknown *tribromoindigotin* may be obtained quantitatively by suspending indigotin in nitrobenzene or nitrotoluene, adding 2—2½ parts of bromine, and boiling the mixture at 225° for forty-five minutes, when the product separates as a violet-brown, crystalline powder. The employment of 3½ parts of bromine leads to the production of *tetrabromoindigotin* in voluminous, violet crystals. The *tetrabromoindigotin* prepared by leaving the indigotin, bromine, and nitrobenzene for twenty-four hours at the ordinary temperature and then heating at 130—135°, has slightly different tinctorial properties to

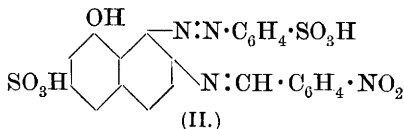
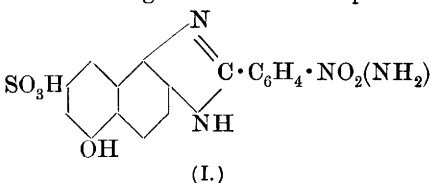
* and J. Russ. *Phys. Chem. Soc.*, 1908, 40, 625—637.

those of the substance produced at 225°. All these preparations are reduced in the hyposulphite vat, and give fast shades of blue on cotton.

G. T. M.

Preparation of Aminohydroxy-derivatives of Phenyl-naphthiminazole. ACTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 193350).—5:6-Diamino- α -naphthol-3-sulphonic acid condenses with benzaldehyde and its derivatives to form benzylidene compounds, which are readily converted into phenyl-naphthiminazole derivatives merely on warming with acids.

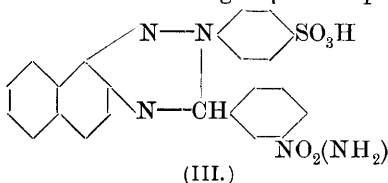
6-Hydroxy-2-m-nitrophenyl- α -naphthiminazole-8-sulphonic acid (I) is thus obtained from 5:6-diamino- α -naphthol-3-sulphonic acid and *m*-nitrobenzaldehyde by condensing these in dilute alcoholic solution and then warming the intermediate product with hydrochloric acid.



6-Hydroxy-2-m-aminophenyl- α -naphthiminazole-8-sulphonic acid results when the foregoing nitro-compound is reduced with iron and acetic acid.

Another naphthiminazole derivative results when the azo-derivative of 7-amino- α -naphthol-3-sulphonic acid and diazobenzenesulphonic acid is condensed with *p*-nitrobenzaldehyde and the resulting condensation product (II) reduced with stannous chloride, when the sulphanilic acid is regenerated and 9-hydroxy-2-*p*-aminophenyl- α -naphthiminazole-7-sulphonic acid is produced.

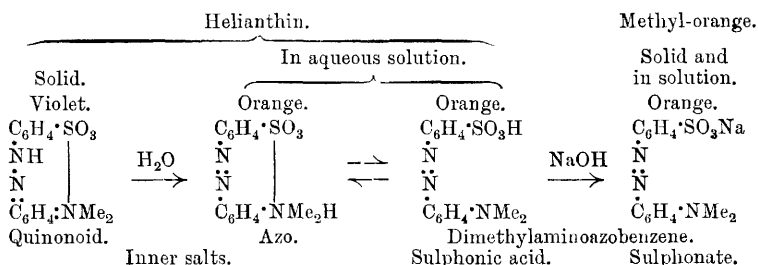
Although the benzylidene derivative gives rise to a naphthiminazole, yet the isomeric triazine (III) from *p*-sulphobenzene-8-azo-7-amino- α -naphthol-3-sulphonic acid can be reduced without fission of the triazine ring to give rise to an aminotriazinesulphonic acid which has the sweet taste characteristic of this group of compounds.



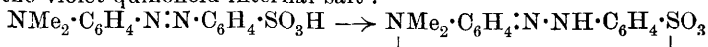
G. T. M.

Establishment of the Isomerism Theory of Indicators in the Case of Methyl-orange and Helianthin. ARTHUR HANTZSCH [and, in part, FRIEDRICH HILSCHER] (*Ber.*, 1908, 41, 1187—1195. Compare Hewitt, this vol., ii, 269).—As in the case of the salts of aminoazo-compounds (this vol., i, 484), the so-

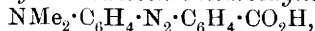
called free aminoazobenzenesulphonic acids, which in the solid state are undoubtedly inner salts, exist in two sharply-divided orange and violet forms. Thus, the so-called aminoazobenzenesulphonic acid and dimethylaminoazobenzenecarboxylic acid are orange, whilst the mono-methyl-, dimethyl- and diethyl-aminoazobenzenesulphonic acids are violet. However, all alkali salts of these orange and violet acids are orange; they all show the same absorption spectrum, which is very similar to that of the free aminoazobenzenesulphonic acid and *p*-bromobenzenediazodimethylaniline, that is, they all have a similar azo-structure. Helianthin in the solid state is violet, and shows the characteristic selective band spectrum of the violet salts of aminoazo-compounds; it must therefore, like these, have a quinonoid structure. Its aqueous solution is, however, orange, and shows the same absorption spectrum as methyl-orange, from which it follows that helianthin, which in the solid state is an internal quinonoid salt, undergoes isomerisation during solution, changing into the azo-form. The relationship existing between these compounds may be shown thus:



Addition of an excess of a strong acid to the aqueous solution of helianthin turns it violet, and then shows the characteristic quinonoid absorption spectrum of the solid indicator and of the quinonoid violet amino-azo-salts. It is shown that the violet substance in the acidified solution of helianthin is not, for example, the quinonoid hydrochloride of helianthin, but the inner salt identical in structure with the solid indicator; the quinonoid hydrochloride can only be obtained, mixed with 10% of helianthin, by crystallising the latter from concentrated hydrochloric acid; further, to turn equivalent solutions of helianthin and benzenediazobromobenzene violet, about 60 times as much acid is required in the latter case as in the former. It is therefore evident that the change of colour produced by adding acid to a dilute solution of methyl-orange or helianthin is due to the isomerisation of the orange dimethylaminoazobenzenesulphonic acid to the violet quinonoid internal salt:



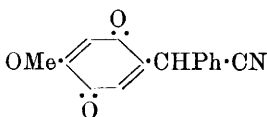
p-Diethylaminoazobenzenesulphonic acid, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, is violet in the solid state; its sodium, potassium, and ammonium salts are orange. *p*-Dimethylaminoazobenzenecarboxylic acid,



prepared by diazotising *p*-aminobenzoic acid and coupling with

dimethylaniline, is orange; the *hydrochloride* is far more stable than the hydrochloride of helianthin; it crystallises in small, violet needles. The orange form of helianthin could not be isolated. W. H. G.

Preparation of Triazans. K. MICHAELIS (*Ber.*, 1908, 41, 1427—1433).—Through the great difference in the molecular magnitudes of the substituents in 5-methoxyquinone-2-benzyl cyanide, annexed



formula, the author hoped to throw some light on the influence of steric hindrance in the formation of hydrazones, but the quinone and also others, such as benzoquinone, diethoxybenzoquinone, dibromodimethoxybenzoquinone, act usually as oxidising

agents on substituted hydrazines. Methoxybenzoquinonebenzyl cyanide (1 mol.) and *as*-phenylbenzylhydrazine hydrochloride (2 mols.), heated in alcoholic solution, yield *diphenyldibenzyltriazan*,



m. p. 107°, which is also obtained by heating equal molecular quantities of *as*-phenylbenzylhydrazine and its hydrochloride at 180°, or by heating the hydrochloride alone. Minunni obtained the same compound in an impure state from carbamide and *as*-phenylbenzylhydrazine (*Abstr.*, 1893, i, 97).

as-Diphenylhydrazine under the preceding conditions yields a violet dye, but equal molecular quantities of *as*-diphenylhydrazine and *as*-phenylbenzylhydrazine hydrochloride at 170—180° yield *triphenylbenzyltriazan*, $\text{NPh}_2\cdot\text{NH}\cdot\text{NPh}\cdot\text{C}_7\text{H}_7$, m. p. 120°, which, like diphenyldibenzyltriazan, is a stable substance, does not form salts, and gives a nitroso-derivative which responds to Liebermann's test.

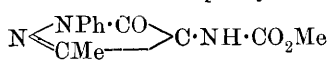
Whilst *as*-phenylmethylhydrazine heated with an excess of carbamide at 170° yields Fischer's *as*-phenylmethylsemicarbazide, m. p. 135°, *as*-diphenylhydrazine and an equivalent quantity of carbamide at 180° give *tetraphenyldiaminobiuret*, $\text{NPh}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}_2$, m. p. 253°, which also results quantitatively from biuret and *as*-diphenylhydrazine at 190°. The same compound is obtained by fusing *diphenylsemicarbazide*, $\text{C}_{13}\text{H}_{13}\text{ON}_3$, m. p. 195°, which is prepared readily by mixing aqueous solutions of equal molecular quantities of potassium cyanate and *as*-diphenylhydrazine hydrochloride.

as-Phenylbenzylsemicarbazide, $\text{C}_7\text{H}_7\cdot\text{NPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 103°, is prepared by adding an aqueous solution of potassium cyanate (1 mol.) to *as*-phenylbenzylhydrazine (1 mol.) dissolved in glacial acetic acid. By fusion with an equal molecular quantity of *as*-phenylbenzylhydrazine, it yields, not a triazan, but *diphenyldibenzyl-diaminobiuret*, $\text{C}_7\text{H}_7\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}\cdot\text{C}_7\text{H}_7$, m. p. 169°.

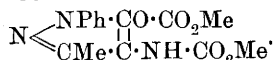
C. S.

Preparation of 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (*D.R.P.* 189842).—4-Amino-1-phenyl-3-methyl-5-pyrazolone is readily oxidised to rubazonic acid by atmospheric oxygen, and on this account cannot be prepared conveniently on a technical scale. Its acyl and alkyl derivatives are more stable, and can be methylated to form 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone (pyramidone).

1-Phenyl-3-methyl-4-methylurethano-5-pyrazolone (I), leaflets and needles, m. p. 198—199°, and 1-phenyl-3-methyl-4-urethano-5-pyrazolone methyl carbonate (II), slender needles, m. p. 153—154°, are obtained respectively by the action of one and two molecules of methyl chloro-carbonate on 4-amino-1-phenyl-3-methyl-5-pyrazolone:

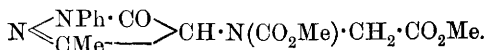


(I.)



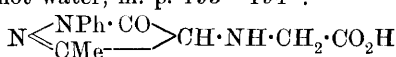
(II.)

Either of the foregoing compounds when treated with methyl chloroacetate in presence of sodium methoxide gives rise to methyl 1-phenyl-3-methyl-4-methylurethano-5-pyrazolonylacetate (III), felted needles, m. p. 135—136°:

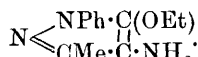


(III.)

When hydrolysed with dilute hydrochloric acid, the foregoing ester furnishes 4-amino-1-phenyl-3-methyl-5-pyrazolonylactic acid (IV), leaflets from hot water, m. p. 193—194°:



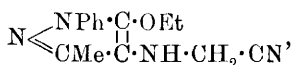
(IV.)



(V.)

4-Amino-5-ethoxy-1-phenyl-3-methylpyrazole (V), a non-crystallisable oil, obtained by reducing 4-benzeneazo-5-ethoxy-1-phenyl-3-methylpyrazole, forms a crystalline hydrochloride, m. p. 183—184°; benzoyl derivative, needles, m. p. 163—164°; acetyl derivative, needles, m. p. 99°.

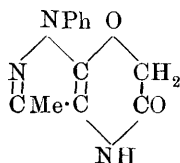
4-Cyanomethylamino-5-ethoxy-1-phenyl-3-methylpyrazole (VI),



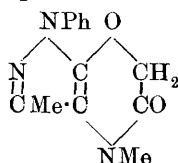
(VI.)

colourless crystals, m. p. 109—110°, is obtained by the action of formaldehyde and hydrocyanic acid on 4-amino-5-ethoxypyrazole.

The *eso-anhydride* of 4-amino-1-phenyl-3-methylpyrazole-5-oxyacetic acid (VII), thick crystals, m. p. 230°, is obtained by successively condensing the alkali derivative of 4-nitro-1-phenyl-3-methyl-5-pyrazolone with ethyl chloroacetate, and reducing the product:



(VII.)



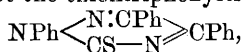
(VIII.)

This anhydride, although sparingly soluble in water, dissolves readily in concentrated hydrochloric acid or dilute aqueous sodium hydroxide. By treatment with methyl sulphate in alkaline solution, the methyl derivative (VIII) is formed, needles, m. p. 167—168°.

When the foregoing compounds are subjected to the action of methylating agents, the alkyl and acyl residues attached to a nitrogen or a pyrazolone oxygen atom are readily eliminated, and the valuable drug, 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone (pyramidone), is produced. G. T. M.

Aminophenylcarbamide and Aminophenylthiocarbamide.

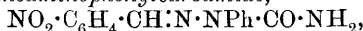
LUIGI ROLLA (*Gazzetta*, 1908, 38, i, 327—349. Compare Pellizzari, Abstr., 1907, i, 873).—Like aminophenylcyanamide (compare Rolla, Abstr., 1907, i, 875), aminophenylcarbamide (α -phenylsemicarbazide) reacts readily with aldehydes and ketones and even with alloxan, yielding well-crystallised derivatives analogous to phenylhydrazones; this reaction is greatly accelerated by a trace of hydrochloric acid. Further, as a diamine, aminophenylcarbamide reacts with various compounds, such as benzil and glyoxal, yielding cyclic derivatives. With malonic acid, aminophenylcarbamide yields aminophenylbarbituric acid (?), a red, crystalline compound which is being studied further. With formic acid, aminophenylcarbamide yields 1-phenyl-1:2:4-triazole-5-one (compare Widman, Abstr., 1894, i, 57), whilst with carbamide it gives phenylurazole, already obtained by Pinner (Abstr., 1888, 687) by the action of carbamide on phenylsemicarbazide. Aminophenylthiocarbamide also reacts readily with aldehydes or ketones, giving phenylhydrazones. With benzil, too, it yields only a phenylhydrazone and not the thiontriphenyltriazine,



thus confirming the view that thiocarbamide reacts in accordance with its tautomeric formula, $\text{NH}_2\cdot\text{C}(\text{SH})\cdot\text{NH}$.

Aminophenylcarbamide picrate, $\text{NH}_2\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, has m. p. 163°.

m-Nitrobenzylideneaminophenylcarbamide,



forms pale yellow crystals, m. p. 232°.

o-Nitrobenzylideneaminophenylcarbamide, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_4$, crystallises in pale yellow needles, m. p. 200°.

p-Nitrobenzylideneaminophenylcarbamide, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_4$, forms pale yellow, silky needles, m. p. 239°.

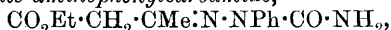
isopropylideneaminophenylcarbamide, $\text{CMe}_2\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$, separates from alcohol in white crystals, m. p. 137°.

Phenylethylideneaminophenylcarbamide, $\text{CPhMe}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$, is deposited from alcohol in white crystals, m. p. 122°.

Isatinaminophenylcarbamide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \text{CO} \end{array} \text{C:N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from alcohol in yellow leaflets, m. p. 212°.

Alloxanaminophenylcarbamide, $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} \text{C:N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$, separates in yellow flocks, m. p. 293°.

Ethyl acetoacetate-aminophenylcarbamide,



forms white crystals, m. p. 190°.

Aminophenylcarbamide forms a copper derivative, the *nitrate* of

which, $\text{Cu}(\text{C}_7\text{H}_8\text{ON}_3)_2 \cdot 2\text{HNO}_3$, separates from water in blue, acicular crystals, m. p. 155° .

Triphenyltriazine, $\text{N} \langle \begin{smallmatrix} \text{CPh} \cdot \text{CPh} \\ \text{CO} - \text{NPh} \end{smallmatrix} \rangle \text{N}$, prepared by the interaction of aminophenylthiocarbamide and benzil in alcoholic solution in presence of a trace of hydrochloric acid, separates from alcohol in pale yellow crystals, m. p. 170° , and gives a brilliant red coloration with concentrated sulphuric acid.

When heated at about 170° , aminophenylthiocarbamide condenses to the *diphenylurazine*, $\text{CO} \langle \begin{smallmatrix} \text{NPh} \cdot \text{NH} \\ \text{NH} \cdot \text{NPh} \end{smallmatrix} \rangle \text{CO}$, which forms white crystals, m. p. 235° (compare Pinner, Abstr., 1888, 687).

Aminophenylthiocarbamide picrate, $\text{C}_7\text{H}_9\text{NS}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, separates from water or alcohol in yellow crystals, m. p. 145° .

m-Nitrobenzylideneaminophenylthiocarbamide,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NPh} \cdot \text{CS} \cdot \text{NH}_2$,
 separates from alcohol in yellow, acicular crystals, m. p. 211° .

isoPropylideneaminophenylthiocarbamide, $\text{CMe}_2 \cdot \text{N} \cdot \text{NPh} \cdot \text{CS} \cdot \text{NH}_2$, crystallises from alcohol in stellate aggregates of colourless needles, m. p. 135° .

Alloxanaminophenylthiocarbamide,
 $\text{CO} \langle \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \rangle \text{C} : \text{N} \cdot \text{NPh} \cdot \text{CS} \cdot \text{NH}_2$,
 forms yellow crystals, m. p. 280° .

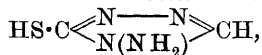
Ethyl acetoacetate-aminophenylthiocarbamide,
 $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CMe} : \text{N} \cdot \text{NPh} \cdot \text{CS} \cdot \text{NH}_2$,
 forms white crystals, m. p. 142° .

Benzylaminophenylthiocarbamide, $\text{CPhBz} : \text{N} \cdot \text{NPh} \cdot \text{CS} \cdot \text{NH}_2$, exists in two stereoisomeric forms, one red, m. p. about 100° , and the other white, m. p. 185° .

5-Thion-1-phenyltriazolone, $\text{NPh} \langle \begin{smallmatrix} \text{N} = \text{CH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix} \rangle$, prepared by the action of formic acid on aminophenylthiocarbamide, crystallises from benzene in colourless, acicular laminae, m. p. 178° , and is isomeric with the 3-thion-1-phenyltriazolone prepared by Pellizzari and Ferro (Abstr., 1899, i, 550) by the action of phosphorus pentasulphide on phenylurazole.
 T. H. P.

Thiocarbohydrazide. ROBERT STOLLÉ and P. E. BOWLES (*Ber.*, 1908, 41, 1099—1102).—A very convenient method of preparing thiocarbohydrazide is to heat a stirred aqueous solution of hydrazine dithiocarbazate (Curtius and Heidenreich, Abstr., 1894, i, 166) with lead oxide, when the filtrate deposits the compound in needles, m. p. 169° . *Dibenzylidenethiocarbohydrazide*, $\text{CS}(\text{NH} \cdot \text{N} : \text{CHPh})_2$, forms pale yellow, glistening needles, m. p. 194° ; the corresponding *ditolylidene* derivative, $\text{C}_{17}\text{H}_{18}\text{N}_4\text{S}$, crystallises from alcohol in yellow leaflets, m. p. 191° ; the *bisnitrobenzylidenethiocarbohydrazide*, $\text{C}_{15}\text{H}_{12}\text{O}_4\text{N}_6\text{S}$, is pale yellow, m. p. 227° .

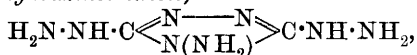
When heated with ethyl orthoformate in a sealed tube at 100° , thiocarbohydrazide forms 1-amino-2-thiol-1 : 3 : 4-triazole,



crystallising from alcohol in needles, m. p. 167°. Its aqueous solution is acid, giving a white precipitate with silver nitrate.

Hydrazine hydrate and thiocarbonylhydrazide when heated in a sealed tube for a long time at 120—130° give 1-amino-5-thiol-2-hydrazino-1 : 3 : 4-triazole, $\text{H}_2\text{N}\cdot\text{NH}\cdot\text{C}\begin{smallmatrix} \text{N} \\ \text{N}(\text{NH}_2) \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}\cdot\text{SH}$, crystallising in slender needles, m. p. 228° (decomp.). It is soluble in alkali; its aqueous solution reduces ammoniacal silver nitrate in the cold; dilute nitric acid and silver nitrate give, however, a white precipitate.

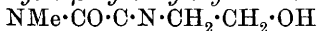
1-Amino-2 : 5-dihydrazinotriazole,



obtained by the action of hydrazine hydrate on guanidine carbonate, crystallises from dilute alcohol in slender, white needles, m. p. 207° (decomp.). Its aqueous solution reduces ammoniacal silver nitrate in the cold; the hydrochloride of its tribenzylidene derivative, $\text{C}_{23}\text{H}_{20}\text{N}_8\cdot\text{HCl}$, separates in needles, m. p. 230°. W. R.

Preparation of Hydroxyalkyl Derivatives of Xanthine Bases. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 191106).—The therapeutic application of the xanthine bases is hindered by the poisonous secondary effect of these substances and their sparing solubility. Their hitherto unknown hydroxyalkyl derivatives, whilst retaining the powerful diuretic action of the parent bases, are free from the harmful secondary reaction and are readily soluble in water. These substances are prepared by the interaction of a xanthine base containing a replaceable hydrogen, and the halogen hydrins in the presence of some agent for fixing acid.

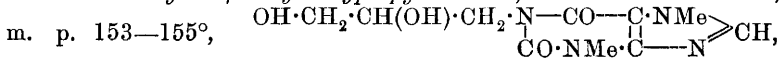
1 : 3-Dimethyl-7-β-hydroxyethylxanthine, colourless leaflets, m. p.



156—158°, $\begin{array}{c} | \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{N} \end{array} \begin{array}{c} || \\ | \end{array} \text{CH}$, is produced by heating to-

gether at 100—120° in aqueous solution theophylline, ethylene chlorohydrin, and sodium hydroxide; it does not form stable salts with acids or alkalis.

3 : 7-Dimethyl-1-α-β-dihydroxypropylxanthine, colourless needles,



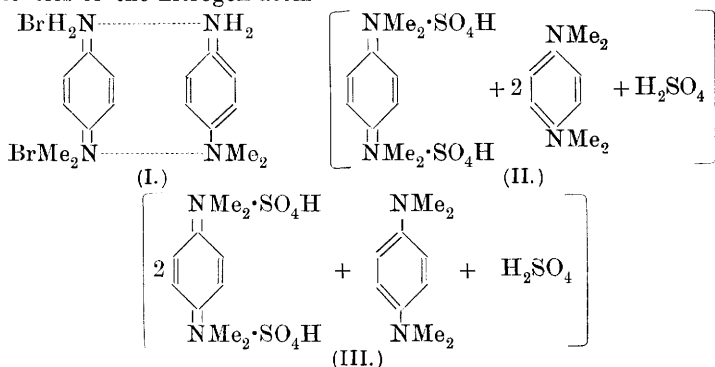
is prepared from theobromine, ethylene monochlorohydrin, and aqueous sodium hydroxide.

3-Methyl-1 : 7-ββ'-dihydroxydiethylxanthine, from ethylene chlorohydrin and 3-methylxanthine, and β-hydroxyethyltheobromine, from this chlorohydrin and theobromine, form colourless needles melting respectively at 168—170° and 189—191°. G. T. M.

Quinonoid Compounds. XV. Wurster's Dye Salts.

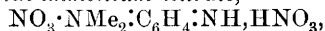
RICHARD WILLSTÄTTER and JEAN PICCARD (*Ber.*, 1908, 41, 1458—1475. Compare *Abstr.*, 1905, i, 669; 1906, i, 996; 1907, i, 641).—Wurster and Sendtner obtained an unstable, red dye by oxidation of *p*-aminodimethylaniline (*Abstr.*, 1880, 110), whilst Wurster and Schobig

obtained a similar, but blue, dye by oxidation of *p*-phenylenetetramethyldiamine (Abstr., 1880, 111). Bernthsen (Abstr., 1886, 53; 1889, 775) considered these dyes to be quinonoid compounds. The present authors have now obtained the two dyes as stable salts. Their constitution is discussed, and partially quinonoid formulæ ascribed to them. The red dye is a *meri** quinonoid salt (I), whilst the blue dye is obtained in two states of oxidation, (II) and (III). In these formulæ, the parts of the molecules are considered to be united by the partial valencies of the nitrogen atoms:



as-meri-Quinonedimethyldi-immonium bromide (I) is best prepared by the action of 1 atom of bromine on 1 mol. of *p*-phenylenedimethyldiamine in glacial acetic acid solution; it crystallises from methyl alcohol in black leaflets with metallic lustre, m. p. 146—147°, is green when powdered, remains unchanged on exposure to air, and forms bluish-red solutions, which are decolorised by addition of hydrochloric acid, or by reduction with stannous chloride or sulphurous acid, or by oxidation with ferric chloride or bromine. In the last case, the colourless solution becomes again red on addition of the leuco-chloride. In dilute hydrochloric acid solution, the dry salt turns potassium iodide-starch paper blue, and in concentrated aqueous solution forms a black, crystalline *iodide* on addition of potassium iodide. On addition of sodium thiosulphate, one-half of the aminodimethylaniline in the molecule is liberated.

as-Quinonedimethyldi-immonium nitrate,



is obtained by the action of nitrous gases on *p*-phenylenedimethyldiamine; it forms colourless crystals, is unstable at the ordinary temperature, detonates when heated, yields Wurster and Sendtner's dye when boiled with alcohol, and forms a blue dye on addition of a salt of *p*-phenylenetetramethyldiamine.

The blue dye has been isolated as the *sulphate* (II); it crystallises in dark prisms with green metallic lustre, is dark violet when powdered, is stable in dry air, but smells of formaldehyde when exposed to moist air, and forms blue solutions. The action of nitrous gases on this dye leads to the formation of the two-thirds quinonoid *sulphate* (III), which is a weaker blue than the one-third quinonoid dye. G. Y.

* *μερικώς*: partial.

Constitution of Hydroxyazo-compounds. KARL AUWERS (*Annalen*, 1908, 360, 11—25).—The evidence as to the constitution of those substances which have been held, on the one hand, to be hydroxyazo-compounds, and, on the other, to be quinonehydrazones, is summarised and discussed. The author considers that the weight of evidence is conclusively in favour of the hydroxyazo-structure for the ortho- as well as for the para-compounds.

Goldschmidt and Brubacher (*Abstr.*, 1891, 1209) having failed to observe transmigration of the acyl group on reduction of *o*-nitrophenyl esters with zinc and acetic acid, considered that such transmigration could not take place on reduction in the same manner of acylated hydroxyazo-compounds. It is now found, however, that *o*-nitro-*p*-tolyl benzoate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OBz}$, which is prepared by Schotten-Baumann's method from *o*-nitro-*p*-cresol, and crystallises from light petroleum in colourless needles, m. p. 102° , when reduced with zinc dust and acetic acid in the cold yields *o*-benzoylamino-*p*-cresol, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHBz}$. G. Y.

Measurement of the Effect of Certain Hypsochrome and Bathochrome Groups on the Colour of Azobenzene. HERBERT GORKE, ERNST KÖPPE, and FRITZ STAIGER (*Ber.*, 1908, 41, 1156—1171).—The work of Hantzsch and Glover (*Abstr.*, 1907, i, 101) has been repeated and extended, using the same form of photometer, but employing as the source of light either a mercury lamp or a hydrogen tube instead of the unsatisfactory thallium flame.

The wave-lengths of the light employed were 576, 546, 486, 436, and $404 \mu\mu$, and the substances examined were azobenzene, *p*-hydroxyazobenzene, and its methyl ether, ethyl ether, *propyl* ether, dark orange-red needles, m. p. 61° , *butyl* ether, orange-red leaflets, m. p. 67° , *phenyl* ether, golden-yellow leaflets, m. p. 116° , acetate, *propionate*, small, reddish-yellow needles, m. p. 75° , *butyrate*, orange leaflets, m. p. 77° , and benzoate. As in the case of the green of the thallium flame, Beer's law is also found to hold good in other parts of the spectrum.

In the fused or solid state, none of the above substances exhibit any marked differences in colour intensity, but in each case examined, the effect of dissolving the substance, even in the most indifferent solvents, is to increase the molecular colour intensity, the effect being most marked in the case of the alkyl derivatives. The statement of Hantzsch and Glover (*loc. cit.*) that the intensities of the acyl and alkyl derivatives of *p*-hydroxyazobenzene in the same solvent are approximately proportional to the molecular weights does not hold good in other parts of the spectrum; in most cases, an increase in the mol. wt. is accompanied by a greater absorption in the green ($546 \mu\mu$) and bluish-green ($486 \mu\mu$) parts of the spectrum than in the blue and violet parts of the spectrum, whereas the introduction of an alkyl group into *p*-hydroxyazobenzene increases the absorption, the introduction of an acyl group decreases the absorption. As was shown by Hantzsch and Glover (*loc. cit.*), equivalent solutions of the same substance in various solvents exhibit varying colour intensities; this does

not, however, appear to be directly related to any physical property of the solvent.

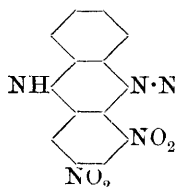
The effect of temperature on the colour intensity of a solution is very complicated; an increase in absorption in one part of the spectrum is accompanied by a decrease in another.

A marked increase in intensity accompanies the formation of a salt of *p*-hydroxyazobenzene; since the salt formation takes place without intramolecular rearrangement (compare Tuck, *Trans.*, 1907, 91, 450), Hantzsch's tenet, "a colourless substance which yields a coloured ion must be a ψ -acid," must be abandoned. W. H. G.

2:4:2':4':6'-Pentanitroazobenzene. H. LEEMANN and EUGÈNE GRANDMOUGIN (*Ber.*, 1908, 41, 1306—1309).—Pentanitrohydrazobenzene could not be obtained by the action of picrylhydrazine on chloro- or bromo-dinitrobenzene or from picryl chloride, chlorodinitrobenzene, and hydrazine hydrate, but when 2:4-dinitrophenylhydrazine (2 mols.) is heated with picryl chloride (1 mol.) at 110—120° for two hours the desired compound is obtained (compare Ciusa, *Abstr.*, 1907, i, 875). Its *monopotassium* salt, $C_{12}H_6O_{10}N_7K$, is a dark explosive powder, dissolving in water with a red colour; the *dipotassium* salt is deep blue in solution and is easily hydrolysed.

2:4:6:2':4'-Pentanitroazobenzene, $C_6H_2(NO_2)_3 \cdot N:N \cdot C_6H_3(NO_2)_2$, obtained by the oxidation of the hydrazo-compound by lead peroxide, crystallises from glacial acetic acid in orange needles, m. p. 213°, and is not oxidised to the azoxy-compound by fuming nitric and chromic acids.

1:3-Dinitro-*N*-dinitroanilindihydrophenazine, annexed formula,



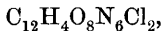
obtained by the action of pentanitroazobenzene on aniline at 100—115°, crystallises from a mixture of benzene and alcohol in lustrous, coppery-blue scales.

As the above substance has similar properties to Kehrman and Messinger's dinitro-*N*-phenyldihydrophenazine (*Abstr.*, 1894, i, 55), the above constitution is assigned to the substance. The parent substance dinitrodihydrophenazine could not be obtained by Kehrman and Messinger's method, but is prepared by heating rapidly picryl-*o*-phenylenediamine in a naphthalene bath to 200°.

Picryl-*o*-phenylenediamine, $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_2(NO_2)_3$, obtained easily by action of picryl chloride on the diamine in alcoholic solution in the presence of potassium acetate at 50°, crystallises from xylene in small, cinnabar-red crystals, m. p. 177—178° (decomp.). W. R.

s-Hexanitroazobenzene. H. LEEMANN and EUGÈNE GRANDMOUGIN (*Ber.*, 1908, 41, 1295—1305. Compare *Abstr.*, 1907, i, 163).—The best method for preparing hexanitrohydrazobenzene is to add the hydrazine hydrate solution to a hot well-stirred alcoholic solution of picryl chloride, and then, as quickly as possible, potassium acetate (3 mols.), when the monopotassium salt separates. This salt,

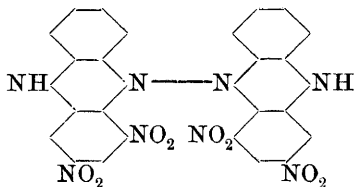
$C_{12}H_5O_{12}N_8K$, separates from its acetone solution on the addition of alcohol in metallic, green crystals, m. p. 188° , and the dipotassium salt, $C_{12}H_4O_{12}N_8K_2$, is also green; both salts are explosive, and the conclusion is drawn that they have a quinonoid structure (compare Hewitt and Mitchell, *Trans.*, 1907, **91**, 1254). The ammonium and potassium salts are sparingly, the sodium salts are easily, soluble. Hexanitroazobenzene (*loc. cit.*) appears to be dimorphous, and is extraordinarily stable towards acids, a mixture of fuming nitric and chromic acids having no action. It is, however, converted by dilute potassium hydroxide into hexanitrohydroazobenzene, picric acid, and decomposition products. Alcoholic hydrogen chloride, when heated with hexanitroazobenzene in a sealed tube at 130 — 150° for one and a half hours, forms 2 : 2'-dichloro-4 : 6 : 4' : 6'-tetranitroazobenzene,



which separates from a mixture of chlorobenzene and alcohol in orange needles, m. p. 244 — 245° . As ammonium sulphide reduces this compound to a hydrazo-derivative dissolving in alkali with a blue colour, the conclusion is drawn that the para positions are occupied by nitro-groups, and therefore that the compound has the above constitution (compare Werner and Stiasny, *Abstr.*, 1900, i, 194).

Like other nitro-compounds, hexanitroazobenzene forms additive compounds with hydrocarbons, which contain 2 mols. of the hydrocarbon. The following have been prepared: that with *naphthalene* forms yellow, glistening needles, m. p. 165° ; with *phenanthrene*, dark orange needles, m. p. 190° ; with *anthracene*, brownish-red needles, m. p. 193° ; an experiment to prepare one containing hexanitroazobenzene, anthracene, and naphthalene gave black needles, m. p. 208 — 210° , which proved to contain 2 mols. of the azo-compound with 1 mol. of anthracene. Also, α -nitronaphthalene, α - and β -ethoxynaphthalene, and α -naphthylamine yield additive compounds containing 2 mols. of the naphthalene derivative, which have m. p's. 124° , 158° , 137° , and 154° (decomp.) respectively.

Primary amines, however, generally react with hexanitroazobenzene to form well-defined compounds. The reaction is a complicated one, and is dependent on the conditions of the experiment. Aniline gives aminoazobenzene, picrylaniline, *o*-trinitrobenzene, and *tetranitrohydrodiphenazine*, annexed formula,



which crystallises from xylene in glistening, bluish-violet leaflets, m. p. 280° , decomp. 291° . It is best prepared by adding hexanitroazobenzene in small portions to a boiling solution of aniline in toluene.

Molecular weight determinations by the boiling-point method in ethylene dibromide gave 569 and 588, calc. 542. When heated with alcoholic hydrochloric acid under pressure at 160° , it resulted in the replacement of the four nitro-groups by chlorine, *tetrachlorohydrodiphenazine*, $C_{24}H_{14}N_4Cl_4$, being formed. It crystallises in red needles, m. p. 350° .

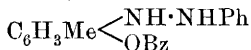
o-Toluidine gives *tetranitrohydrodi-o-toluphenazine*, $C_{26}H_{18}O_8N_8$, crystallising in glistening, copper needles; *m*-toluidine, the corre-

sponding *meta* compound, dark blue, almost black, needles, and *p*-toluidine, the *para* derivative, bluish-violet crystals. *Picryl-m-toluidine*, $C_{13}H_{10}O_6N_4$, forms golden-yellow leaflets, m. p. 126° . *Tetranitrohydrodi- β -naphthophenazine*, $C_{32}H_{18}O_8N_8$, crystallises from xylene in small, green needles. W. R.

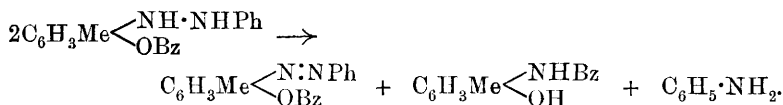
Azo-compounds from the *o*-Aminophenols and 2:8-Dihydroxynaphthalene-6-sulphonic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 191445).—When coupled with the diazotised aminophenols in sodium hydroxide or carbonate solutions, 2:8-dihydroxynaphthalene-6-sulphonic acid furnishes only poor yields of azo-derivatives, but in the presence of calcium hydroxide the condensation occurs extremely readily, and the products, when dyed on wool and subsequently chromed, furnish very fast shades of black.

G. T. M.

Acyl Derivatives of Benzeneazo-*p*-cresol and β -Benzeneazo- α -naphthol and their Transformation Products. KARL AUWERS and M. ECKARDT (*Annalen*, 1908, 359, 336—382).—With the object of throwing light upon the transformation of hydroxyazo-compounds, the investigation of the wandering of acid radicles (Abstr., 1904, i, 736) has been extended. Evidence in favour of the formula

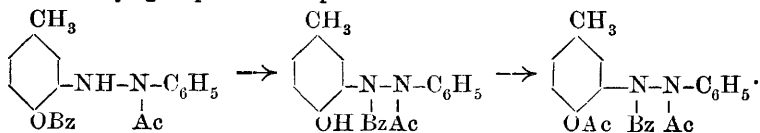


for the reduction product of benzeneazo-*p*-cresol benzoate is found (1) by heating the benzoylhydrazo-compound dissolved in glacial acetic acid, when simultaneous oxidation and reduction take place according to the scheme :

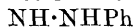


(2) The benzoylhydrazo-compound in alcoholic solution undergoes the benzidine or semidine transformation with hydrogen chloride, the hydrochloride, m. p. 260° , separates out, and from this substance alkalis liberate a crystalline *anhydro-base*, m. p. 154 — 155° , the *sulphate* of which separates from water in silky needles, m. p. 250° . (3) Pyridine solutions of the benzoylhydrazo-compound give with excess of acetyl chloride the *N*- β -monoacetyl derivative, m. p. 143° ; hydroazobenzene behaves in a like manner.

The *benzoyldiacetyl* derivative, m. p. 172.5° , when treated with alcoholic soda, becomes partly hydrolysed to a *monobenzoylacetyl* derivative, m. p. 151° , isomeric with that of m. p. 143° . Experiments show that when boiled with acetic anhydride the benzoyl group wanders from the oxygen to the neighbouring nitrogen atom and a second acetyl group takes its place :



O-N β -Dibenzoylbenzenehydrazo-p-cresol, m. p. 92°, has been prepared, and on reduction this gives *N*-benzoyl-*o*-amino-*p*-cresol and benzanilide. In like manner, the *benzoylanisoylhydrazo*-compound, m. p. 95—100°, gives *N*-benzoyl-*o*-amino-*p*-cresol and anisanilide.



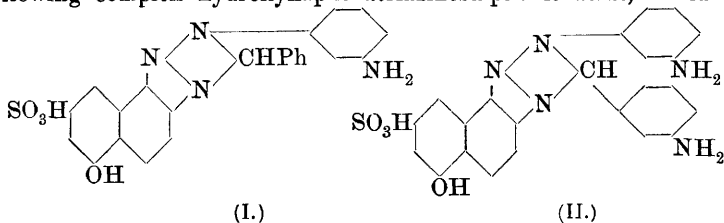
The conclusion is arrived at that $\text{CH}_3\text{—}\langle\text{hexagon}\rangle\text{—OBz}$ represents the reduction product of benzoylbenzeneazo-*p*-cresol. The authors find that at the temperature of the water-bath, the reduction of benzoylbenzeneazo-*p*-cresol proceeds further than Goldschmidt found at 0°, *o*-amino-*p*-cresol, its *N*-benzoyl derivative, aniline, and benzanilide having been isolated. The presence of benzanilide is evidence of the wandering in one part of the molecule of the acid radicle from the oxygen to the nitrogen atom. These and other considerations lead to the conclusion that benzeneazo-*p*-cresol benzoate, like its reduction product, is an *O*-ester. The constitution of the reduction product of acetylbenzeneazo-*p*-cresol (Abstr., 1891, 1209; 1907, i, 554) differs from that of the benzoyl derivative in that the acid radicle is united with nitrogen and not with oxygen; this is shown by the sole formation of acetanilide and free *o*-amino-*p*-cresol when treated with zinc and acetic acid. Only one benzoyl derivative of β -benzeneazo- α -naphthol could be obtained, and this on reduction gives aniline and the *N*-benzoate of β -amino- α -naphthol. Similarly, only one acetyl compound could be prepared, the mode of formation of which shows that a wandering has taken place in the molecule. On reduction by zinc and acetic acid, aniline and acetanilide are produced, showing that the compound is an *O*-ester, although it is also obtained from acetylphenylhydrazine and naphthaquinone, an isomeric change occurring in the latter case.

J. V. E.

α -Anthramine and 1:4-Anthradiamine. ILIE J. PISOVSCHI (*Ber.*, 1908, 41, 1434—1436).—1-Anthramine is obtained in 70—80% yield by heating 1-anthrol with three or four times its weight of ammoniacal calcium chloride at 200—220° for one day, and has m. p. 119° (compare Dienel, Abstr., 1905, i, 767). 4-Anthraceneazo-1-anthramine, $\text{C}_{14}\text{H}_9\cdot\text{N}_2\cdot\text{C}_{14}\text{H}_8\cdot\text{NH}_2$, m. p. 239°, obtained from amyl nitrite (1 mol.) and 1-anthramine hydrochloride (2 mols.) in alcoholic solution, crystallises in reddish-brown needles with a green reflex, and forms unstable salts. Benzeneazo-1-anthramine, $\text{Ph}\cdot\text{N}_2\cdot\text{C}_{14}\text{H}_8\cdot\text{NH}_2$, m. p. 130°, prepared by mixing an aqueous solution of diazobenzene chloride with an alcoholic solution of 1-anthramine, forms red needles, and yields a deep blue *hydrochloride*, $\text{C}_{20}\text{H}_{15}\text{N}_3\cdot\text{HCl}$, which is reduced by zinc dust and dilute hydrochloric acid to 1:4-anthradiamine *hydrochloride*; the corresponding *sulphate* crystallises in sparingly soluble, white needles. The *diacetyl* derivative, $\text{C}_{14}\text{H}_8(\text{NHAc})_2$, has m. p. 322°. An acidified aqueous solution of 1:4-anthradiamine is oxidised by ferric chloride to yellow needles of 1:4-anthraquinone, which darkens at 210°, and has m. p. 218° (decomp.) (compare Dienel, Abstr., 1906, i, 290; Haslinger, *ibid.*, i, 967).

C. S.

[Azo-derivatives of Naphthalenoid Triazines.] LEOPOLD CASSELLA & Co. (D.R.-P. 191024. Compare Abstr., 1907, i, 451).—The following complex hydroxynaphthatriazinesulphonic acids, I and II,



condense with diazonium salts in alkaline solutions, giving rise to azo-dyes, which have the valuable properties of dyeing unmordanted cotton and of undergoing diazotisation on the fibre with subsequent formation of fast ingrain colours with the ordinary developers (β -naphthol, &c.). These triazines are produced by the interaction of 6-amino- α -naphthol-3-sulphonic acid, a benzenoid amine, and benzaldehyde or its derivatives.

m-Nitroaniline and aniline have been employed as bases, and *m*-aminobenzaldehyde has been used instead of benzaldehyde.

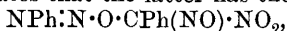
G. T. M.

[Reactivity of Diazo-salts of 2:5-Dichloroaniline.] JOSEF ROHNER (D.R.-P. 193211).—2:5-Dichloroaniline furnishes a diazo-compound which greatly exceeds *p*-nitrodiazobenzene chloride in reactivity; it couples very readily with diethyl-*o*-toluidine and the para-substituted phenols, yielding azo-compounds having valuable tinctorial properties. The base is readily diazotised in 7% hydrochloric acid.

G. T. M.

Action of Diazo-salts on Phenyldinitromethane. [ω -Dinitrotoluene.] GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1908, 43, 303—314; *Gazzetta*, 1908, 38, i, 509—519).—The author describes the diazobenzene derivative of ω -dinitrotoluene and two isomeric compounds, one white and the other red, into which it is readily transformed.

The white compound is either α -nitro- β -nitroso- α -benzoyl- β -phenylhydrazine, $\text{NO}_2 \cdot \text{NBz} \cdot \text{NPh} \cdot \text{NO}$, or $\text{NO}_2 \cdot \text{O} \cdot \text{CPh} : \text{N} \cdot \text{NPh} \cdot \text{NO}$. The ready formation of this compound from the diazobenzene derivative of ω -dinitrotoluene indicates that the latter has the structure



and is a change analogous to the transformation of an azo-compound into a hydrazone observed by Dimroth and Hartmann (Abstr., 1907, i, 1090). The potassium derivative of ω -dinitrotoluene, from which the diazobenzene derivative is obtained, is therefore regarded as having the structure $\text{OK} \cdot \text{CPh}(\text{NO}) \cdot \text{NO}_2$. The red isomeride is ω -benzeneazo- ω -dinitrotoluene, $\text{NPh} : \text{N} \cdot \text{CPh}(\text{NO}_2)_2$, which is the first known compound containing the groups NO_2 and $\cdot \text{N} : \text{NAr}$ united with one and the same carbon atom. Its formation from the diazo-

benzene derivative is explained by assuming that ω -dinitrotoluene can exist in two forms, one stable, $\text{CHPh}(\text{NO}_2)_2$, and the other labile, $\text{NO}_2 \cdot \text{CPh} \cdot \text{NO} \cdot \text{OH}$, which has not yet been isolated; if, then, the diazo-derivative has the structure $\text{NO}_2 \cdot \text{CPh} \cdot \text{NO} \cdot \text{O} \cdot \text{N} \cdot \text{NPh}$, its spontaneous transformation into ω -benzeneazo- ω -dinitrotoluene represents a passage to the stable form.

The *diazobenzene* derivative of ω -dinitrotoluene, $\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_4$, forms golden-yellow crystals, m. p. 70° , and reacts with alcohol, yielding ω -dinitrotoluene, nitrogen, acetaldehyde, and benzene.

α -Nitro- β -nitroso- α -benzoyl- β -phenylhydrazine, $\text{NO}_2 \cdot \text{NBz} \cdot \text{NPh} \cdot \text{NO}$, formed by the isomerisation of the diazobenzene derivative of ω -dinitrotoluene dissolved in benzene, chloroform, or carbon disulphide, forms shining, white laminae, m. p. 127° , gives an emerald-green coloration with concentrated sulphuric acid and phenol, and reacts with cold water, yielding nitrosobenzoylphenylhydrazine (compare Voswinkel, Abstr., 1901, i, 617), and with boiling water, yielding benzoylphenylhydrazine, $\text{NHBz} \cdot \text{NHPh}$.

ω -Benzeneazo- ω -dinitrotoluene, $\text{NPh} \cdot \text{N} \cdot \text{CPh}(\text{NO}_2)_2$, obtained when the isomeric diazobenzene compound is either left for eight to ten days or dissolved in the cold in alcohol, ether, or acetone, crystallises from chloroform in flattened, red needles, m. p. 138 — 147° (decomp.), and is far more stable than its two isomerides. T. H. P.

[Interaction of Diazo-salts and Aromatic Amides of the Higher Fatty Acids.] NATHANAEL SULZBERGER (D.R.-P. 193451. Compare this vol., i, 226).—*p*-Aminostearinamide, prepared either by condensing together stearic acid and *p*-phenylenediamine or by nitrating stearinamide and reducing the resulting *p*-nitrostearinamide, yields a red azo(?)-colouring matter when treated with diazobenzene chloride.

Aminopalmitin- β -naphthalide is produced by condensing β -naphthylamine and palmitic acid at 250 — 300° , nitrating the palmitin- β -naphthalide thus produced, and reducing the mononitro-compound with zinc dust and hydrochloric acid; it couples with diazobenzene chloride and diazotised benzidine to yield respectively brownish-red and yellow colouring matters. G. T. M.

Reaction between Diazo-compounds and Azo-dyes. A. LWOFF (*Ber.*, 1908, 41, 1096—1097).—Griess (this Journ., 1876, ii, 416) has already shown that bisbenzeneazophenol is formed from *p*-hydroxybenzoic acid, carbon dioxide being eliminated. It is now shown that the group $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot$ is displaced from *p*-sulphobenzeneazo- β -naphthol by the action of *p*-nitro- and *o*-chloro-*p*-nitro-diazobenzene chlorides with the formation of the corresponding azo- β -naphthols. W. R.

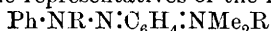
Reaction between Diazo-compounds and Azo-dyes. EUGÈNE GRANDMOUGIN (*Ber.*, 1908, 41, 1403. Compare Lwoff, preceding abstract).—Examples of the removal of the azo-group from an azo-dye have been described previously (Abstr., 1907, i, 987; 1891, 1075). J. J. S.

Yellow Azo- and Violet Quinonoid Salts of Aminoazo-compounds. ARTHUR HANTZSCH and FRIEDRICH HILSCHER (*Ber.*, 1908, 41, 1171—1187).—Although Thiele has shown (*Abstr.*, 1904, i, 208) that *p*-aminoazobenzene hydrochloride can be obtained both in violet and flesh-red modifications, other cases have not hitherto been described. It is found that the salts of aminoazo-compounds exist in two isomeric forms, which are coloured either orange-yellow or bluish-violet. The colour of the salt is determined by the nature of the acid and of the aminoazo-compound; *p*-dimethylaminoazobenzene, *p*-anilinoazobenzene, *p*-dimethylaminoazotoluene, and *p*-bromobenzene-azodimethylaniline generally yield violet salts; dibromotoluene-azodimethylaniline and tribromobenzene-azodimethylaniline give chiefly orange salts, whilst about equal numbers of violet and orange salts are obtained from *p*-aminoazobenzene.

A slight change in the constitution of the aminoazo-compound is sufficient to produce a change in the colour of the salt with the same acid; thus formylaminoazobenzene hydrochloride is orange, whereas the corresponding acetyl compound is violet.

In many cases the same salt has been obtained in the two forms; generally, the orange, labile variety is first precipitated, usually in the form of very thin leaflets, which then more or less readily changes into the violet, stable form, crystallising as a rule in needles. Mixed crystals of the two forms have not been observed.

The orange salts are undoubtedly azo-compounds having the formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\cdot\text{HX}$, since they possess almost the same colour and absorption spectrum as azobenzene and azobenzenetrimethylammonium salts, all of which are orange, since they do not contain a mobile hydrogen atom. On the other hand, the violet salts, since they are also unimolecular, must be isomeric with the orange salts, and must consequently have a quinonoid structure. Attempts to prepare unchangeable representatives of the form



were unsuccessful; nevertheless, a violet solution of a very unstable base, obtained from phenylmethylhydrazine and benzoquinonimine, which must have the formula $\text{NMePh}\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{NH}$, showed the same absorption spectrum as the violet salts.

The orange salts do not change spontaneously at the ordinary temperature into the violet forms, but frequently when heated or crushed. Solutions of the salts contain the two forms in a state of equilibrium, depending largely on the nature of the solvent. Chloroform and indifferent solvents favour the violet form, whilst acetone, alcohol, and ether favour the orange form; for example, the solution of the orange diethylaminoazobenzene hydrochloride in acetone is yellow, whilst in chloroform it is violet; nevertheless, the orange salt is precipitated on adding ether to the chloroform solution.

The following salts were obtained either by adding an ethereal solution of the aminoazo-compound to an excess of acetyl haloid, or by adding a solution of the compound in alcohol or glacial acetic acid to an excess of an aqueous solution of the acid.

p-Aminoazobenzene hydrobromide, hydriodide, and perchlorate are violet; the nitrate is flesh-red, becoming violet when pulverised;

the yellow *sulphate* is very stable, and changes very slowly into the violet form when powdered; the *hydrogen sulphate* is violet; the *oxalate* forms yellow leaflets, and changes into the violet form when heated under paraffin at 100°; the *dithionate* forms flesh-coloured leaflets; the *toluenesulphonate* and *benzenesulphinate* are yellow; the *trichloroacetate* is violet.

p-*Dimethylaminoazobenzene hydrochloride*, *hydrobromide*, *hydriodide*, *sulphate*, *perchlorate*, *nitrate*, *oxalate*, *trichloroacetate*, and *toluenesulphonate* are violet. A solution of the yellow *oxalate* is obtained by mixing the dry base and anhydrous oxalic acid in absolute ethereal solution; the solid salt was not isolated.

p-*Diethylaminoazobenzene* forms golden-yellow crystals, m. p. 95°; the *hydrochloride* and *hydrobromide* are orange-yellow. Only violet salts of *p*-anilinoazobenzene were obtained. *Formylaminoazobenzene hydrochloride* is flesh-coloured; the *sulphate* is yellow. *Acetylaminobenzene hydrochloride* is carmine-red; the *hydrobromide* when dry is carmine-red, but when moistened with ether is violet; the yellow *sulphate* turns violet when powdered.

p-*Tolueneazo-o-toluidine hydrochloride* is carmine-red; the *sulphate* and *oxalate* are orange; the *nitrate* is violet; the *dithionate* and *toluenesulphonate* are flesh-coloured; the *iodate* is carmine-red; the *benzenesulphinate* forms orange needles, which when lightly pressed turn violet, often becoming again orange after some time.

Tolueneazodimethylaniline hydrochloride, *hydrobromide*, *sulphate*, *nitrate*, *iodate*, and *toluenesulphonate* are violet; the *benzenesulphinate* is obtained as a brown precipitate, which quickly turns violet.

Benzeneazo-2:6-dibromoaniline has m. p. 191° (Berju gives m. p. 152°; Abstr., 1884, 1148); the *hydrochloride* and *sulphate* are violet.

p-*Bromobenzeneazodimethylaniline hydrochloride*, *hydrobromide*, *sulphate*, and *nitrate* are violet.

Dibromotolueneazodimethylaniline, $C_7H_5Br_2 \cdot N:N \cdot C_6H_4 \cdot NMe_2$, crystallises in orange needles, m. p. 156°; the *hydrochloride*, *hydrobromide*, *sulphate*, *iodate*, and *toluenesulphonate* are yellow or orange. *Tribromobenzeneazodimethylaniline hydrochloride* and *hydrobromide* are bright orange; violet salts of the last two bases could not be obtained.

W. H. G.

Crystalline Egg-Albumin. EDITH G. WILLCOCK (*J. Physiol.*, 1908, 37, 27—36).—The specific rotation of crystallised egg-albumin is about -31° ; this is a little higher than Hopkins gave, and the result is due to a modification in the method of estimating the protein in solution. Small variations noted are believed to be due to the formation of varying protein-acid substances. If ammonium sulphate is used as the agent in crystallisation, it can be replaced by magnesium sulphate in recrystallisation without affecting the character of the crystals. The dialysed albumin is acid to litmus, but the protein part moves to the cathode and is thus basic. The hypothetical protein-acid can form salts with a weak base. There is some evidence for association with the precipitating salt. The percentage of sulphur in crystallised egg-albumin is 1.324.

W. D. H.

Behaviour of Oxyhæmoglobin towards Reducing Agents.

GUSTAV HÜFNER (*Chem. Zentr.*, 1908, i, 739; from *Arch. Anat. Physiol.*, 1907, 463—465).—The reduction of oxyhæmoglobin seldom proceeds quantitatively; generally, secondary reactions take place, whereby part of the loosely combined oxygen is liberated, oxidising not only other organic substances, but the molecule of the colouring material itself.

J. V. E.

The Influence of Light on the Formation of Carboxymethæmoglobin. A. GRÖBER (*Arch. exp. Path. Pharm.*, 1908, 58, 343—349).—Carboxyhæmoglobin is more rapidly converted into the methæmoglobin derivative by potassium ferri cyanide in the presence of light than in darkness, or in light deprived of the more active chemical rays.

S. B. S.

Hæmin. A. VON SIEWERT (*Arch. exp. Path. Pharm.*, 1908, 58, 386—396).—Hæmin can be prepared by coagulating a solution of red blood corpuscles by heat in the presence of acetic acid, partly drying the coagulum in air, making the latter into a thin paste with alcohol, then adding a small quantity of 10—15% potassium hydroxide solution to the paste, and finally acidifying the viscous solution thus obtained with sulphuric acid; the protein is thereby precipitated and the hæmatin remains in solution. From the latter, by suitable treatment with hydrochloric acid, hæmin can be obtained. The hæmin can be purified by dissolving in dilute sodium hydroxide solution, adding barium hydroxide solution in excess, and treating the barium precipitate thus produced with alcoholic sulphuric acid; the barium sulphate is then filtered off, and alcoholic hydrochloric acid is added to the filtrate at 70°; after a time, the hæmin hydrochloride separates in crystalline form. In addition to the ordinary hæmin, another substance can be prepared, which differs from hæmin in that it is insoluble in sodium hydroxide. This can be obtained by treating the coagulated blood powder (see above) with 95% alcohol containing 1 volume per cent. sulphuric acid and adding alcoholic hydrochloric acid to the solution thus obtained. A mixture of the crystals of hæmin and the alcohol-insoluble substance separates out. The analyses indicate that the latter is an anhydride of the former. The hæmin preparations obtained by the above methods gave, on analysis, numbers agreeing with those previously obtained by Küster.

S. B. S.

Non-existence of Urocarmine as a New and Definite Colouring Matter. LOUIS C. MAILLARD (*J. Pharm. Chim.*, 1908, [vi], 27, 427—437).—Largely polemical. The author maintains that Florence's urocarmine (*ibid.*, 147) is only an impure form of indirubin. When a chloroform solution of urocarmine, prepared according to Florence's directions, is extracted with a 1% sodium hydroxide solution, a bright yellow colouring matter is removed, which is not urobilin, since it shows no fluorescence when treated with an alcoholic solution of zinc chloride or acetate, with or without the addition of ammonia.

If the chloroform solution after treatment with alkali is washed

with dilute acid and with water, evaporated to dryness, and the residue extracted with ether, the ethereal solution has an absorption spectrum identical with that of indirubin, and on evaporation gives a residue having all the characteristics of the latter colouring matter and no longer possessing the tarry appearance of urocarmine.

Removal of the indirubin, which forms the greater part of the chloroform extract, leaves a brownish-black residue. Alcohol extracts a small quantity of indigo-brown from the latter, and leaves a little indigotin. Thus it is shown that urocarmine is a mixture of at least four substances, two of which are definite compounds.

The author suggests that uronigrin is really indigo-brown.

E. H.

The Carbohydrate Group in the Nucleic Acid. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1908, 55, 407—411).—An attempt was made to isolate the reducing group of nucleic acid by treating the sodium salt of the α -acid prepared from thymus with an aqueous extract of thymus gland, which contains a ferment in the presence of which nucleic acids undergo hydrolysis with the scission of phosphoric acid and the alloxuric bases. By this means, only incomplete hydrolysis takes place, and there was evidence of the scission of a reducing substance. The latter was not fermented by yeast, neither could a phenylhydrazine derivative be obtained from it. On hydrolysis with nitric acid, a reducing substance was also obtained, which appeared to be in combination with phosphoric acid (the greater part of which was in organic combination at the end of the experiment).

S. B. S.

Guanylic Acid of the Spleen. WALTER JONES and L. G. ROWN-TREE (*J. Biol. Chem.*, 1908, 4, 289—296).—A true guanylic acid in Bang's sense is obtainable, not only from the pancreas, but also from the spleen nucleoprotein. It is regarded as probable that most nucleic acids yield a similar substance in addition to adenylic acids. Odenius (*Maly's Jahresb.*, 1900, 39) has prepared it from the mammary gland. The character of guanylic acid relied on for its identification is the fact that it does not yield adenine. The pentose and glycerophosphoric acid which Bang states are obtainable from guanylic acid do not appear to have been sought for.

W. D. H.

The Protein Peptones. III. FELIX ROGOZINSKI (*Beit. chem. Physiol. Path.*, 1908, 11, 229—240).—The hydrolysis products of the *Ab* phenylcarbimide fraction previously obtained by Raper (this vol., i, 266) were investigated. The following substances were isolated: a base, m. p. 231—233°, histidine, arginine, glutamic acid, aspartic acid, leucine, tyrosine, aniline, ammonia, and a nitrogen-free substance, m. p. 99—101°. Also the following substances, which were characterised only by qualitative reactions: proline, phenylalanine, and valine or isoleucine. The *Ab* fraction differs from Raper's *Ac* fraction in that the latter contains lysine.

S. B. S.

The Protein Peptones. IV. FELIX ROGOZINSKI (*Beit. chem. Physiol. Path.*, 1908, 11, 241—254).—The peptones obtained by

tryptic digestion of the blood proteins were investigated. The coagulable proteins were separated by heating; the filtrate was saturated with ammonium sulphate, and to the filtrate from the precipitate thus obtained, iron ammonium alum in saturated ammonium sulphate solution was added. After filtering off the resulting precipitate and freeing the liquid from iron by means of hydrogen sulphide, a liquid was obtained which, after saturation with more ammonium sulphate and acidification with dilute sulphuric acid (saturated with ammonium sulphate), gave a precipitate with potassium mercuric iodide solution prepared by Raper's method. The latter precipitate yielded four fractions: (1) a fraction insoluble in 10% potassium iodide, (2) a fraction soluble in water, (3) a fraction soluble in 5% ammonium carbonate, and (4) a fraction soluble in 20% ammonia. The condensation products with phenylcarbimide were prepared from these fractions. From fractions (2) and (3), sub-fractions differing in the solubility of their barium salts could be obtained. It was noticed that the quantity of iron ammonium alum precipitate diminished with a lengthened period of tryptic digestion. Some of the fractions obtained by tryptic digestion appear to be identical with fractions obtained by Raper by similar methods from the products of peptic digestion.

S. B. S.

Tryptophan. EMIL ABDERHALDEN and LOUIS BAUMANN (*Zeitsch. physiol. Chem.*, 1908, 55, 412—415).—Tryptophan was shown by Abderhalden and Kempe to have the specific rotation in *N*-sodium hydroxide solution of $+5.7^\circ$ to $+6.3^\circ$. The correctness of these numbers has been confirmed. In aqueous solution, $[\alpha]_D^{20} - 30.33^\circ$, which is not far removed from that given by Hopkins and Cole (-33°). This fact, perhaps, justifies the designation of tryptophan obtained by the digestion of proteins as the *l*-tryptophan. It can be readily racemised, especially by recrystallisation from pyridine. It is generally found in combination with another substance, *hydroxytryptophan*, $[\alpha]_D^{20} - 11.19^\circ$. The last two facts may account for the varying numbers given for the specific rotation by various observers.

S. B. S.

Protamine as a means of Distinguishing Primary from Secondary Proteoses. ANDREW HUNTER (*Proc. physiol. Soc.*, 1908, v—vi; *J. Physiol.*, 37).—Protamine precipitates other proteins, but protone does not. It also precipitates primary proteoses, but not secondary proteoses, peptones, or polypeptides.

W. D. H.

Protagon. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Soc.*, 1908, i—iv; *J. Physiol.*, 37).—A continuation of the discussion with Cramer; fresh proofs are adduced that protagon is a mixture. An artificial mixture of its constituents manifests the same properties, including specific rotatory power, as "natural protagon."

W. D. H.

The Course of the Fermentative Degradation of Polypeptides. V. EMIL ABDERHALDEN and ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1908, 55, 416—426).—The following poly-

peptides were investigated : *d*-alanylglycine, $[\alpha]_D + 50^\circ$; *d*-alanylglycylglycine, $[\alpha]_D + 30^\circ$, and *d*-alanylglycyl-glycylglycine, $[\alpha]_D + 22.4^\circ$. The rate of change was measured by observing the changes in the optical rotation of the solutions under the influence of various proteoclastic ferments, as the hydrolysis products are either inactive or have very different rotations to the original polypeptide. Parallel experiments were carried out (a) with constant quantities of ferment and varying quantities of polypeptide, and (b) with constant quantities of polypeptide and varying quantities of ferment. The results indicate that in most cases *d*-alanine is the first product of hydrolysis. It is possible that by the method of experiment described, a process may be evolved for the standardisation of enzymes.

S. B. S.

Action of the Juices Expressed from Cells on Polypeptides. EMIL ABDERHALDEN and FILIPPO LUSSANA (*Zeitsch. physiol. Chem.*, 1908, 55, 390—394).—As an extension of previous work, the action of the expressed sap from the cells of the lense and of brain substance was investigated. The former splits *dl*-alanylglycine, glycyl-*l*-tyrosine, diglycylglycine, but only slightly glycyl-*dl*-alanine, into their component amino-acids. The latter juice splits only two of the four dipeptides, namely, *dl*-alanylglycine and diglycylglycine.

W. D. H.

Action of the Juice of *Psalliota campestris* on Polypeptides. EMIL ABDERHALDEN and AUGUSTE RILLIET (*Zeitsch. physiol. Chem.*, 1908, 55, 395—396).—The juice obtained at high pressures from this mushroom splits *dl*-alanylglycine, *dl*-leucylglycine, and diglycylglycine into their component amino-acids. Experiments were also tried with glycyl-*l*-tyrosine, but its decomposition products could not be separated; they are possibly destroyed by a ferment allied to tyrosinase. The results, however, are incomplete, owing to lack of material.

W. D. H.

The Activity of Trypsin and a Simple Method for its Estimation. ERNST FULD (*Arch. exp. Path. Pharm.*, 1908, 58, 468).—A claim for priority (compare Gross, this vol., ii, 234).

S. B. S.

Adsorption of Trypsin by Solids. EDUARD BUCHNER and FRITZ KLATTE (*Biochem. Zeitsch.*, 1908, 9, 436—438).—The following substances were found, after immersion in trypsin solution, to have adsorbed the ferment: fibrin, silk, wool, and cotton threads, linen, paper, agar-agar strips, asbestos, and glass wool. They possessed the power, after removal from the solution, of liquefying gelatin. From the glass wool, the ferment could be readily removed by washing.

S. B. S.

Hydrolytic Enzyme in the Resting Seeds of some Gramineæ. YOSHIO TANAKA (*J. Coll. Eng. Tokyo*, 1908, 4, 39—52).—The optimum temperature for millet diastase is higher than that of barley diastase,

being 50—55°. Millet diastase further differs from that of barley and of other cereals in rapidly liquefying starch to dextrins without producing much maltose until the dextrins have all been converted into achroodextrin. When diastase from millet acts on the glutinous starch of the same plant (*Setaria italica*), the rapid liquefaction and slow saccharification is even more apparent than with ordinary starch. The name α -erythroextrin is suggested for a substance coloured red by iodine and very resistant to millet diastase. A mixture of millet and barley diastases acts much more vigorously than either diastase alone. G. B.

Oxidation Processes in the Living Cell. ALEXIS BACH and ROBERT CHODAT (*Bied. Zentr.*, 1908, 37, 168).—A résumé of the authors' work on this subject (Abstr., 1902, ii, 344, 522; 1903, i, 219, 377, 378, 671; 1904, i, 359, 542, 792). E. J. R.

Some Artificial Peroxydiastases; the Important Rôle of Iron in Their Action. JULES WOLFF (*Compt. rend.*, 1908, 146, 781—783).—The author has indicated previously (this vol., i, 137) the resemblance between the action of certain iron salts and that of the peroxydiastases (name proposed by Bertrand instead of peroxydases). It is now shown that the properties of certain colloidal compounds of iron are practically identical with those of the peroxydiastases. Colloidal ferrous ferrocyanide solution (containing 10 mg. of iron per litre), obtained by interaction of very dilute solutions of an alkali ferrocyanide and a ferrous salt, produces all the reactions of the peroxydiastases. When added to a saturated solution of quinol containing traces of hydrogen peroxide, the reagent gives crystals of quinhedrone in one to two minutes. The action is considerably retarded by traces of ferrous or ferric sulphates, and very small quantities of these salts are sufficient to prevent entirely the formation of quinhedrone. Potassium ferrocyanide has no appreciable effect. Ferric ferrocyanide and ferrous and ferric ferricyanides have an analogous, but smaller, diastatic activity. This artificial peroxydiastase resembles the natural substances also in the following properties. It can be filtered through paper without alteration, but is rendered inactive by filtration through collodion, and it loses part of its activity by one minute's boiling. Traces of mineral acids retard its action, and excess of hydrogen peroxide has the toxic effect discovered by Bach and Chodat (Abstr., 1904, i, 542, 792) for natural peroxydiastases.

In two solutions containing 1 gram of pyrogallol, the amount of hydrogen peroxide corresponding with 28 c.c. of active oxygen, and a quantity of colloidal ferrocyanide equivalent to 0.0004628 gram of iron, to one of which all the hydrogen peroxide was added at first, whilst to the other, half was added at the beginning and the remainder after two hours, the quantities of purpurogallin formed in twenty-four hours were (1) 0.065 gram and (2) 0.123 gram, or 1400 times and 2657 times respectively the weight of iron present. The action was still vigorous after twenty-four hours. E. H.

Proof, by means of the Chromogram Method, that Hydrogenase takes an Active Part in Alcoholic Fermentation. J. GRÜSS (*Ber. Deut. bot. Ges.*, 1908, 26a, 191—196).—A method is indicated, but not as yet described in detail, by means of which the various enzymes contained in plant juices can be identified separately. A drop of the juice is placed on filter paper, when, owing to unequal adsorption by the paper, the enzymes are distributed in various zones and may be identified by colour reactions (thus yielding a "chromogram").

By means of this method, it is shown that, when yeast-juice is added to dextrose solution and powdered sulphur, hydrogenase causes the production of hydrogen sulphide. G. B.

Can the Existence of an Anticatalase be Demonstrated?

H. DE WAELE and ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1908, 9, 264—274).—The catalases used in these experiments were dilute sterile solutions of laked blood. The amount of hydrogen peroxide destroyed at 25° in two hours by the catalases was determined in the presence of various normal sera and antisera produced by the injection of the catalases into different animals. The formation of anticatalases by the methods generally employed in investigations on immunity could not be demonstrated. S. B. S.

The Action of the Electric Current on Yeast-juice.

FRIEDRICH RESENSCHECK (*Biochem. Zeitsch.*, 1908, 9, 255—263).—Experiments were made to determine whether the active substances of the yeast-juice wander to either cathode or anode during the passage of an electric current. It was found that the activity of the solution round the cathode slightly increased, whereas that round the anode slightly diminished, when the time of passage was short (one to three hours). After six hours, the activity round both anode and cathode was diminished. S. B. S.

Action of Beer Yeast on Acid Amides.

JEAN EFFRONT (*Compt. rend.*, 1908, 146, 779—780).—Ehrlich has shown (*Abstr.*, 1907, i, 592) that beer yeast has the property of splitting racemic amino-acids, forming amyl alcohol from leucine. The author finds that yeast contains a diastase *amidase* which decomposes acid amides, giving ammonia and volatile acids. A solution containing 2 grams of asparagine, 10 grams of yeast, and 6 c.c. of *N*-soda in 100 c.c. of water is maintained at 40°; samples removed at intervals, and the ammonia estimated by distillation with magnesia. The amounts of ammonia found indicate that decomposition occurs to the extent of 50% in forty-eight hours, and is complete in seventy-two hours. Control experiments in which (1) asparagine and alkali are present without yeast, and (2) yeast and soda are present but no asparagine, give only trifling amounts of ammonia in seventy-two hours. After sixty hours, the liquid contains the enzyme, amidase, and, if filtered, 100 c.c. of it will completely decompose 1 gram of asparagine in six hours, but the filtrate completely loses its activity when heated at 90°. The diastatic nature of the action of the yeast is confirmed by the

proportionality between the time and the quantity of amide transformed. The active substance of autolysed yeast acts also on aspartic acid, leucine, and glutamic acid. The optimum temperature for its action is $40-45^{\circ}$; alkalis favour, and acids retard, the action. Ten grams of asparagine decomposed by the enzyme gave 5.5 grams of acids, b. p. $110-145^{\circ}$, in which propionic acid was recognised.

The enzyme is invariably present in top-fermentation and aerobic yeasts, and it has been observed in *Amylobacter butylicus*. Its presence in bottom-fermentation yeasts is uncertain. E. H.

Stability of Atoxyl. W. L. YAKIMOFF (*Chem. Zentr.*, 1908, i, 979; from *Deutsch. med. Woch.*, 1908, 34, 200—202).—Dilute atoxyl solutions kept in the dark remain unaltered for some time, although fresh solutions are to be preferred. The stock solution should be made with cold boiled water, stored unsterilised, and screened from the light. Before use, the stock solution must be boiled for one to two minutes. The solution should not be allowed to become alkaline.

J. V. E.

Primary Aromatic Arsonic Acids. OSCAR ADLER and RUDOLF ADLER (*Ber.*, 1908, 41, 931—934).—Béchamp's method (*Compt. rend.*, 1863, 56, i, 1173; Ehrlich and Bertheim, *Abstr.*, 1907, i, 812) of preparing *p*-aminophenylarsonic acid by heating aniline arsenate appears to be a general one for the production of primary aromatic arsonic acids; practically, it is more convenient to heat arsenic acid with an excess of the primary amine at 200° .

2-Aminotolyl-5-arsonic acid, $\text{NH}_2 \cdot \text{C}_7\text{H}_6 \cdot \text{AsO}(\text{OH})_2$, is purified most readily by conversion into the sodium salt, $\text{C}_7\text{H}_9\text{O}_3\text{NAsNa}$, which forms colourless crystals. By treatment with acetic anhydride, it yields an acetyl derivative, $\text{NHAc} \cdot \text{C}_7\text{H}_6 \cdot \text{AsO}(\text{OH})_2$, which is oxidised by alkaline potassium permanganate to 2-acetyl-amino-1-carboxyphenyl-5-arsonic acid, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{AsO}(\text{OH})_2$. The amino-compound resulting from the hydrolysis of the preceding acid is converted by the diazo-reaction into 2-hydroxy-1-carboxyphenyl-5-arsonic acid, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{AsO}(\text{OH})_2$, which crystallises in colourless needles.

Aminonaphthylarsonic acid, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{AsO}(\text{OH})_2$, prepared from α -naphthylamine and α -naphthylamine arsenate at 200° , is purified through the sodium salt, and is converted by the diazo-reaction into hydroxynaphthylarsonic acid, which crystallises in colourless needles.

C. S.

Chemistry of Silicon. ALBERT LADENBURG (*Ber.*, 1908, 41, 966).—The barium triphenylsilicoltrisulphonate described previously (*Abstr.*, 1907, i, 668) is not pure, and contains 3.3% Si instead of 3.9%.

J. J. S.

Organic Chemistry.

Exact Analysis of Marsh Gas. Dissociation of Several Hydrocarbons Effected in the Eudiometer for Measuring Fire-damp. NESTOR GRÉHANT (*Compt. rend.*, 1908, 146, 1199—1200).—A sample of gas collected at the bottom of a shaded pool of water contained 67·7% of methane.

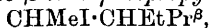
Samples (60 c.c.) of methane, ethylene, and acetylene were introduced respectively into three of the author's eudiometers for measuring fire-damp ("eudiomètre-grisoumètre"), in which spirals of platinum wire are suspended. When these spirals are made red-hot by passing an electric current through them 500—600 times, the methane dissociates gradually, expanding to twice its original volume, hydrogen being liberated and a small amount of carbon deposited; the ethylene gives some small drops of tar, deposits carbon on the walls of the vessel, and increases slightly in volume, whilst the acetylene inflames at the first passage of the current, giving an abundant deposit of carbon on the spiral and on the eudiometer walls, and decreasing considerably in volume.

E. H.

Diethylisopropylmethane [β -Methyl- γ -ethylpentane]. LATHAM CLARKE (*Amer. Chem. J.*, 1908, 39, 572—579).—In an earlier paper (Abstr., 1907, i, 169) an account has been given of the preparation of a new octane (δ -methylheptane). Another octane, β -methyl- γ -ethylpentane (diethylisopropylmethane), has now been synthesised by two different methods.

γ -Ethyl- β -pentanone (diethylacetone), on treatment with magnesium methyl iodide, yields β -methyl- γ -ethyl- β -pentanol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CHEt}_2$, b. p. $156^\circ/760$ mm., which has a strong aromatic odour. On treating this compound with iodine and red phosphorus, β -iodo- β -methyl- γ -ethylpentane, $\text{CMe}_2\text{I}\cdot\text{CHEt}_2$, is obtained, which on reduction with zinc and hydrochloric acid is converted into β -methyl- γ -ethylpentane.

Ethyl ethylisopropylacetoacetate, $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{EtPr})\cdot\text{CO}_2\text{Et}$, b. p. $224^\circ/760$ mm., prepared by Conrad and Limpach's method (Abstr., 1878, 781), is a colourless liquid with a pleasant pine-wood-like odour. On hydrolysis with potassium hydroxide, it yields γ -isopropyl- β -pentanone (*ethylisopropylacetone*), $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{EtPr})$, b. p. $154^\circ/760$ mm., a colourless liquid with a camphor-like odour, which on reduction with sodium in the presence of ether and water furnishes γ -isopropyl- β -pentanol, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{EtPr})$, b. p. $172^\circ/760$ mm., a colourless, oily liquid with an odour like that of sour bread. This substance is converted into β -iodo- γ -isopropylpentane,



which on reduction yields β -methyl- γ -ethylpentane, identical with the product obtained by the preceding method.

β -Methyl- γ -ethylpentane (*diethylisopropylmethane*), $\text{CHMe}_2\cdot\text{CHEt}_2$, b. p. $114^\circ/760$ mm., is a nearly colourless liquid, with D_{15}^{25} 0·7084 and $[\eta]_{\text{D}}^{25}$ 1·3996.

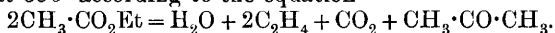
E. G.

Behaviour of Fats and Oils towards Calcium Carbonate.

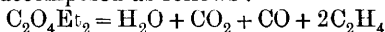
A. KÜNKLER and H. SCHWEDHELM (*Chem. Zentr.*, 1908, i, 1322; from *Seifensieder-Zeit.*, 1908, 35, 165—166).—With the object of throwing light on the origin of petroleum and mineral waxes, the behaviour of fast, oils, waxes, and resins with chalk, common salt, and clay has been investigated. The results indicate the intermediate formation of a calcium salt and a ketone; the latter, especially in the presence of a contact substance like chalk, loses part of its oxygen, probably as water, at moderate temperatures, and as carbon monoxide or carbon dioxide at high temperatures. In these circumstances, it becomes possible to explain the optical activity and high viscosity of these natural oils by the carbon of the keto-group becoming asymmetric in the presence of mixed ketones, and by the formation of complex molecules with branching chains and having high viscosity. As explaining the fact that large quantities of carbon dioxide do not occur with natural oils, it is stated that the elimination of oxygen from the fatty acids only takes place on or near the surface of the earth. J. V. E.

Catalytic Dehydration of Organic Compounds. JEAN B.

SENDERENS (*Compt. rend.*, 1908, 146, 1211—1213. Compare this vol., ii, 166).—The author has extended his work on the dehydration of organic compounds by means of gently-calcined alumina. At 300°, ethyl ether is decomposed into water and ethylene; this is a good method of preparation of the latter gas. Acetic acid at 350° gives acetone, water, and carbon dioxide. Propionic acid is similarly decomposed with formation of diethyl ketone. Ethyl acetate is acted on at 350° according to the equation



Ethyl oxalate is decomposed as follows:



Alumina can also effect the removal of 1 mol. of a halogen hydride; thus, at 250°, chloroisobutane yields isobutylene, chloropropane gives propylene, and ethylene dichloride at 350° furnishes vinyl chloride. Glycerol gives acraldehyde and polyglycerols, and oxalic acid is completely transformed into water and carbon mon- and di-oxide. In all cases, heat alone has no action at the temperatures used. J. C. C.

Mixed Trihalogen Derivatives of Methane. VICTOR AUGER

(*Compt. rend.*, 1908, 146, 1037—1039).—In the preparation of dichloriodomethane by the action of mercuric chloride on iodoform (Serullas, *Ann. Chim. Phys.*, 1827, [ii], 34, 97; Bouchardat, *Annalen*, 1837, 22, 233), chlorodi-iodomethane, HCl_2I , is also formed. Thus distillation under 100 mm. pressure of an intimate mixture of 700 grams of mercuric chloride and 1100 grams of iodoform gives 235 grams of pure dichloriodomethane, CHCl_2I , b. p. 40°/30 mm., 131°/760 mm., D_4^{20} 2.41, and 323 grams of chlorodi-iodomethane, CHClI_2 , a colourless liquid, m. p. -4°, b. p. 88°/30 mm., 200°/760 mm. (decamp.), D_4^{20} 3.17, which is very unstable in the presence of air and light, becoming rapidly coloured violet. It is decomposed by water in the presence of air, giving carbonyl chloride and probably the compound COClI .

The product obtained by Bouchardat (*loc. cit.*) by the action of

bromine on iodoform was a mixture of bromoform and iodine (Löschner, Abstr., 1888, 436), not, as this author thought, dibromiodomethane, CHBr_2 . The latter can be readily prepared by distilling under 150 mm. a mixture of equal parts of iodoform and mercuric bromide. *Dibromiodomethane*, CHBr_2I , is a white, crystalline solid, m. p. 22.5° , b. p. $101-104^\circ/50$ mm., $91^\circ/42$ mm. In the solid state it is stable towards light, but its solutions are very unstable in the presence of air. Bromine converts it even at 0° into bromoform. In the preparation, *bromodi-iodomethane*, CHBrI_2 , is also formed, but cannot be isolated in a pure state; it is readily prepared by the action of cold bromine on iodoform dissolved in carbon tetrachloride, when a mixture of the isomerides is formed which can be separated by fractional crystallisation. Bromodi-iodomethane forms yellow, hexagonal crystals, m. p. 60° , b. p. $110^\circ/25$ mm., unchanged by light when in the solid state, but very unstable in solution. E. H.

Catalytic Dehydration of Alcohols by Calcium Sulphate and by Aluminium Silicate. JEAN B. SENDERENS (*Bull. Soc. chim.*, 1908, [iv], 3, 633—638).—A continuation of work on the dehydration of alcohols by heated inorganic materials (compare Abstr., 1907, ii, 248; i, 577; 1908, ii, 166). Gypsum, dehydrated by careful calcination, and also "plaster of Paris" begin to decompose ethyl alcohol at 370° and dehydrate it rapidly at 420° , yielding a gas containing over 90% of ethylene, the rest being hydrogen. Anhydrite does not decompose ethyl alcohol below 460° , and then only slowly, yielding a gas containing 85.7% of hydrogen and 14.3% ethylene. Gypsum, which has been calcined at a red heat during three hours, approaches anhydrite in its behaviour, acting on alcohol slowly at 485° , and yielding a gas containing 71.2% of hydrogen. These results are explained by assuming that the dehydration is due to the formation of temporary hydrates of the sulphate, and the tendency of the latter to form hydrates is diminished, probably as the result of change in molecular structure, either by heating at a high temperature during a short period or at a low temperature over a long period. In confirmation of this, it is pointed out that finely-powdered gypsum, not previously dehydrated, at first decomposes alcohol rapidly at $420-430^\circ$, and as the heating is continued, the rate falls to 17% of its initial value in the course of ten hours. Aluminium silicate, "modelling clay," and "white clay" also decompose alcohol rapidly at 420° , and, unlike calcium sulphate, their efficiency does not change as the result of their being previously calcined. The gas produced contains 94—98% of ethylene. Kaolin decomposes alcohol slowly at 370° , and more readily at 420° , yielding in the two cases gases containing 87% and 93.5% of ethylene respectively. After being calcined at a red heat, it approaches aluminium silicate and the clays mentioned above in efficiency. The presence of iron oxide or calcium carbonate in the clays modifies their action, and gives rise to a mixture of gases richer in hydrogen. T. A. H.

Studies in Steam Distillation and the Recovery of Amyl Alcohol from the Acid Liquors obtained in the Gerber Process. H. DROOP RICHMOND (*Analyst*, 1908, 33, 209—217).—In

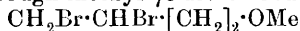
the first part of this paper the author deals with steam distillation from a mathematical and theoretical point of view, whilst in the second part, the results of experiments on the recovery of amyl alcohol from the acid liquid obtained in the Gerber process of estimating fat in milk are described. It appears that a preliminary steam distillation of these liquids yields a crude amyl alcohol, which must be further purified by fractionation before a product boiling at 123—131° is obtained which is suitable for use again in the Gerber process. The readings observed when this recovered amyl alcohol is employed show an excess of about 0.05%.

W. P. S.

Hydrate and Iodo-derivatives of Propargyl Alcohol (Propinol). ROBERT LESPIEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 638—640).—An extension of previous work on propargyl alcohol and some of its derivatives (Abstr., 1898, i, 116; 1899, i, 184). In previous papers it was stated that this alcohol crystallises at -17° . The substance which separates in this way is a *monohydrate*, C_3H_4O, H_2O . *Propargyl phenylurethane* crystallises from benzene on addition of light petroleum, and has m. p. 62—63°. Iodopropargyl alcohol, $Cl:C\cdot CH_2\cdot OH$, previously described (Abstr., 1899, i, 184), changes in part when kept or when treated with boiling water into tri-iodoallyl alcohol, $Cl_2\cdot Cl\cdot CH_2\cdot OH$, which is more readily obtained by adding iodine solution in slight excess to the copper derivative of propinol, suspended in potassium iodide solution and kept at 100°, and may be used for the characterisation of propargyl alcohol; *tri-iodoallyl acetate*, m. p. 41—41.5°, crystallises from acetic acid.

T. A. H.

Propargylcarbinol. ROBERT LESPIEAU and PARISELLE (*Compt. rend.*, 1908, 146, 1035—1037).—By passing a slow current of hydrogen bromide through methyl $\gamma\delta$ -dibromobutyl ether,



(Abstr., 1907, i, 580), kept at 100° until methyl bromide ceases to be evolved, cooling the product to 0°, saturating with hydrogen bromide, and heating in a sealed tube at 100° for ten hours, $\alpha\beta\delta$ -tri-bromobutane, $CH_2Br\cdot CHBr\cdot [CH_2]_2\cdot Br$, a liquid, b. p. 112—113°/13 mm., is formed. When this is heated to boiling with 20% by weight of solid potassium hydroxide, it is partly transformed into a *dibromobutylene*, b. p. 57—60°/14 mm., to which the authors ascribe the formula $CH_2\cdot CBr\cdot [CH_2]_2\cdot Br$.

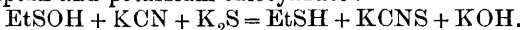
If the action of the potash is carried too far, acetylenic compounds are produced. β -Bromo- Δ^a -butene- δ -ol, $CH_2\cdot CBr\cdot CH_2\cdot CH_2\cdot OH$, a liquid, b. p. 69—72°/11 mm., 175°/760 mm. (decomp.), is formed by the saponification of the corresponding *acetalin*, a liquid, b. p. 75—78°, which results from the action of potassium acetate on $\beta\delta$ -dibromo- Δ^a -butylene. When β -bromo- Δ^a -butene- δ -ol is acted on by a 50% solution of potassium hydroxide, *butinol*, $CH\equiv C\cdot CH_2\cdot CH_2\cdot OH$, a liquid, b. p. 133—136°/760 mm., is formed. This gives a *phenylurethane*, m. p. 66—67°. By treating butinol with an ammoniacal cuprous chloride solution, a yellow precipitate is formed, which, when suspended in a solution of iodine in potassium iodide and gradually heated at 100°, is converted into $\alpha\alpha\beta$ -tri-iodo- Δ^a -butene- δ -ol, $Cl_2\cdot Cl\cdot CH_2\cdot CH_2\cdot OH$, a

substance, m. p. 112—113°, which becomes rose-coloured on exposure to light, and gives an *acetyl* derivative, m. p. 51—52°. E. H.

Alkylene Glycol-chlorohydrin Ethers and Tiffeneau's Wandering of Phenyl. PAUL HOERING (*Ber.*, 1908, 41, 1889—1893).—A reply to Houben (this vol., i, 307). G. Y.

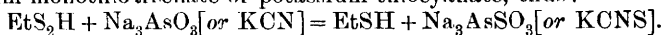
New Method for the Preparation of Diamyl Ether and Ethers of the Higher Alcohols. GEORG SCHROETER and WALTER SONDAG (*Ber.*, 1908, 41, 1921—1925. Compare Schroeter and Herzberg, *Abstr.*, 1905, i, 85; Krafft and Roos, *Abstr.*, 1892, 1219).—Large amounts of methyl ether are formed when methyl alcohol is heated with methionic acid at 120° under pressure, whilst ethyl ether and water distil continually when ethyl alcohol is run into a mixture of ethyl alcohol and methionic acid at 140°, the methionic acid being afterwards regained unchanged. Amyl and higher ethers are readily prepared by heating the corresponding alcohols with small amounts of methionic acid in an open vessel at about 40°. In this manner, amyl ether, b. p. 168—172°, can be obtained from commercial amyl alcohol in a 90—95% yield, taking into account the amount of alcohol regained. After fractionation over sodium, this amyl ether has b. p. 59·5—60°/10 mm. or 169·9—170·6°/760 mm., $\alpha_D + 0·187^\circ$. The commercial amyl alcohol had $\alpha_D - 1·03^\circ$ (compare Guye and Gautier, *Abstr.*, 1895, ii, 149, 195; Marckwald, *Abstr.*, 1904, i, 362). It is found, further, that benzenesulphonic acid and sulphuric acid can be employed in the same manner in the preparation of the higher ethers (compare Norton and Prescott, *Abstr.*, 1885, 496; Mamontoff, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 230). The method of preparation can be employed only in the case of alcohols and ethers with b. p. above 130—140°, and of alcohols which have not too great a tendency to intramolecular fission of water. G. Y.

Action of Alkalis on Sodium Ethyl Thiosulphate. II. AUGUST GUTMANN (*Ber.*, 1908, 41, 1650—1655. Compare *Abstr.*, 1907, i, 671).—Sodium ethyl thiosulphate when boiled with an alcoholic solution of potassium hydroxide is decomposed with the formation of sodium potassium sulphite, and not sulphate or thiosulphate. Since analysis shows that 1 mol. of sulphite is produced from 1 mol. of sodium ethyl sulphite, the reaction which takes place may be represented thus: $\text{NaEtS}_2\text{O}_3 + \text{KOH} = \text{NaKSO}_3 + \text{EtSOH}$. The exact nature of the *substance*, EtSOH, which has not been isolated, is not yet known. It is converted by sodium arsenite in alcoholic sodium hydroxide solution, under pressure, into ethyl mercaptan and sodium arsenate: $\text{EtSOH} + \text{Na}_3\text{AsO}_3 = \text{EtSH} + \text{Na}_3\text{AsO}_4$, and by potassium cyanide and potassium sulphide in aqueous solution into ethyl mercaptan and potassium thiocyanate:



Similarly, sodium ethyl thiosulphate is decomposed by an alcoholic solution of potassium hydrogen sulphide, yielding potassium sodium

sulphite and a *substance*, EtS_2H , thus: $\text{NaEtS}_2\text{O}_3 + \text{KSH} = \text{NaKSO}_3 + \text{EtS}_2\text{H}$. The alcoholic solution of the compound EtS_2H , when treated with sodium arsenite or potassium cyanide, yields ethyl mercaptan and sodium monothioarsenate or potassium thiocyanate, thus:



Attempts will be made to isolate the compound EtS_2H . W. H. G.

Hydrates of the Fatty Acids, according to Measurements of the Viscosity of their Solutions. D. E. TSAKALOTOS (*Compt. rend.*, 1908, 146, 1146—1149. Compare this vol., ii, 260; Dunstan, *Abstr.*, 1904, ii, 805).—The viscosities of aqueous solutions of formic, acetic, propionic, and *n*-butyric acids of different strengths have been measured at 20° by the Poiseuille-Ostwald method, the densities of the liquids being determined by means of a Sprengel-Ostwald pyknometer. The viscosity-coefficients (η) were calculated from the formula $\eta = kdt$, where k is the constant of the apparatus, d the density of the solution, and t its time of flow. To determine k , an experiment was made with benzene, the value of η/d being found from Guye and Friderich's table. The results are given in tabular form. Whilst the viscosity of pure formic acid is greater than those of its homologues, the aqueous solutions of the latter are more viscous than those of formic acid. When the viscosities of the solutions are plotted against their concentrations, the curves obtained for acetic, propionic, and *n*-butyric acid exhibit well-defined maxima corresponding with concentrations of equal molecular quantities of acid and water, indicating the existence of the hydrates $\text{CH}_3 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$, $\text{C}_2\text{H}_5 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$, and $\text{C}_3\text{H}_7 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$. The curve for formic acid, on the contrary, shows a regular decrease in viscosity from pure acid to pure water. *iso*Butyric acid and water form two layers at concentrations between 20% and 50% of acid; the viscosities of the homogeneous solutions are higher than the values calculated by the rule of mixtures. E. H.

Action of Concentrated Sulphuric Acid on Glycerol Esters of Saturated Monobasic Fatty Acids. B. W. VAN ELDIK THIEME (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 855—860).—As is well known, the hydrolysis of esters is a reversible reaction: $\text{R} \cdot \text{CO}_2\text{R}' + \text{H}_2\text{O} \rightleftharpoons \text{R} \cdot \text{CO}_2\text{H} + \text{R}' \cdot \text{OH}$; the equilibrium between the reacting molecules is dependent on the temperature, the nature of the medium, and the nature of the ester. The velocity of the hydrolysis, which is low, is accelerated by hydrogen ions, but, so long as the amount of acid added is insufficient to modify markedly the nature of the medium, the equilibrium is unchanged. Hence the saponification of fats by dilute sulphuric acid cannot be carried to completion, but if concentrated sulphuric acid is employed, not only is the nature of the medium altered, but the reaction now takes place according to the equation: $\text{R} \cdot \text{CO}_2\text{R}' + \text{H}_2\text{SO}_4 \rightleftharpoons \text{R} \cdot \text{CO}_2\text{H} + \text{R}' \cdot \text{O} \cdot \text{SO}_3\text{H}$, and the equilibrium may be shifted completely to the right if the acid is anhydrous, if an excess of the acid is added to the dry fat, and if the temperature is maintained within certain limits. The following experiments show the influence of these three conditions on the saponification. Contrary to Bunte's statement (*Abstr.*, 1895, ii, 95), butter-fat cannot be

saponified completely by 93.5% sulphuric acid at 30—32°. It is found that at that temperature 81% of the butter-fat is hydrolysed by 93.5% sulphuric acid, 89.7% by 98.5% acid, and 92.2% by 100% acid. At 18°, 86.6% of trilaurin is saponified by 6.5 mols. of 100% sulphuric acid, 95.5% by 26 mols. of the same acid, and 100% by 52 mols. of the acid. If the mixture of sulphuric acid and completely saponified trilaurin is heated for one hour at 60°, 12.9% of trilaurin is again formed (compare Grün and Schacht, *Abstr.*, 1907, i, 462). Lauric and sulphuric acids must form a molecular compound, as dry benzene extracts both acids from a mixture of trilaurin and 100% sulphuric acid (compare Hoogewerff and van Dorp, *Abstr.*, 1899, i, 672; Meiger, *Monatsh.*, 1903, 24, 840). When heated with 52 mols. of 94.6% sulphuric acid, trilaurin yields 80% of lauric acid and 20% of mixed glycerides. It is considered that the mono- and di-laurins in this mixture are formed by the action of water on the compounds $C_{11}H_{23} \cdot CO \cdot O \cdot C_3H_5(O \cdot SO_3H)_2$ and $C_3H_5(O \cdot CO \cdot C_{11}H_{23})_2 \cdot O \cdot SO_3H$.

Grün and Schacht (*loc. cit.*) state that the action of sulphuric acid on glycerol leads to the formation of only glycerolmono- and glyceroldi-sulphuric acids. Experiments are now quoted showing that, on the contrary, the product of the action of 98.3% sulphuric acid is chiefly the tri- and di-sulphuric acids, only small amounts of glycerolmonosulphuric acid being formed, but that if the mixture is diluted with water the trisulphuric acid undergoes partial hydrolysis to the di- and mono-sulphuric acids (compare Claësson, *Abstr.*, 1879, 1033).

G. Y.

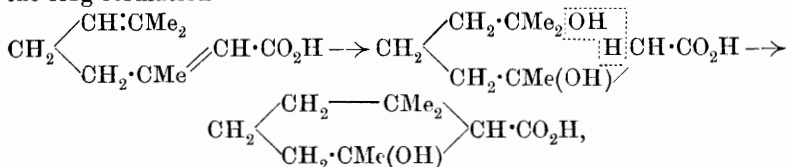
Theory of the Saponification of the Glycerides. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 233—234).—Corrections of a few errors in a previous paper (this vol., ii, 165).

W. H. G.

Theory of Saponification. IV. RICHARD FANTO and MILAN J. STRITAR (*Monatsh.*, 1908, 29, 299—316).—A continuation of the authors' investigation on the hydrolysis of fats (compare *Abstr.*, 1907, i, 464).—The hydrolysis of tallow, beef-fat, tripalmitin, and olive-oil by solutions of potassium hydroxide in absolute, 95%, and 90% alcohol, sometimes in the presence of benzene, has been studied in the manner previously described (*Abstr.*, 1904, i, 843; 1907, i, 277). The mixture of fats which is obtained on treating tripalmitin with an insufficient quantity of potassium hydroxide has also been investigated. The results obtained may be summarised as follows: (1) The hydrolysis of fats by aqueous potassium hydroxide (heterogeneous system) takes place directly. (2) The transformation of fats into ethyl esters under the influence of alcoholic potassium hydroxide solutions ("alcoholysis") in homogeneous systems proceeds throughout in separate stages. The same reaction also takes place in apparently heterogeneous systems; a perfect heterogeneous system cannot, however, be obtained with the constituents employed in studying this change, owing to the miscibility of the various substances produced by the esters. (3) The higher the percentage of water in the alcoholic potassium hydroxide solutions the closer does the course of the reaction approach to the direct hydrolysis of the true heterogeneous system.

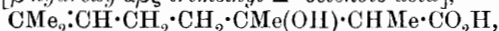
W. H. G.

Mechanism of the Ring Formations in the Geranic Series; Synthesis and Structure of Dihydromyrcene. MARC TIFFENEAU (*Compt. rend.*, 1908, 146, 1153—1155).—Tiemann (Abstr., 1898, i, 374) has explained the formation of isomeric cyclic compounds from derivatives of the geranic series by successive fixation and elimination of two molecules of water, although Barbier and Bouveault had shown (Abstr., 1897, i, 537) that, strictly, a single molecule was sufficient for the ring formation

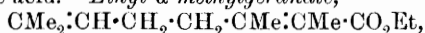


subsequent elimination of the second molecule of water being possible in two ways, thus giving rise to isomeric derivatives. To test the validity of this hypothesis, the author has studied the isomeric change of geranic compounds, in which the hydrogen atoms (one or both) combined with the carbon atom joined to the carboxyl group are substituted by alkyl groups.

When methylheptenone is condensed in the presence of zinc or magnesium with ethyl α -bromopropionate or ethyl or amyl α -chloropropionate, the ethyl or amyl ester of β -hydroxy- α -methyl- $\alpha\beta$ -dihydrogeranic acid [β -hydroxy- $\alpha\beta\zeta$ -trimethyl- Δ^8 -octenoic acid],



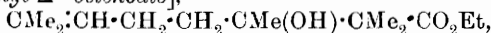
is formed. The *ethyl* ester has b. p. 145—146°/15 mm., D_0 0.9694; the *amyl* ester, 175—185°/14 mm. (decomp.), D_0 0.953. Each of these esters is transformed by acetyl chloride into the corresponding ester of α -methylgeranic acid. *Ethyl α -methylgeranate*,



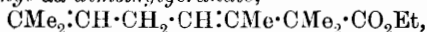
has b. p. 239—240°, D_0 0.9259; the *amyl* ester has b. p. 275—277°, D_0 0.9134. Both esters on saponification give α -methylgeranic acid, b. p. 156—158°/13 mm., D_0 0.964, which when distilled slowly at ordinary pressure loses carbon dioxide and forms Semmler's dihydromyrcene, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CHMe}$ (Abstr., 1901, i, 732), thus showing that the dehydration of the β -hydroxy- α -methyl- $\alpha\beta$ -dihydrogeranic acid is effected at the expense of the hydrogen combined with the neighbouring tertiary carbon atom.

α -Methylgeranic acid, but not its amyl ester, is transformed by sulphuric acid into a cyclic acid, b. p. 155—158°/11 mm., D_0 1.0071, which on distillation at ordinary pressure loses carbon dioxide, giving Semmler's cyclodihydromyrcene (*loc. cit.*), $\text{CMe}_2\begin{matrix} \text{CHMe}\cdot\text{CMe} \\ \text{CH}_2\text{---CH}_2 \end{matrix}\text{CH}$, b. p. 168—170°/70 mm., D_0 0.8325, D_{14}^{20} 0.8217, n_D^{14} 1.460.

Condensation of methylheptenone with ethyl bromoisobutyrate gives *ethyl β -hydroxy- $\alpha\alpha$ -dimethyl- $\alpha\beta$ -dihydrogeranate* [*ethyl β -hydroxy- $\alpha\alpha\beta\zeta$ -tetramethyl- Δ^8 -octenoate*],



b. p. 160—163°/14 mm., D_0 0.9644, which on dehydration by acetyl chloride gives *ethyl $\alpha\alpha$ -dimethylgeranate*,



b. p. 248—251°, D_D^{20} 0.9208, n_D^{20} 1.4609. The corresponding acid has b. p. 166—168°/15 mm. The ester does not undergo ring formation when treated with sulphuric acid. E. H.

The Lactone of $\beta\gamma$ -Dihydroxybutyric Acid. P. CARRÉ (*Compt. rend.*, 1908, 146, 1282—1284. Compare Wagner, Abstr., 1894, i, 563).—When $\beta\gamma$ -dihydroxybutyric acid is distilled in a vacuum and the distillate fractionated, there are obtained at 92—93°/12 mm. the lactone of hydroxycrotonic acid (Lespieau, Abstr., 1904, i, 471) and the lactone of $\beta\gamma$ -dihydroxybutyric acid, $\begin{array}{c} \text{CH}_2\text{---CO} \\ | \quad \diagup \text{O} \\ \text{CH(OH)}\cdot\text{CH}_2 \end{array}$, b. p. 174—175°/12 mm. With alkalis, the acid is regenerated. The benzoyl derivative, $\begin{array}{c} \text{CH}_2\text{---CO} \\ | \quad \diagup \text{O} \\ \text{CH(OBz)}\cdot\text{CH}_2 \end{array}$, has m. p. 101°. J. C. C.

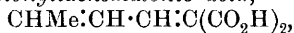
Condensation of Aldol and Crotonaldehyde with Malonic Acid. ADOLF RIEDEL (*Annalen*, 1908, 361, 89—95).—When heated with pyridine in a reflux apparatus, aldol and malonic acid condense, forming sorbic acid and anhydrohydroxydihydrosorbic acid. It is considered that the first product of the reaction is probably $\beta\delta$ -dihydroxybutylmalonic acid, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH(OH)}\cdot\text{CH(CO}_2\text{H)}_2$, which loses carbon dioxide and water, forming β -hydroxydihydrosorbic acid, $\text{CHMe}\cdot\text{CH}\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, two molecules of this then forming the anhydro-acid.

Anhydrohydroxydihydrosorbic acid, $\text{C}_{12}\text{H}_{18}\text{O}_5$, is obtained as a viscid, yellow oil, which loses water, changing into sorbic acid, slowly at the ordinary temperature, but more rapidly when boiled with concentrated hydrochloric acid or when distilled in a vacuum. The silver,

$\text{C}_{12}\text{H}_{16}\text{O}_5\text{Ag}_2$, barium, $\text{C}_{12}\text{H}_{16}\text{O}_5\text{Ba}\cdot 4\text{H}_2\text{O}$, and copper, $\text{C}_{36}\text{H}_{50}\text{O}_{15}\text{Cu}_2$, salts decompose when heated, forming the corresponding sorbates.

When heated together in quinoline, aldol and malonic acid yield an acid, $\text{C}_{12}\text{H}_{16}\text{O}_4\cdot\text{H}_2\text{O}$, which is obtained as a resinous, reddish-yellow oil, and is considered to be a polymeride of sorbic acid. The silver, $(\text{C}_{12}\text{H}_{14}\text{O}_4\text{Ag}_2)_x$, and copper, $(\text{C}_{12}\text{H}_{14}\text{O}_4\text{Cu})_x$, salts are described.

The action of crotonaldehyde on malonic acid in pyridine solution at the ordinary temperature leads to the formation of sorbic acid and small amounts of crotonylidenemalonic acid,



which separates from a mixture of benzene and light petroleum in yellow, granular crystals, m. p. 76°, and on further heating loses carbon dioxide, forming sorbic acid. G. Y.

The System Chloral-Water. C. VAN ROSSEM (*Zeitsch. physikal. Chem.*, 1908, 62, 681—712. Compare this vol., ii, 361).—The freezing points and boiling points of mixtures of chloral and water in various proportions have been determined. The pure chloral used had m. p. -57.5° and b. p. 97°/740 mm.

The form of the freezing-point curve indicates the existence of three compounds of chloral and water containing these components in the

molecular proportions 2:1, 1:1, and 1:7. The first of these is formed very slowly from the components, and undergoes a slow dissociation when fused. Its natural freezing point is about 49° , but the crystals may be heated rapidly to 80° without melting. The ordinary monohydrate, which occurs in two pseudo-symmetric modifications (compare Pope, *Trans.*, 1899, 455), also undergoes a slow dissociation when fused. Its natural freezing point is 47.4° , and the highest melting point observed was 54° . The heptahydrate is rapidly formed from the components, and has a constant melting point of -1.4° ; in this case there is no process of slow dissociation in the liquid phase.

When mixtures of chloral and water are boiled under a pressure of 740 mm., the composition of the vapour is for all concentrations only very slightly different from that of the liquid. When the boiling temperature is plotted against composition, a curve is obtained with a minimum and two points of inflexion. The boiling point of chloral hydrate is lower than that of either component, but does not coincide with the minimum on the boiling-point curve.

At the ordinary temperature, mixtures of chloral and water form two layers to begin with, but after a time become homogeneous, a considerable amount of heat being developed. At high temperatures (170° and above), homogeneous mixtures of chloral and water separate into two layers, the temperature of separation varying with the composition. The lowest temperature of separation observed was in the case of a mixture containing 60 molecular per cent. of chloral.

J. C. P.

Preparation of Methyl α -Chloropropyl Ketone. GEORG KORSCHUN (*Bull. Soc. chim.*, 1908, [iv], 3, 595—596. Compare Vladesco, *Abstr.*, 1891, 1183).—This chloro-ketone was prepared by a method already used for methyl α -chloroethyl ketone (*Abstr.*, 1905, i, 373), namely, the passage of a mixture of chlorine and carbon dioxide through methyl propyl ketone, cooled in a freezing mixture, and contained in a glass vessel connected to a second vessel containing distilled water. The passage of the two gases is continued until the increase in weight of the two vessels and their contents is equal to about 80% of the weight of ketone taken. The chloro-ketone is then isolated by fractional distillation, the portion having b. p. $63^{\circ}/95$ mm. being collected. The yield is 56.4 per cent.

T. A. H

Acetylacetone Compounds of Metals of Group II. SEBASTIAN M. TANATAR and E. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 580—584).—In continuation of their work on the atomic weight of glucinum (*Abstr.*, 1907, i, 888; ii, 261), the authors have prepared the acetylacetone compounds of the metals of the second group in order to compare them with the corresponding glucinum compound. The only one of these compounds resembling that of glucinum is the zinc derivative. But whilst zinc and also cadmium readily form basic acetylacetone derivatives, no basic glucinum compound is formed even on boiling a solution of the normal acetylacetone compound with glucinum carbonate and oxide.

Magnesium acetylacetone, $\text{Mg}(\text{CHAc}_2)_2$, forms long, white crystals and exhibits normal ebullioscopic behaviour in alcohol.

Calcium acetylacetone, $\text{Ca}(\text{CHAc}_2)_2 \cdot 2\text{H}_2\text{O}$, forms white, acicular crystals.

Zinc acetylacetone, $\text{Zn}(\text{CHAc}_2)_2$, forms yellow crystals, m. p. 130° , can be distilled at a pressure of 350 mm., and has the normal molecular weight in boiling alcohol.

Strontium acetylacetone, $\text{Sr}(\text{CHAc}_2)_2 \cdot 2\text{H}_2\text{O}$, is insoluble in any of the ordinary solvents.

Basic cadmium acetylacetone, $\text{Cd}(\text{CHAc}_2)_2 \cdot \text{CdO}$, is amorphous; the normal salt could not be prepared.

Barium acetylacetone, $\text{Ba}(\text{CHAc}_2)_2 \cdot 2\text{H}_2\text{O}$, crystallises in plates.

Mercuric acetylacetone, $\text{Hg}(\text{CHAc}_2)_2$, forms white crystals.

T. H. P.

Application of Barfoed's Reagent to Show the Hydrolysis of Disaccharides by Enzymes. HERBERT E. ROAF (*Bio.-Chem. J.*, 1908, 3, 182—184).—The presence of lactase and maltase may be determined readily by the use of Barfoed's reagent, which when used with certain precautions is not reduced by disaccharides, but is reduced by the monosaccharides into which they are decomposed.

W. D. H.

The Properties of Starch in Relation to its Colloidal Condition. EUGÈNE FOUARD (*Compt. rend.*, 1908, 146, 978—981. Compare this vol., i, 138).—The physical properties of true "soluble starch," filtered through a membrane of collodion, have been further investigated.

The freezing-point depression is nil, so that soluble starch has no osmotic pressure. If the freezing-point depression be taken as less than 0.001° , the molecular weight must be more than 15,000, equivalent to a cluster of 45 molecules of maltose. This, however, is not the initial condition of the molecules, since the act of freezing brings about a slight opalescence of the solution.

Ultramicroscopic examination shows that the particles are much smaller than those in colloidal starch solution, soluble starch being, in fact, indistinguishable from many other true solutions.

Soluble starch may have $[\alpha]_D$ $183^\circ 15'$ to $191^\circ 50'$, according to the texture of the collodion filter employed. The greater the proportion of starch which passes through the filter the higher the specific rotatory power. The various collodion filters may be compared with a set of sieves of different mesh which sort out molecular aggregates of various sizes.

When a solution which passed entirely through the filter was evaporated down in a vacuum at 15° or in the drying-oven at 60° , it would no longer pass through entirely. Dilution of this solution increased the amount which passed from 71.1% to 91.0% of the total starch present. Thus partial evaporation and subsequent dilution served to destroy the condition of perfect solubility of the starch. The author concludes that water itself is an essential factor in modifying the molecular aggregation of pure starch. The action is a reversible

hydrolysis in accordance with the law of mass action. Soluble starch molecules are not necessarily already formed in natural starch, but are more probably formed by the hydrolysing action of water on it. When a true solution of starch is allowed to age, it sets to a compact magma. This change is reversible, is accelerated by acids or low temperature, and retarded by alkalis or heat.

When a starch solution is converted into the granular condition, the conductivity increases from about 73.4×10^{-6} to a constant value of 226.7×10^{-6} . Since the solutions contain a very slight trace of a weak acid, perhaps an acid phosphate (compare Abstr., 1907, i, 391), the increase in conductivity is ascribed to the liberation of the molecules of this electrolyte which remain combined with the soluble starch until the latter is polymerised. When the above-mentioned maximum conductivity is reached, no further granulation occurs, although only a small fraction of the total starch has been coagulated.

A very important relationship must subsist between the organic starch molecule and its saline environment. R. J. C.

Highly Nitrated Cellulose, Hydrocellulose, and Oxycellulose.

ERNST BERL and R. KLAYE (*Chem. Zentr.*, 1908, i, 1381; from *Zeitsch. Schiess. Sprengstoffwesen*, 1907, 2, 381—387. Compare Abstr., 1907, i, 390).—With the object of ascertaining whether highly nitrated cellulose (13.5% N) is true cellulose nitrate, oxycellulose nitrate, hydrocellulose nitrate, or a mixture of these substances, nitration experiments have been carried out with cellulose, hydrocellulose, and oxycellulose under exactly similar conditions. The substances used were cellulose, hydrocellulose, hydracellulose, KMnO_4 -cellulose, Br-oxy-cellulose, HNO_3 -oxycellulose, KClO_3 -oxycellulose, bleaching powder-oxycellulose, and a new *oxycellulose* prepared by the authors by means of calcium permanganate, all of which, besides being freed from fat, were analysed, microscopically examined, and tested with methylene-blue, Fehling's solution, &c. The results show that the product of nitrating pure cellulose at the ordinary temperature is pure cellulose ester; hydrocellulose and oxycellulose, under the same conditions, are not capable of being so highly nitrated as pure cellulose. The solubility of the nitrate from hydro- or oxy-cellulose in a mixture of ether and alcohol is the same as that of the product from pure cellulose which has the same nitrogen content. Hydro- and oxy-cellulose nitrate exhibit a greater attraction for methylene-blue than does the HNO_3 -ester of pure cellulose of identical nitrogen content. Cellulose, hydro- and oxy-cellulose have a greater attraction for methylene-blue than their nitric acid-esters. The viscosity of acetone solutions of nitrates of pure cellulose is considerably greater than that of similar solutions of the nitrates of hydro- and oxy-cellulose having the same nitrogen content and prepared at the same temperature. J. V. E.

Gradual Nitration of Cellulose and Denitrification of Cellulose Nitrate by means of Acid Mixtures. ERNST BERL and R. KLAYE (*Chem. Zentr.*, 1908, i, 1381—1382; from *Zeitsch. Schiess. Sprengstoffwesen*, 1907, 2, 403—406).—It is shown that a cellulose

nitrate (13.86% N), prepared by means of nitrogen pentoxide, is stable when treated with hot water, so the cause of the esterification of cellulose by means of nitric and sulphuric acids not taking place to the theoretical extent (14.14% N) is not due to the instability of the product when containing more than 13.5% N. Rather is it to be ascribed to the sulphuric acid, which, besides favouring the nitration by removing water, has a tendency to hydrolyse the nitric acid-ester, as also have the H-ions of the nitric acid. Equilibrium is established between the ester formed and the acid, and it follows that for every acid mixture a definite cellulose nitrate should be produced. The validity of this explanation is shown by the examination of the product obtained from treating pure cellulose and three different cellulose nitrates with acid mixtures of various strengths, the time of action and the temperature being also varied.

J. V. E.

Cellulose Nitrates and Cellulose Acetonitrates. ERNST BERL and WATSON SMITH, jun. (*Ber.*, 1908, 41, 1837—1844).—When treated with nitric acid and an excess of acetic anhydride, cellulose yields highly nitrated products; acetylation does not occur. Similar products are formed when Pictet and Khotinsky's acetyl nitrate (*Abstr.*, 1907, i, 175) is used. When, however, sulphuric acid is present, acetyl nitrates of cellulose are formed, probably owing to the sulphuric acid hydrolysing several of the nitrate groups and subsequent acetylation. The percentage of nitrogen in these mixed esters tends to increase as the proportion of acetic anhydride to the acid mixture is decreased. The nitrates obtained in the absence of sulphuric acid appear to be less soluble in concentrated sulphuric acid than the ordinary nitrates.

When the proportion of acetic anhydride is small, nitrates are not formed to any appreciable extent.

J. J. S.

A Lævorotatory Substance Found in Altered Beetroot. JULIUS WEISBERG (*Bull. Soc. chim.*, 1908, [iv], 3, 601—604; *Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 946—949*).—Examination of juice expressed from beetroot, which had become "frosted" and partly rotten, showed that it contains a lævorotatory substance, which is precipitated by lead subacetate solution and by milk of lime, and which on boiling with dilute mineral acids decomposes, forming dextrorotatory products (arabinose and dextrose?) which reduce Fehling's solution. The substance appears therefore to differ from Fremy's parapectic acid only in being lævorotatory in place of dextrorotatory, and it is proposed to call it *l*-parapectic acid. There is reason to believe that it is formed from the dextrorotatory pectous matter originally present in the roots.

T. A. H.

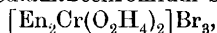
Double Phosphate of Magnesium and Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1908, 146, 1284—1287).—The author has investigated Quantin's method (*Abstr.*, 1893, ii, 104) of separating ammonia from the methylamines, and finds that, contrary to Quantin's statement, monomethylamine is precipitated by magnesium phosphate, giving *magnesium methylamine phosphate*,

* and *Zeitsch. Ver. deut. Zuckerind.*, 1908, 505—508.

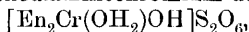
$\text{Mg}(\text{NH}_3\text{Me})\text{PO}_4 \cdot 6\text{H}_2\text{O}$. This is even exclusively formed when equal molecular quantities of ammonia, monomethylamine, and magnesium phosphate are mixed. The latter reagent does not precipitate solutions of di- or tri-methylamine. The conclusion is drawn, therefore, that Quantin's method cannot be applied to the separation of ammonia and monomethylamine, but only to the separation of mixtures of di- and tri-methylamine and ammonia. J. C. C.

Stereochemistry of Chromium. V. Stereoisomeric Aquo- and Hydroxy-salts. PAUL PFEIFFER [with R. PRADÉ and R. STERN] (*Zeitsch. anorg. Chem.*, 1908, 58, 228—256. Compare Abstr., 1907, i, 895; this vol., i, 79).—The preparation and properties of certain stereoisomeric aquo- and hydroxy-salts of chromium are described, including two new examples of structural isomerism.

cis-Dibisaquodiethylenediaminechromium bromide,

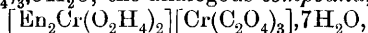


has already been described (*loc. cit.*). The corresponding *chloride*, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{Cl}_3$, prepared by the action of hydrochloric acid on *cis*-hydroxyaquadithylenediaminechromium dithionate,

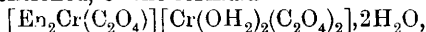


forms lustrous, orange-red plates. Both salts are considerably hydrolysed in aqueous solution, and from these, by the action of pyridine, the basic salts, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{OH}]\text{X}_2$ ($\text{X} = \text{Cl}$ or Br), are obtained in claret-red crystals, soluble with neutral reaction in water. By the action of mineral acids on these salts, the dibisaquo-salts are regenerated, as represented by the equation $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{X}_3 \rightleftharpoons [\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{OH}]\text{X}_2 + \text{HX} + \text{H}_2\text{O}$. By the action of potassium iodide and dithionate respectively on the hydroxy-salts, the corresponding *iodide*, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)\text{OH}]\text{I}_2$, lustrous, claret-red, compact crystals, and *dithionate*, $[\text{En}_2\text{Cr}(\text{OH}_2)\text{OH}]\text{S}_2\text{O}_6$, small, claret-red needles, have been prepared; the latter contains a molecule of water less than the other salts.

By interaction of the *cis*-dibisaquo-bromide, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{Br}_3$, and potassium chromium thiocyanate, $\text{K}_3\text{Cr}(\text{SCN})_6$, in dilute acetic acid solution, the *compound*, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2][\text{Cr}(\text{SCN})_6] \cdot \text{H}_2\text{O}$, is obtained as a red powder. From the same bromide and blue potassium chromium oxalate, $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, the analogous *compound*,



is obtained in lustrous, violet-brown leaflets. A compound isomeric with the last-mentioned, of the formula



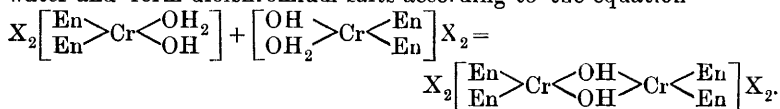
is obtained in small, lustrous, reddish-yellow crystals by interaction of the oxalato-chloride, $[\text{En}_2\text{CrC}_2\text{O}_4]\text{Cl}$, and red potassium chromium oxalate, $[\text{Cr}(\text{OH}_2)_2(\text{C}_2\text{O}_4)_2]\text{K} \cdot 4\text{H}_2\text{O}$, and subsequent addition of alcohol.

The *trans*-salts are prepared by methods analogous to those just described. The green *trans*-compound, $[\text{En}_2\text{CrBr}_2]\text{Br}$, is considerably hydrolysed in aqueous solution, and on adding potassium bromide and pyridine the basic salt, *trans-hydroxyaquadithylenediaminechromium bromide*, $[\text{En}_2\text{Cr}(\text{OH}_2)\text{OH}]\text{Br}_2$, is obtained as lustrous, flesh-coloured leaflets. From the bromide by double decomposition, the corresponding *iodide* and *dithionate* have been prepared; both form flesh-

coloured crystals, and, like the bromide, dissolve in water with neutral reaction. By treating the bromide with hydrobromic acid (compare *cis*-series above), *trans*-dibisaquodiethylenediaminechromium bromide, $[\text{En}_2\text{Cr}(\text{O}_2\text{H}_4)_2]\text{Br}_3$, is obtained in lustrous, prismatic, orange-brown needles; whether two of the water molecules are outside or inside the nucleus is not yet conclusively settled. On treatment with alcohol, or after keeping over phosphoric oxide for some time, the salt loses $2\text{H}_2\text{O}$, and *trans*-di aquodiethylenediaminechromium bromide, $[\text{En}_2\text{Cr}(\text{OH}_2)_2]\text{Br}_3$, is obtained in orange-brown crystals. The *chloride*, *nitrate*, *thiocyanate*, and *oxalate* corresponding with the last-mentioned salt have also been prepared, but the last three salts have not yet been analysed. These salts are considerably hydrolysed in solution, the chief products being the *hydroxyaquo*-salts, $[\text{En}_2\text{Cr}(\text{OH}_2)\text{OH}]\text{X}_2$, mentioned above as being obtainable by other methods.

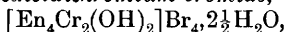
The properties of the corresponding compounds belonging to the *cis*- and *trans*-series are compared in detail. G. S.

Stereochemistry of Chromium. VI. Polynuclear Chromium Salts. PAUL PFEIFFER [with W. VORSTER and RICHARD STERN] (*Zeitsch. anorg. Chem.*, 1908, 58, 272—296. Compare foregoing abstract).—When *cis*-hydroxyaquadidiethylenediaminechromium salts, or the corresponding hydroxybisaquo-salts, are heated, they lose water and form diolchromium salts according to the equation



The bromide of this series is obtained by the action of pyridine on the dilute aqueous solution of *cis*-dibisaquodiethylenediaminechromium bromide, the hydroxybisaquo-salt being formed as intermediate product.

Tetraethylenediaminediolchromium bromide,



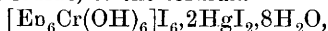
forms lustrous, bluish-violet crystals, soluble with neutral reaction in water; the bromine is precipitated quantitatively by silver nitrate. The salt is decomposed on heating with mineral acids; with concentrated hydrochloric acid the *cis*-dichloro-chloride, $[\text{En}_2\text{CrCl}_2]\text{Cl} \cdot \text{H}_2\text{O}$, is obtained, and with hydrochloric acid the *cis*-bromobisaquo-bromide,



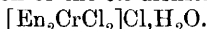
By double decomposition of the diolbromide with potassium iodide, the corresponding *iodide*, $[\text{En}_4\text{Cr}_2(\text{OH})_2]\text{I}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, is obtained in small, bluish-violet, lustrous needles.

A number of hexaethylenediaminehexoltetrachromium salts, which appear to have the general formula $\{\text{Cr}[\text{En}_2\text{Cr}(\text{OH})_2]_3\}\text{X}_6$, have been prepared as follows. Partly dehydrated chrome alum is heated for some time with ethylenediamine monohydrate, and the product is then treated with a little water and filtered; the residue is the crude sulphate of the series in question. When the sulphate is treated with hydrochloric acid in moderate excess, *hexaethylenediaminehexoltetrachromium chloride*, $[\text{En}_6\text{Cr}_4(\text{OH})_6]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$, is obtained in small, red needles. From this salt by double decomposition, the corresponding

bromide and iodide, with $4\text{H}_2\text{O}$, thiocyanate, with H_2O , dithionate, with $7\text{H}_2\text{O}$, nitrate, with $6\text{H}_2\text{O}$, and chromate, with $5\text{H}_2\text{O}$, have been obtained; all occur in red needles except the chromate, which forms a brownish-red, apparently amorphous powder. A double salt of the iodide and mercuric iodide, of the formula



has also been obtained as a yellowish-red precipitate. These salts are slightly alkaline in reaction, do not unite with hydrochloric acid like the hydroxy-salts, and on heating with concentrated hydrochloric acid are decomposed with production of the *cis*-dichloro-chloride,



It is pointed out that these red hexol salts appear to be closely related to the rhodoso-salts of Jörgensen. G. S.

Stereochemistry of Chromium. VII. Mixed Luteo-salts.

PAUL PFEIFFER [with TH. GASSMANN and H. PIETSCH] (*Zeitsch. anorg. Chem.*, 1908, 58, 297—316. Compare foregoing abstracts).—As the isomerism persists when the nucleus halogen atoms in the *cis*- and *trans*-diaciodiethylenediaminechromium (and cobalt) salts, $[\text{En}_2\text{CrX}_2]\text{X}$, are ionised by displacing them by water molecules (previous abstract, Part V), the question was investigated as to whether the *cis-trans*-isomerism also persists when a halogen in the nucleus is displaced by an ethylamine or propylamine group. This is found not to be the case, identical simple and mixed luteo-salts being obtained from the *cis*- and *trans*-compounds. The change of configuration takes place with the *trans*-compounds.

The salts were either prepared directly by heating the respective dichloro-chlorides, $[\text{En}_2\text{CrCl}_2]\text{Cl}$ and $[\text{En}_2\text{CoCl}_2]\text{Cl}$, with ethylenediamine and propylenediamine (Pn) respectively until the product became yellow, and then adding the alkali salt of the appropriate acid, or by double decomposition. *Diethylenediaminepropylenediaminechromium bromide*, $[\text{En}_2\text{Cr Pn}]\text{Br}_3 \cdot 2\text{H}_2\text{O}$, forms lustrous, yellow needles; the *iodide*, with $2\text{H}_2\text{O}$, and the *thiocyanate*, with $\frac{1}{2}\text{H}_2\text{O}$, also form lustrous, yellow needles. *Diethylenediaminepropylenediaminecobalt bromide* $[\text{En}_2\text{Co Pn}]\text{Br}_3 \cdot 3\text{H}_2\text{O}$, and the *iodide*, with $3\frac{1}{2}\text{H}_2\text{O}$, occur in brownish-yellow needles; the *thiocyanate*, with $\frac{1}{2}\text{H}_2\text{O}$, in small, yellow crystals. The solubility of the cobalt salts in water has been determined.

By interaction of the complex chromium and cobalt bromides just mentioned with potassium chromium oxalate and potassium cobalt oxalate respectively in aqueous solution, the four compounds, $[\text{En}_2\text{Cr Pn}][\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 4\frac{1}{2}\text{H}_2\text{O}$, silver-grey leaflets,

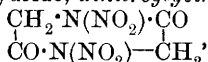
$[\text{En}_2\text{Cr Pn}][\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 4\frac{1}{2}\text{H}_2\text{O}$, green needles, $[\text{En}_2\text{Co Pn}][\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 5\text{H}_2\text{O}$, small green crystals, and $[\text{En}_2\text{Co Pn}][\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 4\frac{1}{2}\text{H}_2\text{O}$, lustrous, silver-grey crystals, have been prepared. The compounds are decomposed into their components by heating with hydrochloric acid. By an analogous method, the four corresponding *cyanides* have been prepared, all of which occur in yellow crystals. G. S.

Distillation of Esters of Amino-acids by means of the Geryk Pump. PHOEBUS A. LEVENE and D. D. VAN SLYKE (*Biochem. Zeitsch.*, 1908, 10, 214).—A sufficiently low pressure for the fractional

distillation of esters of amino-acids was obtained by the use of the Geryk pump, and the use of liquid air avoided, the vessel immersed in liquid air being replaced by one filled with cotton wool saturated with sulphuric acid and immersed in a freezing mixture.

W. D. H.

Nitration and Acetylation of Glycine Anhydride and its Methyl Homologues: Alanine Anhydride and α -Aminoisobutyric Anhydride. ANTOINE P. N. FRANCHIMONT and H. FRIEDMANN (*Rec. trav. chim.*, 1908, 27, 192—206. Compare Donk, Abstr., 1907, i, 831).—When glycine anhydride is added to a mixture of absolute nitric acid and acetic anhydride, *dinitroglycine anhydride*,



is obtained. This compound separates from ethyl acetate in large, glistening plates, which decompose at 145—146°. When dissolved in alcoholic ammonia, it furnishes nitroaminoacetamide, whilst sodium hydroxide converts it into the sodium salt of nitroaminoacetic acid.

Alanine anhydride dissolves in absolute nitric acid with formation of a *dinitrate*, which on treatment with acetic anhydride yields *dinitroalanine anhydride*, $\text{CHMe} < \begin{array}{c} \text{N}(\text{NO}_2) \cdot \text{CO} \\ \text{CO} \cdot \text{N}(\text{NO}_2) \end{array} > \text{CHMe}$. This forms colourless needles decomposing at 136°.

Methyl α -aminoisobutyrate, $\text{C}_5\text{H}_{11}\text{O}_2\text{N}$, b. p. 136°/749 mm., D_4^{25} 0.9787, was prepared from α -aminoisobutyric acid; *hydrochloride*, decomp. 183°. When the ester is heated in a closed vessel for thirty-six hours at 230—240°, it forms *α -aminoisobutyric anhydride*, $\text{C}_8\text{H}_9\text{O}_2\text{N}_2$, which sublimes without melting. *α -Aminoisobutyramide*, $\text{C}_4\text{H}_9\text{ON}_2$, m. p. 127°, is very soluble in water, alcohol, and chloroform. *α -Nitroaminoisobutyric*

anhydride, $\begin{array}{c} \text{CMe}_2 \cdot \text{N}(\text{NO}_2) \cdot \text{CO} \\ | \\ \text{CO} - \text{NH} - \text{CMe}_2 \end{array}$, crystallises from hot water in fine colourless needles, m. p. 166° (decomp.). When treated with absolute nitric acid and acetic anhydride, this compound is transformed quantitatively into *dinitro- α -aminoisobutyric anhydride*, $\text{C}_8\text{H}_9\text{O}_6\text{N}_4$, rhombohedra, m. p. 108°, insoluble in water, but soluble in alcohol, ether, and benzene.

Diacetylglycine anhydride, $\text{C}_8\text{H}_{10}\text{O}_4\text{N}_2$, m. p. 102°, is very soluble in water and alcohol, and is readily prepared by dissolving glycine anhydride in acetic anhydride.

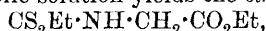
Diacetylalanine anhydride, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$, m. p. 132°, crystallises from hot water in shining needles. α -Aminoisobutyric anhydride is not attacked when boiled with acetic anhydride and sodium acetate, or with acetyl chloride.

W. O. W.

Derivatives of Dithiocarbaminoacetic Acid. H. KÖRNER (*Ber.*, 1908, 41, 1901—1905).—A study of the action of carbon disulphide on amino-acids.

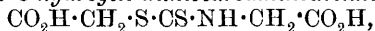
A solution of *potassium dithiocarbaminoacetate* (*potassium glycine-N-dithiocarboxylate*), $\text{CS}_2\text{K} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{K}$, is obtained by the action of carbon disulphide on a solution of glycine in aqueous potassium hydroxide. The *acid* is unstable, and on liberation decomposes,

forming carbon disulphide. The potassium salt reacts easily with alkyl haloids, forming salts of the type $\text{CS}_2\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$, which on acidification yield stable, crystalline acids, $\text{CS}_2\text{R}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The *S*-ethyl *O*-hydrogen ester, $\text{CS}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, formed by shaking the potassium salt with ethyl bromide, crystallises in white prisms, m. p. 123—124°, and when treated with hydrogen chloride in ethyl-alcoholic solution yields the *ethyl* ester,



crystallising in white needles, m. p. 72°. The *O*-methyl *S*-ethyl ester, $\text{CS}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, has m. p. 75°.

S-Carboxymethyl *O*-hydrogen dithiocarbaminoacetate,

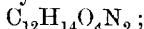


prepared from the potassium salt and potassium chloroacetate, crystallises in white prisms, decomp. 80°, m. p. 120°, and changes when heated at 100°, or more slowly over sulphuric acid at the ordinary temperature, into *rhodaninacetic acid* (4-*keto*-2-thiothiazolidine-3-acetic acid), $\text{S} \begin{smallmatrix} \text{CS} - \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix}$, which is formed also by the

action of ethyl chloroacetate on potassium dithiocarbaminoacetate. It crystallises in yellow needles, m. p. 148°, and, when dissolved in hot water, again forms *S*-carboxymethyl *O*-hydrogen dithiocarbaminoacetate. *Ethyl rhodaninacetate*, $\text{C}_7\text{H}_9\text{O}_3\text{NS}_2$, crystallises in yellow needles, m. p. 58°. The *methyl* ester is obtained as a yellow oil which rapidly solidifies.

The action of α -bromopropionic acid on potassium dithiocarbaminoacetate leads to the formation of 4-*keto*-2-thio-5-methylthiazolidine-3-acetic acid, $\text{S} \begin{smallmatrix} \text{CS} - \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{CHMe} \cdot \text{CO} \end{smallmatrix}$. G. Y.

Hydroxyprolines. HERMANN LEUCHS and HEINRICH FELSER (*Ber.*, 1908, 41, 1726—1735).—The two synthetical hydroxyprolines (*Abstr.*, 1905, i, 545) when reduced with hydriodic acid and red phosphorus at 140—150° yield proline (pyrrolidine-2-carboxylic acid). Both acids combine with phenylcarbimide, yielding *derivatives*,



that from the α -acid crystallises from water in four-sided plates, m. p. 194—195° (corr., decomp.), and that from the β -acid forms six-sided plates, m. p. 187° (corr.). The phenylcarbimide derivatives readily yield *phenylhydantoins*, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_2$, when heated with dilute hydrochloric acid, these melt respectively at 164—165° (corr.) and 156—158° (corr.).

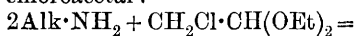
In order to determine whether one of the two artificial hydroxyprolines is the racemic form of the hydroxyproline obtained by hydrolysing gelatin, attempts have been made to racemise the natural product, but without success; the stability of this acid indicates that the hydroxy-group is in the β - or γ -position. Attempts to resolve the artificial acids did not meet with success.

δ -Chloro- α -bromovalerolactone reacts with aqueous methylamine, yielding a mixture of two hydroxyhygric acids. The two are readily separated by means of their copper salts, one of which is insoluble in alcohol.

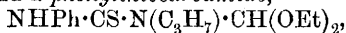
The *b*- γ -hydroxy-*N*-methylproline (*hydroxyhygric acid*), $C_6H_{11}O_3N$, obtained from this insoluble copper salt is identical with the product obtained by methylating *b*- γ -hydroxyproline. It crystallises from methyl alcohol in irregular polyhedra, m. p. 226—227° (corr.) (decomp.). The isomeric *a*- γ -hydroxy-*N*-methylproline crystallises in needles, m. p. 207—208° (corr.) (decomp.). J. J. S.

α -Amino-*n*-hexoic Acid [Leucine]. H. KUDIELKA (*Monatsh.*, 1908, 29, 351—358).—The author has prepared leucine by Fischer's method (Abstr., 1900, i, 646) from both natural and synthetical *n*-hexoic acids. Using Kahlbaum's preparations, 100 parts of the latter gave 37 parts of leucine, whilst 100 parts of the former gave only 6 parts. The copper salt, pale blue leaflets, nickel salt, greenish-blue salt, and cobalt salt, red leaflets, are described. The methylated base forms an aurichloride, $C_9H_{19}O_2N \cdot HAuCl_4$, yellow leaflets, m. p. 142°. The solubilities of *d*- and *l*-leucine and of their copper salts in water are recorded. J. C. C.

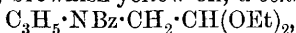
sec.-Aminoacetals. CARL PAAL and LEO VAN GEMBER (*Arch. Pharm.*, 1908, 246, 306—314).—The authors have prepared a number of sec.-aminoacetals by the action of primary alkylamines on chloroacetal:



Tertiary bases are also formed in this reaction, which, however, were not investigated. The alkylaminoacetals are basic oils with an unpleasant odour, and are soluble in water. *n*-Propylaminoacetal, b. p. 185—192°, forms a hydrochloride, white, hygroscopic needles, m. p. 103—105°, a hydrogen oxalate, m. p. 175°, a nitrosoamine, viscid, yellow oil, and a phenylthiocarbamide,



white needles, m. p. 44—47°. Allylaminoacetal, b. p. 194—197°, forms a hydrochloride, m. p. 110—112°, a hydrogen oxalate, m. p. 175°, a nitrosoamine, a viscid, brownish-yellow oil, a benzoyl derivative,



viscid, yellow oil, a phenylcarbamide, yellow oil, and a phenylthiocarbamide, white, stellate needles, m. p. 81—82°. *n*-Butylaminoacetal, b. p. 207—210°, is a colourless, mobile liquid, of which the hydrogen oxalate, m. p. 190°, the nitrosoamine, brown, viscid oil, the benzoyl derivative, yellow, viscous oil, the phenylcarbamide, m. p. 50—52°, and the phenylthiocarbamide, m. p. 51—54°, were prepared. isoAmylaminoacetal, b. p. 215—220°, gives a hydrochloride, colourless plates, m. p. 33°, a hydrogen oxalate, m. p. 204°, a nitrosoamine, yellow oil; a benzoyl derivative, viscid oil, and a phenylthiocarbamide, m. p. 38—42°. J. C. C.

Properties of the Metallic Dithiocarbamates. MARCEL DELÉPINE (*Compt. rend.*, 1908, 146, 981—984; *Bull. Soc. chim.*, 1908, [iv], 3, 643—652. Compare Abstr., 1907, i, 594).—The author has prepared well-crystallised specimens representative of various types of dithiocarbamides, namely:

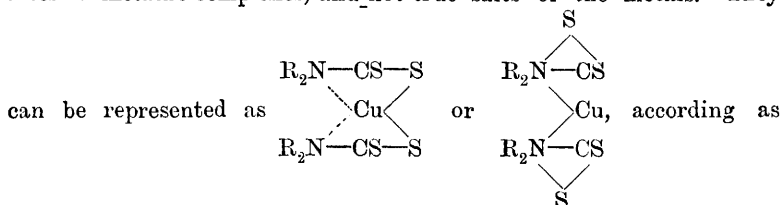
- I. $(\text{NH}_2 \cdot \text{CS}_2)_2\text{Ni}$ and $(\text{NH}_2 \cdot \text{CS}_2)_3\text{Co} \cdot 2\text{C}_4\text{H}_9\text{O}$ (acetone).
 II. $\text{NHPr} \cdot \text{CS}_2\text{Na} \cdot 4\text{H}_2\text{O}$, $\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS}_2\text{Na} \cdot 4\text{H}_2\text{O}$, and $\text{NHPh} \cdot \text{CS}_2\text{Na} \cdot 3\text{H}_2\text{O}$.
 III. $(\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS}_2)_2\text{Ba} \cdot 2\text{H}_2\text{O}$, $\text{NMe}_2 \cdot \text{CS}_2\text{Na} \cdot 2\frac{1}{2}\text{H}_2\text{O}$, and $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2\text{Na} \cdot 4\text{H}_2\text{O}$.
 IV. $\text{NHPr} \cdot \text{CS}_2\text{Cu}'$; $(\text{C}_4\text{H}_9 \cdot \text{NH} \cdot \text{CS}_2)_2\text{Zn}$, and $(\text{NHPh} \cdot \text{CS}_2)_3\text{Co}$.
 V. $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2\text{Ag}$; $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Pb}$; $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Cu}$, and $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_2\text{Ni}$.
 VI. $(\text{NMe}_2 \cdot \text{CS}_2)_3\text{Co} \cdot 2\text{CHCl}_3$; $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_3\text{Co}$, and $[\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CS}_2]_3\text{Fe}$.

The salts, which are often soluble in ether, chloroform, benzene, and carbon disulphide, have a tendency to crystallise with their solvent. Salts of alkali and alkaline-earth metals, also of zinc, are colourless; those of copper, nickel, cobalt, and iron are intensely and variously coloured, but without regard to the ordinary colours of these metals, in their salts. Ferrous and cobaltous salt could not be obtained, but, on the other hand, cupric salts rapidly and spontaneously change into cuprous salts. The salts $\text{NHPr} \cdot \text{CS}_2\text{Na}$ and $\text{NMe}_2 \cdot \text{CS}_2\text{Na}$ produce twice the theoretical freezing-point depression in aqueous solution.

In benzene or ethylene dibromide, the salts $[\text{NBu}_2\text{CS}_2]_2\text{Ni}$ and $[\text{NBu}_2\text{CS}_2]_3\text{Co}$ [$\text{Bu} = \text{C}_4\text{H}_9$], as also the ferric salt, give normal freezing-point depressions, showing that they correspond with the type RX_3 , and not with the type R_2X_6 .

The copper salt, $[\text{NBu}_2\text{CS}_2]_2\text{Cu}$, gives a non-conducting solution in benzene, although the dry compound becomes electrified when pulverised. The absence of conductivity in solutions of these salts in moist organic solvents corresponds with a considerable indifference towards reagents. Thus copper is not precipitated by hydrogen sulphide, or nickel, cobalt, or iron by ammonium sulphide. $\text{NBu}_2 \cdot \text{CSAg}$ produces no precipitate even after ten minutes with hydrochloric acid. Lead, however, is easily precipitated from the dithiocarbamates by sulphuric acid or hydrogrogen sulphide.

The author contends that metallic dithiocarbamates are really internal metallic complexes, and not true salts of the metals. They

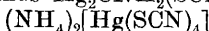


Werner's or Blomstrand and Jörgensen's notation is adopted. The alkali metals, which form true salts, can be replaced by copper present as oxide, and the copper dithiocarbamates are also stable in presence of sulphuric acid. Furthermore, several of the compounds are volatile; thus nickel and copper diisobutyldithiocarbamates distil unchanged in a vacuum.

R. J. C.

Hydrolysis of Aqueous Solutions of Ammonium Thiocyanate in Presence of Metallic Hydroxides. HERMANN GROSSMANN (*Zeitsch. anorg. Chem.*, 1908, 58, 265—271).—The freshly-

precipitated, well-washed hydroxides were boiled with a 10% aqueous solution of ammonium thiocyanate until no further change occurred. In these circumstances, the hydroxides of the alkalis and alkaline earths, including lithium and magnesium, decomposed the ammonium salt completely, the thiocyanates of the respective metals remaining in solution. With hydroxides of less basic character, there are three possible cases: (1) salts with complex cations are formed, for example, $\text{Zn}(\text{NH}_3)_2(\text{SCN})_2$ and $\text{Cu}(\text{NH}_3)_2(\text{SCN})_2$; (2) salts with complex anions are formed, for example, $\text{NH}_4[\text{Ag}(\text{SCN})_2]$ and $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4] \cdot 4\text{H}_2\text{O}$; (3) both complex cations and anions may be formed. As examples of the last class, the compounds $\text{Hg}_2\text{ONH}_2(\text{SCN})_2$ and



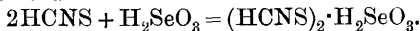
(Fleischer, 1875), as well as the cadmium compounds, $\text{Cd}(\text{NH}_3)(\text{SCN})_2$, $\text{Cd}(\text{NH}_3)_2(\text{SCN})_2$, and $(\text{NH}_4)_2\text{Cd}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}$, are already known, and by slightly modified methods the compounds $\text{Ni}(\text{NH}_3)_2(\text{SCN})_2$, bluish-green crystals, and $\text{Ni}(\text{NH}_3)_4(\text{SCN})_2$, dark blue crystals, have been prepared.

Hydroxides of very slight basic character, such as those of glucinum, aluminium, iron (ferric), and chromium, have practically no action on ammonium thiocyanate at boiling temperature. G. S.

[Hexathiocyno-salts of Molybdenum.] JOHANNA MAAS and JULIUS SAND (*Ber.*, 1908, 41, 1861).—A correction. It has been found possible to prepare the characteristic yellow zinc salt of the hexathiocyno-series as follows: an excess of ammonium thiocyanate is added to a solution of the green molybdenum trichloride containing hydrochloric acid, and kept at the ordinary temperature for twelve hours, air being excluded; the resulting liquid is then rendered ammoniacal, and finally treated with an ammoniacal solution of zinc chloride.

Since the yellow salts are formed in the absence of air, they must be aquo-salts having the general formula $\text{Mo}(\text{SCN})_6(\text{OH}_2)\text{R}_3$, and not compounds of the type $\text{Mo}(\text{SCN})_6(\text{OH})\text{R}_3$ as stated previously (this vol., i, 397). W. H. G.

Thiocyanoselenious Acid: New Method for Estimating Selenium. W. I. IWANOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 661—664).—*Thiocyanoselenious acid*, $(\text{HCNS})_2 \cdot \text{H}_2\text{SeO}_3$, is formed by the interaction of a thiocyanate and selenious acid in presence of hydrochloric acid, the reactions being expressed by the equations:
 $\text{NH}_4\text{CNS} + \text{HCl} = \text{HCNS} + \text{NH}_4\text{Cl}$ and



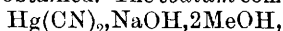
It separates as a voluminous precipitate, composed of pyramidal crystals. By heating or by the action of water, alcohol, glycerol, acid, or alkali, it decomposes with precipitation of red selenium. When treated with benzene or carbon disulphide, it dissolves partly, giving a yellow solution, which, on shaking with water, yields a colloidal selenium solution having at first a rose-red, and later a purple, colour. Nitric acid dissolves and oxidises it into selenious and sulphuric acids.

Attempts to prepare an analogous tellurium compound were unsuccessful.

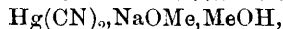
The instability of thiocyanoselenious acid affords a ready means of estimating selenium. To a solution containing from 0.1 to 0.4 gram of selenium, and diluted to about 600 c.c. with water, are added 20—30 c.c. of ammonium or potassium thiocyanate solution, and, after thorough stirring, about 150 c.c. of 25% hydrochloric acid. After being heated on a water-bath for twelve hours, the solution is filtered through a filter previously dried at 105° and weighed, the amorphous selenium on the filter being well washed with hot water, dried at 105°, and weighed. The precipitate often contains a small proportion of sulphur, which may be estimated by oxidising the precipitate in a glass or porcelain beaker with aqua regia, evaporating with hydrochloric acid to expel the nitric acid, dissolving the residue in hydrochloric acid and hot water, filtering, and precipitating with barium chloride. This method gives much better results than washing the precipitate with carbon disulphide, as in some cases part of the selenium is dissolved by this solvent, whilst in others, both sulphur and selenium remain undissolved.

T. H. P.

Compounds of Mercuric Cyanide with Alkalis and Nitric Acid. KARL A. HOFMANN and H. WAGNER (*Ber.*, 1908, 41, 1628—1634. Compare this vol., i, 143).—Mercuric cyanide solution decolorises a solution of phenolphthalein made alkaline with a little sodium hydroxide; this result cannot be due to hydrolysis, as only concentrated solutions of alkali precipitate oxide or basic salt, and from the agreement amongst themselves of the constants, determined by means of the solubility, depression of freezing point, conductivity, and hydrolysis of ethyl acetate, the conclusion is arrived at, that in dilute solutions the complex ion $\text{Hg}(\text{CN})_2 \cdot \text{OH}$ is present. Hexagonal crystals having the composition $\text{Hg}(\text{CN})_2 \cdot \text{KOH} \cdot 1\frac{1}{2} \text{H}_2\text{O}$ have been obtained from a solution of 13 grams of mercuric cyanide, 40 grams of potassium hydroxide, and 60 c.c. of water. An aqueous solution of this salt gives crystals of mercuric cyanide on concentration. Oxidising agents, such as hydrogen peroxide, precipitate mercury, and the aqueous solution gives silver cyanide with silver nitrate, mercury acetylide with acetylene, and cyanate with permanganate, showing that this solution is much more reactive than mercuric cyanide solution. The corresponding sodium compound, $\text{Hg}(\text{CN})_2 \cdot \text{NaOH} \cdot 1\frac{1}{2} \text{H}_2\text{O}$, forms long prisms, which in a vacuum over phosphoric oxide lose $\frac{1}{2}$ mol. of water. When the operations are carried out in alcoholic instead of aqueous solution, analogous alcohol compounds are obtained. The sodium compound,



forms hexagonal, doubling refracting prisms, which lose 1 mol. of methyl alcohol in a vacuum over phosphoric oxide; the potassium compound is similar, and the sodium methoxide derivative,



forms rectangular prisms and is stable in a vacuum, but decompose in the light.

A hot solution of mercuric cyanide and 68% nitric acid deposits on cooling the compound, $\text{Hg}(\text{CN})_2 \cdot \text{HNO}_3$, which crystallises in needles. It is explosive, and the strongly acid aqueous solution does not give precipitates with either ammonia or alkali, a distinction from the double salt, $\text{Hg}(\text{CN})_2 \cdot \text{AgNO}_3$.

W. R.

Constitution of Certain Mercuric Salts with Complex Cations. VINCENZO BORELLI (*Gazzetta*, 1908, 38, i, 361—426).—The author has studied the reactions, cryoscopic behaviour, electrical conductivity, and transport numbers of the complex salts which mercuric cyanide forms with the strongly dissociated mercuric perchlorate and nitrate, and with the feebly dissociated mercuric chloride and acetate. The results indicate that all these complex salts are constitutionally analogous, and all contain the same cation, HgCN^+ . They are hence to be regarded as salts of "cyanomercury" having the constitutions $\text{HgCN}\cdot\text{ClO}_4$, $\text{HgCN}\cdot\text{NO}_3$, $\text{HgCN}\cdot\text{Cl}$, and $\text{HgCN}\cdot\text{OAc}$, since they all dissociate according to the scheme $(\text{HgCN})\text{A} \rightleftharpoons \text{HgCN}^+ + \text{A}'$. The complex cyanomercury ion, HgCN^+ , is very stable in all these compounds, and its dissociation according to the equation $\text{HgCN}^+ \rightleftharpoons \text{Hg}^{++} + \text{CN}'$ is extremely small in amount. Further, a study of mercuric oxycyanide indicates that its properties are expressed, not by the formula $\text{Hg}(\text{CN})_2\cdot\text{HgO}$, but by $\text{O}(\text{HgCN})_2$, so that it is really cyanomercury oxide, which yields the corresponding hydroxide when dissolved in water. In concentrated, but not in dilute, aqueous solutions, cyanomercury perchlorate, nitrate, and chloride give a precipitate of mercuric oxide on the addition of sodium hydroxide solution, whilst cyanomercury acetate gives a precipitate of cyanomercury oxide under similar conditions. Solutions which are not precipitated by sodium hydroxide give a precipitate with ammonia solution, whilst still more dilute solutions are precipitated only by hydrogen sulphide. With silver nitrate, solutions of the perchlorate, nitrate, or acetate give no precipitate, whilst the chloride gives a precipitate consisting entirely of silver chloride; the concentration of the cyanogen ions is, hence, very small in all cases.

Cyanomercury perchlorate, $(\text{HgCN})\text{ClO}_4$, obtained by evaporating a concentrated aqueous solution of mercuric perchlorate (1 mol.) and mercuric cyanide (1 mol.) in a vacuum over sulphuric acid at the ordinary temperature, forms white, acicular prisms, soluble in water or alcohol. In solution it undergoes gradual reduction, with partial formation of mercurous salt. Cryoscopic determinations show that it is dissociated to the extent of 0.80, 0.83, and 0.97 in solutions containing 1, 0.5, and 0.2 mol. respectively per litre. The conductivity in aqueous solution increases considerably with the dilution ($\Lambda_{1024} = 349.9$; $\Lambda_{32} = 174.4$), the dissociation being of the same order of magnitude as that occurring in solutions of mercuric perchlorate ($\Lambda_{1024} = 296.9$; $\Lambda_{32} = 126.9$). The transport number of the cation HgCN^+ with respect to the anion ClO_4^- in solutions of medium concentration (0.2 mol. per litre) and at about 20° is about 0.338.

Cyanomercury nitrate, $(\text{HgCN})\text{NO}_3$, chloride, $(\text{HgCN})\text{Cl}$, and acetate, $(\text{HgCN})\text{C}_2\text{H}_3\text{O}_2$ (compare Prussia, *Abstr.*, 1899, i, 318), exhibit behaviour in general similar to that of the perchlorate. The transport number of the cation HgCN^+ with respect to the anion NO_3^- in solutions of medium concentration at the ordinary temperature is about 0.323. Examination of the products of electrolysis of the chloride in aqueous solution shows that the ion $(\text{HgCN})^+$ may give rise to two other ions, namely, the cyanic ion, $(\text{CNO})'$, at the anode and the cyanogen ion, $(\text{CN})'$, at the cathode; the former of these is

probably formed by the addition of an atom of oxygen to the cyanogen ions existing in small quantity near the electrode, and the latter by the dissociation of the cyanomercury ion.

That cyanomercury oxide (compare Richard, *J. Pharm. Chim.*, 1903, 18, 553) forms the corresponding hydroxide, $(\text{HgCN})\text{OH}$, in solution is shown by cryoscopic and ebullioscopic measurements. The solution has a conductivity of the same order of magnitude as that of mercuric cyanide, so that the compound is dissociated to only a slight extent.

T. H. P.

Experiments to Obtain Aliphatic Substituted Oxytriazines and Oxydihydrotriazines. HEINRICH BILTZ [With P. HORRMANN] (*Ber.*, 1908, 41, 1880—1886).—An account of fruitless attempts to prepare oxytriazines and oxydihydrotriazines of the aliphatic series by methods employed with success in preparing similar aromatic compounds (compare Biltz, *Abstr.*, 1905, i, 491, 673). The work of Diels *Abstr.*, 1902, i, 205; 1903, i, 862), carried out with the same object, has been confirmed.

Diacetyl monosemicarbazone dissolves in aqueous sodium hydroxide without forming an oxytriazine derivative. The sodium salt, $\text{C}_5\text{H}_8\text{O}_2\text{N}_3\text{Na}$, crystallises in nodular aggregates. A mixture of diacetyldioxime and dimethylacetyleneurein (compare Franchimont and Klobbie, *Abstr.*, 1889, 125) is obtained by treating an alcoholic solution of carbamide and diacetyloxime with a few drops of concentrated sulphuric acid.

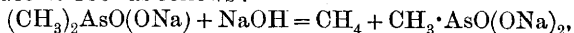
Diacetyloximesemicarbazone, $\text{C}_5\text{H}_{10}\text{O}_3\text{N}_4$, prepared by treating diacetyl oxime with semicarbazide hydrochloride and sodium acetate, has m. p. 247° (decomp.); with a short thermometer, m. p. 259 — 260° (decomp.); the acetate crystallises in aggregates of needles, m. p. 216° .

Dimethylketolsemicarbazone, $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained by acting on dimethylketol with semicarbazide hydrochloride and sodium acetate, has m. p. 194 — 195° (short thermometer). The solution in concentrated sulphuric acid when carefully diluted yields a substance, m. p. about 270° (decomp.), which is probably diacetyl-disemicarbazone. Dimethylketolsemicarbazone decomposes at 200° , yielding a yellow, vitreous mass.

W. H. G.

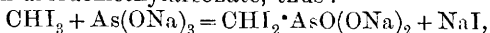
Action of Alkalis on Mono- and Di-methylarsonic Acids and their Iodo-derivatives. VICTOR AUGER (*Compt. rend.*, 1908, 146, 1280—1282).—When sodium methylarsonate is heated with excess of sodium hydroxide at 250 — 280° , it is decomposed according to the equation: $\text{CH}_3\cdot\text{AsO}(\text{ONa})_2 + \text{NaOH} = \text{CH}_4 + \text{AsO}(\text{ONa})_3$.

Sodium cacodylate undergoes a similar decomposition, the first stage taking place at 180° as follows:



the sodium methylarsonate then being decomposed at 260° according to the preceding equation.

The fact that methylene iodide is formed by the action of trisodium arsenite on iodoform is explained by assuming the intermediate formation of sodium di-iodomethylarsonate, thus:



which then decomposes into methylene iodide and sodium arsenate (this vol., i, 13). Details are given for the preparation of methylene iodide by this method.

J. C. C.

Conversion of *cyclo*Pentene into the Mono- and Di-aldehydes of Glutaric Acid. CARL D. HARRIES and LUDWIG TANK (*Ber.*, 1908, 41, 1701—1711).—In a future communication, the authors will give a comparison of the stability of different ring systems, based on the rate of decomposition of ozonides by water. The present paper deals with *cyclopentene*, the ozonide of which is readily decomposed by water, whilst that of *cyclohexene* is only decomposed with difficulty, although the stability of the two ring systems should be of the same order according to the tension theory of Baeyer.

It is very probable that only those aliphatic compounds which contain two carbonyl groups in the β -position to one another are capable of existing in the enolic form, since such compounds are very rarely obtained by the decomposition of ozonides, the substance in its enolic form undergoing further oxidation. *cyclo*Pentene, b. p. 45—46°, D_4^{14} 0.7754, n_D^{14} 1.42080, obtained by the distillation of *cyclopentanol* with phosphoric oxide, yields when ozonised in excess of cold hexane a viscous *ozonide*, $C_5H_8O_3$, which has the usual odour and properties of such compounds. It is rapidly attacked by boiling water, yielding hydrogen peroxide, glutaric acid, glutardialdehyde, and γ -aldehydobutyric acid.

Glutardialdehyde, $CHO \cdot [CH_2]_3 \cdot CHO$, b. p. 71—72°/10 mm. or 187—189°/760 mm., is a colourless, mobile liquid, which resembles succindialdehyde in many respects (this vol., i, 133). In the presence of a trace of water, it changes into a "glassy" polymeride, which reverts to the unimolecular form by distillation in a vacuum. It has D_4^{20} 1.1238 and n_D^{20} 1.45523, and the molecular refraction indicates that the substance is a true dialdehyde. The *bisnitrophenylhydrazone* has m. p. 79—80°.

γ -*Aldehydobutyric acid*, $CHO \cdot [CH_2]_3 \cdot CO_2H$, b. p. 240°/760 mm. or 136—138°/9 mm., is a viscous liquid with a strongly acid reaction, which reduces ammoniacal silver and Fehling's solutions, is resinified by sodium hydroxide, and very readily oxidises to glutaric acid. It has $D_4^{18.5}$ 1.1657, $n_D^{18.5}$ 1.44973, and the molecular refraction indicates that the substance is a true aldehyde. The high dielectric constant, 23.86 (aniline = 7.2), indicates that the aldehydic character is more pronounced than the acid. The *oxime* has m. p. 110—111°, or, after repeated crystallisation from water, 107—108°. The *semicarbazone* has m. p. 165—166° (decomp.), and the *nitrophenylhydrazone*, 148.5°. The analyses of these three compounds are not very accurate.

*cyclo*Heptene, D_4^{20} 0.823, n_D^{20} 1.45301, ozonised in carbon tetrachloride, yields a viscous, and in some cases a solid, *ozonide*, the analyses of which give numbers between $C_7H_{12}O_3$ and $C_7H_{12}O_4$. The ozonide is decomposed only slowly by boiling water, but the amount is too small to allow of the identification of the products. C. S.

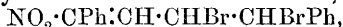
Addition of the Higher Oxides to Doubly Unsaturated Hydrocarbons. A New Case of Addition in the 1:4-Position. HEINRICH WIELAND and HANS STENZL (*Annalen*, 1908, 360, 299—322).—As the evidence in favour of Thiele's theory of conjugated linkings has consisted so far chiefly in the addition of hydrogen, bromine, and

hydrohaloids, it seemed of importance to study the behaviour of conjugated linkings towards other addenda. Moreover, the investigation of the positions assumed by the group NO_2 , on addition to conjugated ethylene linkings, offered some points of interest in connexion with previous studies on the form in which the higher oxides of nitrogen combine with unsaturated compounds (Abstr., 1904, i, 54, 415, 596; 1905, i, 706). The authors have therefore investigated the constitution of the compounds formed by addition of NO_2 groups to $\alpha\delta$ -diphenylbutadiene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}$ (compare this vol., i, 35), cyclopentadiene, $\text{CH}_2\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}\cdot\text{CH} \end{smallmatrix}$, and dicyclopentadiene, the constitution of which has not as yet been established.

The following new evidence is brought forward in favour of the formulation of the additive compound of $\alpha\delta$ -diphenylbutadiene and nitric peroxide as $\alpha\delta$ -dinitro- $\alpha\delta$ -diphenyl- Δ^{β} -butylene.

On reduction with the usual reagents and in the ordinary way, the dinitro-compound forms $\alpha\delta$ -diphenylbutadiene, a reaction further exemplifying the analogy of the behaviour of the nitro-group with that of the halogens, but, on reduction with zinc and hydrochloric acid under special conditions, it yields small amounts of *diphenylbutadienediamine*, $\text{NH}_2\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}\cdot\text{NH}_2$, which crystallises in colourless needles, m. p. 149° (decomp.), decolorises permanganate in acid solution, and when treated with nitrous acid evolves nitrogen and yields an *oil*. The diamine forms colourless, crystalline *salts* with acetic and hydrochloric acids, and a *picrate*, $\text{C}_{16}\text{H}_{18}\text{N}_2\cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, yellow needles, decomp. about 220° . When suspended in chloroform, cooled by ice, and oxidised with ozone, the dinitro-compound yields large amounts of nitrophenylmethane, $\text{CH}_2\text{Ph}\cdot\text{NO}_2$, the decomposition product of nitrophenylacetic acid, $\text{NO}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, together with small amounts of benzoic acid and benzaldehyde, arising probably from the intermediate formation of α -nitro- $\alpha\delta$ -diphenylbutadiene. If the additive compound was $\alpha\beta$ -dinitro- $\alpha\delta$ -diphenyl- $\Delta\gamma$ -butylene, oxidation would lead to the formation of a dinitro-carboxylic acid, $\text{NO}_2\cdot\text{CHPh}\cdot\text{CH}(\text{NO}_2)\cdot\text{CO}_2\text{H}$.

α -Nitro- $\alpha\delta$ -diphenylbutadiene forms a *dibromide*,



which crystallises in yellow needles, m. p. 106° , decomp. about 165° , and gives a cherry-red coloration with concentrated sulphuric acid.

When suspended in cooled ether and treated with nitrous gas, α -phenylcinnamylacrylic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$, evolves carbon dioxide and yields a *dinitro*-compound, which is probably $\beta\gamma$ -*dinitro- $\alpha\delta$ -diphenylbutadiene*, $\text{CHPh}\cdot\text{C}(\text{NO}_2)\cdot\text{C}(\text{NO}_2)\cdot\text{CHPh}$; this crystallises in yellow prisms, m. p. 218° , is stable towards acids or cold alkalis, and does not form an additive compound with bromine.

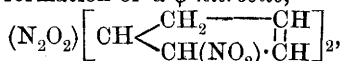
The bearing of these facts on the nature of the ethylene linkings in diphenylbutadiene is discussed. It is considered that the partial



formula.

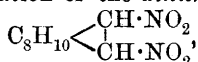
valencies of the α - and δ -carbon atoms are neutralised by those of the benzene rings, the behaviour of the compound being best expressed by the annexed

The action of nitrogen trioxide on *cyclopentadiene* in ethereal solution leads to the formation of a *ψ-nitrosite*,



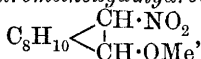
which is obtained in yellow crystals, m. p. 38° , decomposes slightly above its m. p., readily polymerises, gives Liebermann's reaction, and is converted by amyl nitrite and alcoholic hydrogen chloride into the *nitrosochloride*, $(\text{N}_2\text{O}_2) \left[\text{CH} \begin{array}{c} \text{CH}_2 - \text{CH} \\ \diagdown \quad \diagup \\ \text{CHCl} \cdot \text{CH} \end{array} \right]_2$; this crystallises in colourless needles, detonates at about 142° , decolorises permanganate, forms potassium chloride with potassium hydroxide in methyl-alcoholic solution, and gives an orange coloration with phenol and concentrated sulphuric acid.

The action of nitrogen dioxide on *dicyclopentadiene* in ethereal solution leads to the formation of the *dinitro-compound*,



which crystallises in needles, m. p. 122° , is readily attacked by permanganate, does not give Liebermann's reaction, forms a crystalline *dibromide*, and loses 1 mol. of hydrogen nitrite when boiled with alcohol, or alcoholic potassium hydroxide or ammonia.

The *ψ-nitrosite*, $(\text{N}_2\text{O}_2) \left[\text{CH} \begin{array}{c} \text{CH} \cdot \text{NO}_2 \\ \diagdown \quad \diagup \\ \text{C}_8\text{H}_{10} \end{array} \right]_2$, formed by the action of nitrogen trioxide on *dicyclopentadiene*, crystallises in hexagonal leaflets, m. p. $144\text{--}146^\circ$ (decomp.), forms green solutions, reacts slowly with permanganate, does not give Liebermann's reaction, and when boiled with potassium in methyl-alcoholic solution evolves nitrous oxide and forms *nitromethoxydihydrodicyclopentadiene*,



which crystallises in rhombohedra, m. p. 68° , gives a blood-red coloration with alcoholic ferric chloride, forms *precipitates* with zinc, silver, and copper salts in neutral solution, and reacts slowly with permanganate.

The *nitro-oxime*, $\text{C}_8\text{H}_{10} \begin{array}{c} \text{CH} \cdot \text{NO}_2 \\ \diagdown \quad \diagup \\ \text{C} \cdot \text{NOH} \end{array}$, formed by boiling the *ψ-nitrosite* with alcohol or aniline in alcoholic solution, crystallises from benzene in prisms or needles, m. p. $138\text{--}139^\circ$, gives an intense green coloration with ferric chloride, and yields hydroxylamine when boiled with 20% sulphuric acid.

G. Y.

Compounds of Platinous Chloride with Dicyclopentadiene.

KARL A. HOFMANN and J. VON NARBUTT (*Ber.*, 1908, **41**, 1625—1628). —It has been already found that mercuric chloride, *dicyclopentadiene*, and alcohols give compounds of the class $\text{HgCl} \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OR}$ (Hofmann and Seiler, *Abstr.*, 1906, **i**, 786), and it has since been discovered that platinous chloride in aqueous alcohols reacts in a similar way to form the stable ethers, $\text{PtCl} \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OR}$.

Chloroplatomethoxydicyclopentadiene, $\text{PtCl} \cdot \text{C}_{10}\text{H}_{12} \cdot \text{OMe}$, obtained by mixing an aqueous solution of potassium platinichloride with a methyl-

alcoholic solution of dicyclopentadiene, crystallises in pale yellow plates, decomp. 190° . At 15° , the experiment requires several weeks; at 40° , several days. Hot potassium hydroxide decomposes it into hydrocarbon, and 20% hydrochloric acid at 15° slowly converts the plates into prisms, probably the compound $\text{PtCl}\cdot\text{C}_{10}\text{H}_{12}\text{Cl}$. The *ethoxy*-compound, $\text{PtCl}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OEt}$, forms pale yellow prisms; propyl alcohol does not give an analogous compound, but the *compound*, $\text{PtCl}\cdot\text{C}_{10}\text{H}_{12}\text{Cl}$, which separates in needle aggregates. The conclusion is drawn that these compounds owe their stability partly to their containing the linking $\text{ClPt}\cdot\overset{|}{\text{CH}}\cdot\overset{|}{\text{CH}}\cdot\text{Cl}$ or OMe .

W. R.

The Optical Behaviour of cycloHexadiene Derivatives. KARL AUWERS (*Ber.*, 1908, 41, 1828—1831. Compare Abstr., 1906, i, 947; Brühl, *Trans.*, 1907, 91, 115).—The author draws attention to the fact that many cyclohexadienes which contain conjugated ethylene linkings do not show the exaltation in molecular refraction and dispersion usually characteristic of such compounds. It is pointed out that many of these unsaturated hydrocarbons tend to polymerise, and that determinations should be made with freshly-prepared specimens. The low values obtained for some of the compounds may possibly be due to the fact that polymerised products were examined.

Methyl 1:4-dimethyl- $\Delta^{1:3}$ -hexadiene-2-carboxylate also does not exhibit the usual exaltation.

J. J. S.

Dihydrotoluene ($\Delta^{1:3}$ -Methylcyclohexadiene). CARL D. HARRIES (*Ber.*, 1908, 41, 1698—1701).—The dihydrotoluene obtained by the dry distillation of hexahydro-*m*-tolylenediamine phosphate (Abstr., 1901, i, 194; 1902, i, 361) yields by suitable oxidation with potassium permanganate the same 1:2-dihydroxymethylcyclohexane-3-one as is obtained from methylcyclohexenone (Abstr., 1898, i, 402), and is consequently $\Delta^{1:3}$ -methylcyclohexadiene. Klages found, however (Abstr., 1907, i, 597), that the observed and calculated molecular refractions agreed, although it is well known that substances containing a conjugated double linking exhibit an exaltation of this constant. The author has therefore redetermined the physical constants of this dihydrotoluene, and, with D_4^{20} 0.8354 and n_D^{20} 1.47628, the observed molecular refraction, 31.72, shows a small increment over the calculated value, 31.43. This result points to the presence in the dihydrotoluene of an isomeride which does not contain a conjugated double linking. Evidence in the same direction is obtained by the action of bromine, more than one molecular proportion of the halogen being absorbed. The action of ozone on dihydrotoluene gives a gelatinous product, which is apparently a mixture of a mono- and a di-ozonide, but the decomposition of the substance by water does not give conclusive results as to its structure.

C. S.

Contact Oxidation of Hydrocarbons. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 652—658. Compare this vol., i, 306).—The author has investigated the oxidation of various hydrocarbons under the conditions of the former experiments (*loc. cit.*).

With light petroleum, D 0.71, the gaseous products of oxidation

included 8—10% of carbon dioxide and 6·8—2·4% of carbon monoxide, other products being about 10% of close-chain and ethylene hydrocarbons of the compositions C_6H_{12} and C_5H_{10} . Further aldehydic derivatives of the benzene series with the aldehyde group in the meta- or para-position were also obtained. Heavier oils yield similar products.

Benzene yields (1) a gaseous product containing 12·44% of carbon dioxide, 2·44% of oxygen, 6·78% of carbon monoxide, 6·94% of methane, and 71·4% of nitrogen; (2) aldehydic and carboxylic derivatives of benzene. From a study of the various products, the author concludes that the benzene undergoes a series of condensations and oxidations; for instance, $2C_6H_6 = H_2 + C_6H_5 \cdot C_6H_5$ (the latter being then oxidised to "acroleinphenol," benzaldehyde, and a hydroxybenzoic acid) and $3C_6H_6 = 2H_2 + C_6H_5 \cdot C_6H_4 \cdot C_6H_5$, the latter being then transformed into hydroxydiphenylcarboxylic acid or the corresponding aldehyde.

Toluene yields, in addition to the gaseous products, 2·5—4% of benzaldehyde and various substances with reducing and phenolic properties, and similar to the corresponding products obtained from benzene.

In the case of turpentine, the gas obtained has the following composition: CO_2 , 7·55%; O, 1·77%; CO, 7·55%; H, 4·8%; CH_4 , 3·6%; C_2H_4 , 1·2%; N, 73·5%. The other products obtained indicate that the turpentine loses part of its hydrogen and condenses to hydrocarbons of the diphenyl series, the latter then undergoing oxidation as in the case of benzene (*vide supra*).

The results so far obtained indicate that many gases, for example, natural methane and illuminating gas, may be converted by contact oxidation into more valuable products, such as formaldehyde.

T. H. P.

1:2-Dibromo-3-nitrobenzene and the Nitration of *o*-Dibromobenzene. ARNOLD F. HOLLEMAN [with P. C. J. EUWES] (*Rec. trav. chim.*, 1908, 27, 153—161. Compare Abstr., 1906, i, 345).—An improved method for the preparation of 1:2-dibromo-3-nitrobenzene from *o*-nitroaniline is described.

The m. p. previously ascribed to this compound (*loc cit.*) is too low. When crystallised from light petroleum, it has m. p. 84—85°. Pure *o*-dibromobenzene, m. p. 5·6°, has been treated at 0° with nitric acid (D 1·5). By an examination of the solidifying point and density, the product of nitration is found to consist of 84% 1:2-dibromo-4-nitrobenzene with 16% 1:2-dibromo-3-nitrobenzene. These two isomerides cannot be separated by fractional crystallisation.

W. O. W.

Halogen Derivatives of Dinitrohydrocarbons. GIACOMO PONZIO and G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1908, 43, 475—482; *Gazzetta*, 1908, 38, i, 648—654).—Whereas two forms of ω -nitrotoluene are known having the structures $CH_2Ph \cdot NO_2$ and $CHPh \cdot NO \cdot OH$ respectively, only one form of ω -dinitrotoluene, $CHPh(NO_2)_2$,

has been obtained (compare Ponzio, Abstr., 1906, i, 735, and Hantzsch, Abstr., 1906, i, 500); two potassium salts of ω -dinitrotoluene are, however, known, one colourless and probably having the structure $NO_2 \cdot CPh \cdot NO \cdot OK$, and the other yellow and capable

of being represented by two formulæ, $\text{OK}\cdot\text{N}:\text{CPh}\cdot\text{O}\cdot\text{NO}_2$ and $\text{OK}\cdot\text{CPh}(\text{NO}_2)\cdot\text{NO}$. The nature of the product of the action of hypochlorites on the yellow salt is in favour of the latter structure, a chlorine derivative being obtained which probably has the constitution $\text{NO}\cdot\text{CPh}(\text{NO}_2)\cdot\text{OCl}$, as it gives with alcoholic potash, potassium nitrate, nitrite, and benzoate in addition to the potassium salt of ω -dinitrotoluene. The alternative formula $\text{CPhCl}(\text{NO}_2)_2$ does not so well explain the facts. The yellow diazobenzene derivative obtained by the action of diazobenzene acetate on the yellow potassium salt of ω -dinitrotoluene is therefore probably $\text{NO}\cdot\text{CPh}(\text{NO}_2)\cdot\text{O}\cdot\text{N}:\text{NPh}$, a formula which is in good accord with the easy transformation of the substance into nitronitrosobenzoylphenylhydrazine, $\text{NO}_2\cdot\text{NBz}\cdot\text{NPh}\cdot\text{NO}$ (compare this vol., i, 482).

ω -Chlorodinitrotoluene, $\text{CPhCl}_2\text{NO}_4$, separates immediately on adding a dilute solution of potassium ω -dinitrotoluene to an alkaline solution of chlorine at 0° as a colourless oil which is stable under ordinary conditions; when warmed with water, it gives benzoic acid and nitrous fumes.

ω -Bromodinitrotoluene, obtained similarly, is a slightly yellow oil. The phenylhydrazine salt, $\text{CHPhN}_2\text{O}_4\cdot\text{PhN}_2\text{H}_3$, of ω -dinitrotoluene, obtained by mixing aqueous solutions of potassium ω -dinitrotoluene and phenylhydrazine hydrochloride, forms yellow leaflets, m. p. 87° .

ω -Chlorodinitroanisole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CClN}_2\text{O}_4$, and ω -bromodinitroanisole, prepared from ω -dinitroanisole, are colourless oils, which are stable at the ordinary temperature and give anisic acid when boiled with water; alcoholic potash converts both substances into potassium ω -dinitroanisole. The phenylhydrazine salt of ω -dinitroanisole forms yellow leaflets, m. p. 79° .

ω -Chlorodinitro-3:4-methylenedioxytoluene, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CClN}_2\text{O}_4$, prepared from ω -dinitro-3:4-methylenedioxytoluene, crystallises from alcohol in large, slightly yellow plates, m. p. 55° ; ω -bromodinitro-3:4-methylenedioxytoluene, m. p. 81° , crystallises from light petroleum.

W. A. D.

Reduction of Nitro-compounds by Zinin's Method. RICHARD WILLSTÄTTER and HEINRICH KUBLI (*Ber.*, 1908, 41, 1936—1940).—The authors find that when aromatic nitro-compounds are treated in alcoholic solution with ammonium sulphide in the cold, good yields of the corresponding aryl-hydroxylamines are obtained. From nitrobenzene was prepared phenylhydroxylamine; from *p*-nitrotoluene, *p*-tolylhydroxylamine, and α -nitronaphthalene gave α -naphthylhydroxylamine.

The latter crystallises with $1\text{H}_2\text{O}$, forming colourless, glistening prisms, m. p. 79° (compare Scheiber, *Abstr.*, 1904, i, 867). The anhydrous substance has the same m. p. When α -naphthylhydroxylamine is dissolved in anhydrous ether and shaken with dry silver oxide in presence of anhydrous copper sulphate or sodium sulphate, it yields α -nitrosonaphthalene in clear yellow crystals dissolving to a green solution. When heated, α -nitrosonaphthalene turns green at 80° , and has m. p. 85 — 86° ; it then solidifies, and has m. p. 98° . J. C. C.

Picrates. WILHELM SUIDA (*Ber.*, 1908, 41, 1909—1913).—Anthranilic acid forms two picrates, $C_7H_7O_2N, C_6H_3O_7N_3$, yellowish-brown prisms, and $2C_7H_7O_2N, C_6H_3O_7N_3$, red, or when containing $1\frac{1}{2}H_2O$ yellow, crystals, depending on the proportions in which concentrated solutions of anthranilic and picric acids are mixed. In the same manner, *p*-toluidine and picric acid combine in the molecular proportion 1:1, forming a brownish-yellow, or in the proportion 2:1, forming a bright yellow, salt.

α -Naphthylamine also forms a greenish-yellow picrate containing 1 mol., and a copper-red picrate containing 2 mols., of the base and 1 mol. of picric acid. Aniline, on the other hand, forms only one brownish-yellow picrate. G. Y.

Tri-*p*-halogen Substitution Products of Triphenylmethane and Triphenylcarbinol. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 789—798. Compare Abstr., 1907, i, 1050).—Crystallographical determinations with the following substances: tri-*p*-iodotriphenylmethane, rhombic [$a:b:c=0.5765:1:0.8798$]; tri-*p*-iodotriphenylmethane containing benzene of crystallisation, triclinic [$a:b:c=0.5719:1:1.4298$; $\alpha=109^\circ 8'$; $\beta=126^\circ 21'$; $\gamma=107^\circ 32'$]; tri-*p*-chlorotriphenylcarbinol, rhombic [$a:b:c=0.6009:1:0.9781$]; tri-*p*-bromotriphenylcarbinol, rhombic [$a:b:c=0.8407:1:0.8081$]; tri-*p*-iodotriphenylcarbinol, rhombic [$a:b:c=0.8543:1:0.817$], and tri-*p*-iodotriphenylcarbinol containing benzene of crystallisation, triclinic [$a:b:c=1.3991:1:1.6135$; $\alpha=109^\circ 16'$; $\beta=117^\circ 36'$; $\gamma=62^\circ 52'$]. G. Y.

Mercury Salts of the Three Nitroanilines. C. LORING JACKSON and R. W. PEAKES (*Amer. Chem. J.*, 1908, 39, 567—572).—During a study of the abnormal replacement of bromine by hydrogen in 1:3:5-tribromo-2:4-dinitrobenzene, this substance was treated with the nitroanilines, but reaction did not take place under any conditions. The mercury salts of the nitroanilines were therefore prepared with a view to ascertaining if they would react with 1:3:5-tribromo-2:4-dinitrobenzene, but they gave no better results.

These salts, $(NO_2 \cdot C_6H_4 \cdot NH)_2Hg$, are precipitated when a strong solution of potassium hydroxide is added to a solution of the nitroaniline and mercuric nitrate. The salt of *p*-nitroaniline is crimson, that of the *m*-derivative is maroon-coloured and contains $1H_2O$, and that of the *o*-compound is bright red. The *o*-salt is formed the most rapidly, the *m*-salt next, and the *p*-salt most slowly. E. G.

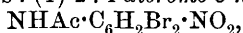
Action of Bromine or of Sodium Hypobromite on *m*-Nitroaniline and Some of its Halogen Substitution Derivatives. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 465—480).—The authors have studied the action of bromine or sodium hypobromite on *m*-nitroaniline and some of its halogenated derivatives with the hope of obtaining new mono- and di-substituted derivatives of *m*-nitroaniline, and of ascertaining in what

order the three hydrogen atoms of *m*-nitroaniline, capable of substitution, are replaced by the halogen.

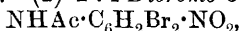
Bromination of *m*-nitroaniline with bromine in chloroform solution yields tribromo-*m*-nitroaniline, m. p. 102·5°, *p*-bromo-*m*-nitroaniline, and a small quantity of 2 : 4-dibromo-5-nitroaniline (*vide infra*).

Bromination of *m*-nitroaniline (1 mol.) with sodium hypobromite (1 atom of bromine) in acetic acid solution gives (1) 4-bromo-3-nitroacetanilide; (2) 2-bromo-5-nitroacetanilide, $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NO}_2$, which crystallises from alcohol in slender, monoclinic needles or prisms [ARTINI: $a:b:c = 3:3702:1:1 \cdot 2522$; $\beta = 77^\circ 3'$], m. p. 180°, D 1·831. When treated with concentrated sulphuric acid at 120°, it is converted into 2-bromo-5-nitroaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NO}_2$, which crystallises from alcohol in orange-yellow needles, m. p. 141°.

The action of sodium hypobromite on *p*-bromo-*m*-nitroaniline in acetic acid solution yields: (1) 2 : 4-dibromo-5-nitroacetanilide,



which crystallises from ethyl acetate in flattened needles or long plates, m. p. 172°, and can also be obtained, mixed with 2 : 4-dibromo-6-nitroacetanilide, by nitrating 2 : 4-dibromoacetanilide in sulphuric acid. De-acetylation of this compound yields 2 : 4-dibromo-5-nitroaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{NO}_2$, which crystallises from alcohol in slender, pale yellow, monoclinic laminae [ARTINI: $a:b:c = 2:1598:1:3 \cdot 0212$; $\beta = 73^\circ 51'$], m. p. 114·2°. (2) 2 : 4-Dibromo-3-nitroacetanilide,

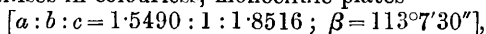


which crystallises from benzene in slender, white needles, m. p. 150°. When treated with nitrous acid, it is converted into 1 : 3-dibromo-2-nitrobenzene, which may be prepared conveniently in this way.

When 1 : 3-dibromo-2-nitrobenzene is treated with nitric acid, D 1·54, it yields 1 : 3-dibromo-2 : 4-dinitrobenzene, $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$, which crystallises from alcohol in long, almost colourless needles or in yellowish-green plates, m. p. 83°, and, under the action of alcoholic ammonia solution, is converted into 2 : 4-dinitrophenylene-1 : 3-diamine, $\text{C}_6\text{H}_2(\text{NH}_2)_2(\text{NO}_2)_2$, which crystallises from alcohol in orange-yellow needles, m. p. 250°. When treated with potassium hydroxide solution, the latter yields the potassium salt of 2 : 4-dinitroresorcinol, $\text{C}_6\text{H}_2(\text{OK})_2(\text{NO}_2)_2$.

Nitration of 1 : 3-dibromo-2-nitrobenzene with excess of nitric acid, or with a mixture of nitric and sulphuric acids, results in the formation of 1 : 3-dibromo-2 : 4 : 6-trinitrobenzene, which, when treated with alcoholic ammonia solution, yields 2 : 4 : 6-trinitrophenylene-1 : 3-diamine (compare Noelting and Collin, Abstr., 1884, 1004). The latter, under the action of dilute potassium hydroxide solution, gives potassium stypnate.

Reduction of 1 : 3-dibromo-2-nitrobenzene with tin and hydrochloric acid, and replacement of the amino-group of the resultant product by bromine, leads to the formation of 1 : 2 : 3-tribromobenzene, $\text{C}_6\text{H}_3\text{Br}_3$, which crystallises in colourless, monoclinic plates



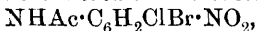
m. p. 87·4°, D 2·658. 2-Chloro-1 : 3-dibromobenzene, $\text{C}_6\text{H}_3\text{ClBr}_2$, obtained in a similar manner, m. p. 73°, and 2-iodo-1 : 3-dibromobenzene, $\text{C}_6\text{H}_3\text{Br}_2\text{I}$, m. p. 99·8°, crystallise in forms similar to that of the

tribromo-derivative. 2:6-Dibromoacetanilide, $C_6H_3Br_2 \cdot NHAc$, crystallises from alcohol in colourless, trimetric prisms

$$[a:b:c = 0.734:1:0.392],$$

m. p. 210° , $D_{16} 1.923$.

The action of sodium hypobromite on *p*-chloro-*m*-nitroaniline in acetic acid yields (1) 4-chloro-2-bromo-5-nitroacetanilide,



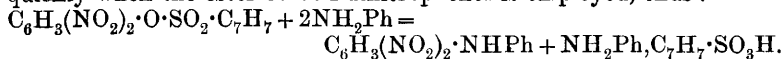
which crystallises from alcohol in long, white needles, m. p. 147.4° , and is also obtained by nitrating 4-chloro-2-bromoacetanilide in sulphuric acid solution. The corresponding 4-chloro-2-bromo-5-nitroaniline, $NH_2 \cdot C_6H_2ClBr \cdot NO_2$, crystallises from alcohol in yellow, monoclinic prisms [$a:b:c = 2.1321:1:3.0222$; $\beta = 73^\circ 17'$], m. p. 108° , $D 1.739$. Replacement of the amino-group in this compound by hydrogen gives 1-chloro-3-bromo-6-nitrobenzene, m. p. 42.4° (compare Körner, this Journ., 1876, i, 204). (2) 4-Chloro-2-bromo-3-nitroacetanilide, $NHAc \cdot C_6H_2ClBr \cdot NO_2$, which crystallises from aqueous alcohol in colourless plates or faintly yellow prisms, m. p. $135-136^\circ$. The corresponding 4-chloro-2-bromo-3-nitroaniline, $NH_2 \cdot C_6H_2ClBr \cdot NO_2$, m. p. $99-100^\circ$, is similar in crystalline habit and chemical properties to the analogous dibromonitroaniline.

2-Bromo-5-nitroaniline is converted quantitatively into 2:4-dibromo-5-nitroaniline on bromination.

These results show that, in the bromination of *m*-nitroaniline, the positions accessible to the halogen are the para-position and, in a less degree, the ortho-position non-adjacent to the nitro-group; in no case does the halogen enter the meta-position. When the para-position in *m*-nitroaniline is already occupied by a halogen atom, the new halogen atom assumes indifferently either of the two ortho-positions. If the ortho-position is occupied, the halogen atom assumes the para-position.

Partial bromination of 3:5-dinitroaniline yields (1) 2-bromo-3:5-dinitroaniline, $NH_2 \cdot C_6H_2Br(NO_2)_2$, which crystallises from alcohol in golden-yellow laminae, m. p. 181° , and, on treatment with alcoholic ammonia solution gives 3:5-dinitrophenylene-1:2-diamine (compare Nietzki and Hagenbach, Abstr., 1897, i, 277), m. p. 215° . (2) 2:4:6-Tribromo-3:5-dinitroaniline (compare Blanksma, *Rec. trav. chim.*, 1902, 21, 255). T. H. P.

Preparation of *o*-Nitroamines from the Corresponding Phenol Derivatives. FRITZ ULLMANN and GÉZA NÁDAI (*Ber.*, 1908, 41, 1870—1878).—The authors find that when arylsulphonic esters of *o*-nitrophenol and its derivatives are treated with amines, they are converted into the corresponding *o*-nitroamines. Aniline acts only slowly on the ester of *o*-nitrophenol, but the reaction proceeds very quickly when the ester of 2:4-dinitrophenol is employed, thus:



It was not found possible to prepare the arylsulphonic ester of picric acid, and in presence of pyridine, quinoline, or diethylaniline, picryl chloride was obtained. 2:4-Dinitrophenol, when treated with toluenesulphonyl chloride and diethylaniline, also gave a mixture of chlorodinitrobenzene and the sulphonic ester, but *o*- and *p*-nitrophenols

gave, under the same conditions, only the corresponding esters, whilst benzoic and cinnamic acids furnished the corresponding acid chlorides.

The 2:4-dinitrophenyl ester of *p*-toluenesulphonic acid crystallises from alcohol or glacial acetic acid in colourless prisms, m. p. 121°. When treated with gaseous ammonia in boiling nitrobenzene solution, it gives ammonium toluenesulphonate and 2:4-dinitroaniline, and, when warmed with aniline, 2:4-dinitrodiphenylamine is obtained. On reduction, the dinitro-ester gives the 2:4-diaminophenyl ester of *p*-toluenesulphonic acid, white leaflets, m. p. 125°; the diacetyl derivative, white needles, m. p. 167°. The dinitro-ester with pyridine gives dinitrophenylpyridinium toluenesulphonate, $C_{18}H_{15}O_7N_3S$, white needles.

When picric acid is heated with toluenesulphonyl chloride in presence of diethylaniline and nitrobenzene, and the product poured into ammonia, picramide is formed; when aniline is employed instead of ammonia, 2:4:6-trinitrodiphenylamine results, and with *p*-toluidine, 2:4:6-trinitrophenyl-*p*-tolylamine, red needles, m. p. 169°, is obtained. The 3:5-dinitrotolyl ester of *p*-toluenesulphonic acid, prepared from 3:5-dinitro-*p*-cresol and the acid chloride, feathery needles, m. p. 154°, when warmed with aniline in benzene solution gives phenyl-2:6-dinitro-*p*-tolylamine, orange leaflets, m. p. 174°.

Trinitro-*m*-cresol, when condensed with *p*-toluenesulphonyl chloride in presence of diethylaniline, yields 3-chloro-2:4:6-trinitrotoluene (Reverdin, Dresel, and Delétra, Abstr., 1904, i, 580). J. C. C.

A Violet *aci*-Ether of Hexanitrodiphenylamine. ARTHUR HANTZSCH and ST. OPOLOSKI (*Ber.*, 1908, 41, 1745—1749).—It has been found possible to isolate a *aci*-methyl ether of hexanitrodiphenylamine. The compound is deep violet in colour, and corresponds with the red *aci*-ethers of the nitrophenols.

The constitutional formula $C_6H_2(NO_2)_3 \cdot N:C_6H_2(NO_2)_2 \cdot NO \cdot OMe$ is suggested, whereas the ordinary yellow methyl ether is regarded as the *N*-ether, $C_6H_2(NO_2)_3 \cdot NMe \cdot C_6H_2(NO_2)_3$.

The silver derivative of hexanitrodiphenylamine is obtained most readily by the action of silver oxide on an acetone solution of the nitro-compound and subsequent precipitation with ether. It forms brilliant violet crystals, and decomposes above 200°. The salt reacts with a benzene solution of acetyl chloride, yielding the pale yellow acetyl derivative, $C_6H_2(NO_2)_3 \cdot NAc \cdot C_6H_2(NO_2)_3$, m. p. 240° (decomp.). The *N*-methyl and ethyl ethers are both yellow (compare Mulder, Abstr., 1906, i, 493), and give a red coloration with dilute alkalis only after hydrolysis. The ethers cannot be obtained by the action of picryl chloride or alkyl derivatives of picramide. A small amount of the violet *aci*-methyl ether (*O*-ether) is obtained when the dry silver salt is treated with excess of methyl iodide at 0° without the addition of a solvent. It crystallises from an absolutely dry mixture of benzene and hexane in black needles; it melts and decomposes at 140—141° when heated rapidly, or at 120° when heated slowly. Its solutions in benzene have a violet colour, and are comparatively stable.

The acetone solution is very unstable, and readily yields hexanitrodiphenylamine.

J. J. S.

Mutual Solubility of Solid Aromatic and the Corresponding Hexahydrogenated Compounds (Equilibrium in the System: Phenol-*cyclo*Hexanol.) LUIGI MASCARELLI and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 601—609. Compare Abstr., 1907, ii, 936).—The composition-freezing point diagram for mixtures of phenol and *cyclo*hexanol consists of three branches: (1) from 0 to about 20% of *cyclo*hexanol the freezing point falls continuously from 40° to about 19°; (2) from 20, to about 80—90% it rises slightly at first and afterwards falls rapidly to about -50°; (3) from 80—90 to 100% of *cyclo*hexanol the freezing point rises from about -50° to +20°. In order to ascertain whether the slightly marked maximum of the second branch corresponds with the formation of an additive compound between the phenol and *cyclo*hexanol, the equilibrium was studied in the presence of ethylurethane, which satisfies the conditions laid down by Mascarelli (compare this vol., ii, 94). As the maximum undergoes appreciable displacement towards the ordinate axis, it cannot correspond with an additive compound. On determining the composition of the separated crystals by Bylert's method (Abstr., 1891, 1411), using benzil as third substance, it is found that a solid solution is formed.

The results show that the two substances, phenol and *cyclo*hexanol, are dimorphous, but only one form of the one compound can give solid solutions with one of the other. The ordinary forms of phenol and *cyclo*hexanol are incapable of dissolving in the solid state, and should give a curve consisting of two straight lines, of which the first and third branches of the experimental curve form parts. The other forms of phenol and *cyclo*hexanol are completely soluble in the solid condition, so that they should give a curve rising to a maximum; the second branch of the experimental curve represents part of this ideal curve. The existence of two forms of phenol is in accord with the observations of Tammann (*Krystallisieren und Schmelzen*, 1903, 308), who gave the m. p. of the unstable form of phenol as about 30°; the authors' results lead to the value 10—20°.

T. H. P.

Chlorinating Action of Phosphorus Pentachloride and the Action of Thionyl Chloride on Carbonyl Compounds. PAUL HOERING and F. BAUM (*Ber.*, 1908, 41, 1914—1918).—When boiled with a mixture of phosphorus tri- and penta-chlorides, *isosafrole* is converted into *disosafrole* (Angeli and Mola, Abstr., 1895, i, 24). Dibromo- and tribromo-*isosafrole*, on the other hand, when heated with phosphorus pentachloride, form mixtures of stereoisomeric dichlorides, which are separated only partly and with difficulty. From dibromo*isosafrole* there is obtained a *dichloride*, $C_{10}H_8O_2Cl_2Br_2$, m. p. 97—99°, and from the tribromo-compound a crystalline mixture, m. p. 134—145°, from which was isolated a *dichloride*, $C_{10}H_7O_2Cl_2Br_3$, m. p. 173·5—174·5°, or in one case 176—177°. This is stable towards water, but when heated gently with sodium ethoxide yields a crystalline product, m. p. 90—90·5°, containing only 1 atom of chlorine,

and when boiled with sodium acetate in glacial acetic acid solution is converted into an *acetate*, which, on hydrolysis with alcoholic potassium hydroxide, forms tribromoisosafole oxide, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{Br}_3 \cdot \text{CH} < \begin{smallmatrix} \text{CHMe} \\ \text{O} \end{smallmatrix}$;

hence the addition of chlorine must have taken place at the ethylene linking in the propenyl side-chain of the *isosafole*. In agreement with this, it is found that the action of phosphorus pentabromide on di- and tri-bromoisosafole leads to the formation of the dibromides, which are obtained also by direct addition of bromine.

Piperonal dichloride is formed by the action of thionyl chloride on piperonal, and, when heated with phosphorus pentachloride at $110\text{--}120^\circ$, yields dichloropiperonal dichloride, b. p. $163^\circ/18$ mm. (compare Barger, *Trans.*, 1908, 41, 1768). An attempt to found on this a general method of preparing dichlorides by the action of thionyl chloride on aldehydes was unsuccessful. Benzaldehyde, treated with thionyl chloride, yields benzyl chloride almost quantitatively; salicylaldehyde reacts with thionyl chloride or phosphorus pentachloride, forming disalicylide; anisaldehyde under similar conditions yields an unstable *product*, b. p. $125\text{--}130^\circ/14$ mm., which could not be purified; acetaldehyde and paraldehyde yield a mixture of products, b. p. $118\text{--}125^\circ$, whilst acetone reacts energetically with thionyl chloride, forming a *product* which decomposes on distillation and does not contain even traces of dichloropropane.

G. Y.

Derivatives of Diphenylene Oxide. WALTHER BORSCHKE and W. BOTHE (*Ber.*, 1908, 41, 1940—1944).—Although Galewsky (*Abstr.*, 1891, 1234) was unable to obtain a mononitro-derivative of diphenylene oxide, the authors have prepared 4-nitrodiphenylene

oxide, $\text{O} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_3 \cdot \text{NO}_2 \end{smallmatrix}$, by warming a glacial acetic acid solution of diphenylene oxide with nitric acid, D 1.52. It crystallises from acetic acid in yellow, silky needles, m. p. $181\text{--}182^\circ$. On reduction with tin and hydrochloric acid, it yields 4-aminodiphenylene oxide, m. p. 94° . The *hydrochloride*, decomp. 220° , the *stannichloride*, the *diacetyl* derivative, colourless needles, m. p. 83° , and the *benzoylamino*-derivative, m. p. 201° , are described. When the *diazo-chloride* is stirred into a solution of sodium sulphide and sodium hydroxide, sodium diphenylene-oxide-azosulphonate, $\text{C}_{12}\text{H}_7\text{O} \cdot \text{N}_2 \cdot \text{SO}_3\text{Na}$, separates in yellow crystals. On acidification with acetic acid and treatment with zinc dust, sodium diphenylene-oxide-hydrazinesulphonate is formed, which on boiling with hydrochloric acid yields hydrazinodiphenylene oxide, $\text{C}_{12}\text{H}_{10}\text{ON}_2$, in leaflets, m. p. 152° . The *hydrochloride* has m. p. 225° . The chloride of diazodiphenylene oxide is not decomposed by boiling a solution with concentrated sulphuric acid; with phenol it forms phenolazodiphenylene oxide, reddish-brown crystals, m. p. 199° , and suffers the usual Sandmeyer decomposition, by means of which is obtained 4-iododiphenylene oxide, yellow leaflets, m. p. 182° , and the

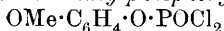
nitrile, $\text{O} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_3 \cdot \text{CN} \end{smallmatrix}$, colourless needles, m. p. 120° , which on hydrolysis

furnishes *diphenylene-oxide-4-carboxylic acid*, colourless needles, m. p. 266°. This is also formed by treating acetyldiphenylene oxide (Galewsky, *loc. cit.*) with sodium hypochlorite. *Benzoyldiphenylene oxide*, $O \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_5Bz \end{smallmatrix}$, obtained from diphenylene oxide by treatment with benzoyl chloride and aluminium chloride, forms white needles, m. p. 167—168°, and gives an *oxime*, m. p. 234—235, the *benzoyl* derivative of which has m. p. 246°. J. C. C.

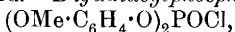
Hydrogenation of Polyphenols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 146, 1193—1196).—The authors have applied Sabatier and Senderens' method of hydrogenation by means of finely-divided nickel to quinol, catechol, and pyrogallol. At 160—170°, quinol yields a mixture of phenol, *cyclohexanol*, and *cis*- and *trans*-*cyclohexane-1:4-diols*. At 130°, the *cis*-compound is obtained exclusively. Catechol gives *cis-cyclohexane-1:2-diol*, rhombic crystals, m. p. 75—76°, b. p. about 225°. Pyrogallol is converted into *cyclohexane-1:2:3-triol*, tabular crystals, m. p. 67°. No definite product could be obtained from resorcinol, although a very small amount of a substance, m. p. 65°, was isolated, which was probably *cis-cyclohexane-1:3-diol*. J. C. C.

Melting Point of Resorcinol. CHARLES T. BENNETT (*Pharm. J.*, 1908, [iv], 26, 758).—After repeated crystallisation from benzene, resorcinol has m. p. 110°, although higher figures (up to 119°) are given in the literature. The sample was pure as estimated by Richard's method (titration with *N*/5-iodine), and contained neither catechol nor quinol. J. C. C.

Guaiaacylphosphoric Acids. VICTOR AUGER and P. DUPUIS (*Compt. rend.*, 1908, 146, 1151—1153).—The authors have prepared mono- and di-guaiaacylphosphoric acids by the following three methods: (1) by boiling guaiacol with phosphoryl chloride, and hydrolysing the resulting guaiaacylphosphoryl dichloride and diguaiaacylphosphoryl chloride; (2) by treating a mixture of guaiacol and pyridine in the cold with phosphoryl chloride, and decomposing the pyridine salt with alkali (especially suitable for the preparation of diguaiaacylphosphoric acid), and (3) by hydrolysing guaiacol phosphate with the calculated amount of alcoholic soda. *Guaiaacylphosphoryl dichloride*,



is a colourless oil, b. p. 178—180°/30 mm., readily hydrolysed to *monoguaiaacylphosphoric acid*, slender, deliquescent needles, m. p. 94°. The alkali salts are soluble in water, and the salts of the alkaline earths and of the heavy metals are insoluble; the *sodium*, *calcium*, and *copper* salts are described. *Diguaiaacylphosphoryl chloride*,



is a colourless oil, b. p. 258°/15 mm., slowly hydrolysed by water to *diguaiaacylphosphoric acid*, colourless tablets, m. p. 97°. The *sodium*, *calcium*, and *copper* salts are described. The two latter are soluble in water, and may be used for the separation of mono- and di-guaiaacylphosphoric acids, as the corresponding salts of the mono-acid are

insoluble. The authors find that when guaiacol is heated with phosphoryl chloride and excess of pyridine, the methyl group is eliminated with formation of catechol. J. C. C.

Tautomerism. IV. PAUL RABE (*Annalen*, 1908, 360, 289—298. Compare Abstr., 1906, i, 89).—The author finds that ethyl methyl-*cyclohexenonedicarboxylate* exists in two desmotropic modifications, namely, a solid enolic form (I) and an oily ketonic form (II):



Both modifications distil at the same temperature (200°/17 mm.), but do not yield an identical distillate; in each case about 20% of the one being converted into the other. This is the first proof of the existence of two desmotropic forms in a state of vapour.

[With DAVID SPENCE and RICHARD EHRENSTEIN.]—1-Methyl- Δ^1 -*cyclohexen-3-one-4:6-dicarboxylate* is obtained as an oil when ethyl 1-methyl-*cyclohexan-1-ol-3-one-4:6-dicarboxylate* is allowed to remain for two days in contact with hydrogen chloride in ethereal solution. After several days, crystals of the *enolic* form, m. p. 72°, separate, the residual oil consisting of the *ketonic* form. This has D_4^{20} 1.1687, n_D^{20} 1.4885; it is almost completely transformed into the enolic form by contact with piperidine or tripropylamine. Both modifications give a *sodium* salt, which, however, regenerates the enolic form. The same *p-nitrophenylhydrazones*, m. p. 165°, and *semicarbazones*, m. p. 162—164° (decomp.), were obtained from both the enolic and ketonic tautomerides.

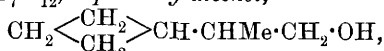
J. C. C.

The Action of Aluminium Chloride on Phenyl Mercaptan. J. J. B. DEUSS (*Rec. trav. Chim.*, 1908, 27, 145—148).—The addition of an excess of aluminium chloride to phenyl mercaptan, dissolved in large excess of light petroleum, results in the formation of diphenyl sulphide and diphenylene disulphide. Hydrogen sulphide is evolved together with a small quantity of hydrogen chloride. W. O. W.

Transformations of cycloButyldimethylcarbinol. II. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 676—698. Compare Abstr., 1905, i, 772).—The author has examined further the hydrocarbon C_7H_{12} , b. p. 100—102° (*loc. cit.*), and finds it to be identical with Rénard's heptene and with the hydrocarbon obtained by Maquenne from perseitol (Abstr., 1893, i, 635). The constitution of this

hydrocarbon is probably $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CMe} \\ | \\ \text{CH}_3 \cdot \text{CMe} \end{array}$.

The action of oxalic acid on *cyclobutyldimethylcarbinol* yields, besides the hydrocarbon C_7H_{12} , a *primary alcohol*,



b. p. 157°/773 mm., m. p. 27—28°, D_0^{20} 0.9057, n_D^{20} 1.4489, molecular refraction 33.75 (calc. for cyclic alcohol, 33.74). Its *phenylurethane*, $\text{NHPh} \cdot \text{CO} \cdot \text{OC}_7\text{H}_{13}$, crystallises from light petroleum in long needles, m. p. 88—89°, and its *acetate*, $\text{C}_7\text{H}_{13} \cdot \text{OAc}$, has b. p. 171°/751 mm.,

D_0^{15} 0.9403, n_D^{15} 1.4359. On oxidation with potassium dichromate and sulphuric acid, it yields an *aldehyde*, $C_6H_{11}\cdot CHO$, b. p. $144^\circ/751$ mm., $D_0^{18.5}$ 0.9072, D_0^{20} 0.8985, $n_D^{18.5}$ 1.4359, which forms a *semicarbazone*, $C_6H_{11}\cdot CH:N\cdot NH\cdot CO\cdot NH_2$, m. p. $188-189^\circ$, and an *oxime*, $C_6H_{11}\cdot CH:NOH$, m. p. 65° . The same aldehyde is obtained on oxidising *cyclobutyl*dimethylcarbinol, the oxidation in this case being preceded by transformation into the primary alcohol described above.

The action of hydrobromic acid on this primary alcohol also yields a hydrocarbon, C_7H_{12} , identical with that obtained by the action of oxalic acid on *cyclobutyl*dimethylcarbinol. The following are the physical characters of this hydrocarbon, which vary slightly with the source from which it is obtained, probably owing to admixture with the hydrocarbons $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH\cdot CMe\cdot CH_2$ and $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>C\cdot CMe_2$.

On treatment with concentrated sulphuric acid or hydriodic acid, the hydrocarbon C_7H_{12} is reduced to the compound C_7H_{14} (compare Maquenne, *loc. cit.*), b. p. $94-96^\circ/755-772$ mm., D_0^{20} 0.7546—0.7579, n_D^{20} 1.4144. Aschan (*Chemie der alicyclischen Verbindungen*, 473) regards this hydrocarbon C_7H_{14} as possibly identical with 1:3-dimethylcyclopentane, but the author regards it as, more probably, a mixture of 1:2-dimethylcyclopentane with a small proportion of methylcyclohexane.

The union of hydrogen bromide with the compound C_7H_{12} yields an unstable bromo-derivative, as also does the action of hydrobromic acid on the primary alcohol $C_7H_{13}\cdot OH$. The nitrosochloride, $C_7H_{12}\cdot NOCl$, prepared from the hydrocarbon C_7H_{12} , has m. p. $73-75^\circ$, and the dibromide, $C_7H_{12}Br_2$, m. p. $115-115.5^\circ$. The hexabromo-derivative, m. p. 134° , was also prepared (compare also Rénard, *Abstr.*, 1887, 565; Maquenne, *Abstr.*, 1889, 32, 361; 1892, 1065; Markownikoff, *Abstr.*, 1904, i, 384).

T. H. P.

Cholesterol. STEFAN MINOVICI (*Ber.*, 1908, 41, 1561—1565).—A study of the action of sulphuric and hydrochloric acids on cholesterol (compare Mauthner, *Abstr.*, 1906, i, 579). Gradual addition of concentrated hydrochloric acid to cholesterol in boiling alcoholic solution leads to the formation of *cholesteryl ether*, $(C_{27}H_{43})_2O$ or $(C_{27}H_{45})_2O$, which crystallises in yellow needles, m. p. 74.5° , forms a viscid *additive* compound with bromine, gives a yellow, fluorescent coloration with concentrated hydrochloric acid, and is isomeric with Mauthner and Suida's ether (*Abstr.*, 1896, i, 425).

When heated on the water-bath with equal volumes of concentrated sulphuric acid and water, cholesterol yields (a) a *cholesteryl ether*, which forms white crystals, m. p. 201° , gives a yellow coloration, and fluorescence with concentrated sulphuric acid, and is considered to be isomeric with the preceding ether and Mauthner and Suida's ether; it forms a *tetrabromide*, $(C_{27}H_{43}Br_2)_2O$ or $(C_{27}H_{45}Br_2)_2O$, crystallising in needles, m. p. 174.5° (decomp.). (b) The *cholesteryl ether*, m. p. 74.5° ; and (c) a *substance*, which crystallises in spangles, m. p. $135-136^\circ$, and appears to form cholesterol on repeated recrystallisation.

G. Y.

Cholesterol, Cholic Acid, and a Common Degradation Product of the Same. HUGO SCHRÖTTER, RICHARD WEITZENBÖCK, and REINHOLD WITT (*Monatsh.*, 1908, 29, 245—254).—Both cholesterol and cholic acid, when heated with concentrated sulphuric acid in the presence of a small quantity of mercury, yield a mixture of acids, which when treated with strong nitric acid yields *rhizocholic acid*, $C_8H_6O_7$, crystallising in small, white needles, m. p. 228—230°; the *silver* salt, $C_8H_3O_7Ag_3$, is a white precipitate; the *barium* and *calcium* salts are more soluble in cold than in hot water.

Since the acid is so stable towards concentrated sulphuric acid and nitric acid, the three carboxylic groups are evidently attached to three different carbon atoms. It is therefore suggested that the acid is a hydroxycyclopentadienetetracarboxylic acid having the composition

$$\begin{array}{c} \text{CH} \cdot \text{C}(\text{CO}_2\text{H}) \\ | \\ \text{OH} \cdot \text{C} \cdot \text{CH}(\text{CO}_2\text{H}) \end{array} \rangle \text{C} \cdot \text{CO}_2\text{H}$$
; the position of the ethylene linking and of the hydroxyl group is still uncertain. Since this carbon nucleus is characteristic of terpenes and camphenes, it is concluded that not only do cholesterol and cholic acid have a similar structure, but are also connected with the terpenes. W. H. G.

Non-hydrolysable Constituents of Cacao Butter. HERMANN MATTHES and O. ROHDICH (*Ber.*, 1908, 41, 1591—1592).—The two phytosterols, obtained previously from cacao butter (this vol., i, 199), are best prepared from crude phytosterol acetate; this is brominated in glacial acetic acid solution, and the bromides separated, reduced, and hydrolysed. Phytosterol acetate tetrabromide yields phytosterol, which crystallises in monoclinic leaflets, m. p. 162—163° (stigmasterol, m. p. 146°: *loc. cit.*). Phytosterol acetate dibromide yields phytosterol, which forms doubly refracting, hexagonal crystals, m. p. 139° (135—136°: *loc. cit.*).

Phytosterol and a yellow, unsaturated oil with a pleasant odour are obtained on hydrolysis of the fat extracted from cacao shells by light petroleum. G. Y

Hydrogenation of cyclobutanecarboxylic Acid. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 673—676).—In order to throw light on the formation of a 5-carbon atom ring compound from cyclobutyldimethylcarbinol by the action of hydriodic acid (compare Abstr., 1905, i, 772), the author has investigated the action of hydriodic acid (D 1.96) on cyclobutanecarboxylic acid. When these compounds are heated together in a sealed tube at 200—210° for nine hours, the products obtained are: (1) a small quantity of a substance, b. p. about 150°, having a hydrocarbon-like odour; (2) *n*-valeric acid, which represents the main product. The hydrogenation of cyclobutanecarboxylic acid thus differs from that of cyclobutyldimethylcarbinol in that it leads merely to the breaking of the tetramethylene ring at a position adjacent to the carboxyl group with formation of an open-chain compound. T. H. P.

The Six Dinitrobenzoic Acids. H. A. SIRKS (*Rec. trav. Chim.*, 1908, 27, 207—250).—This paper consists chiefly of work already published (compare Abstr., 1907, i, 131). Full details are given of

the preparation of the dinitrotoluenes and the corresponding dinitrobenzoic acids. Determinations of the constants of dissociation and esterification disclose the fact that these acids may be divided into two classes. The first includes the two acids in which a nitro-group does not adjoin the carboxyl group; these are only slightly dissociated in solution, and show a comparatively high value for the esterification constant. The four remaining acids, however, are much more highly dissociated, and exhibit correspondingly small values for the esterification constant.

A description and sketch is given of an apparatus suitable for the extraction of large quantities of liquid by means of ether.

W. O. W.

Chloromethyl Sulphate. II. Action on Amino-groups.

JOSEF HOUBEN and HANS R. ARNOLD (*Ber.*, 1908, 41, 1565—1580. Compare *Abstr.*, 1907, i, 1000).—The action of water on chloromethyl sulphate, $\text{CH}_2\text{Cl}\cdot\text{SO}_4\text{Me}$, was found previously to lead to the formation of methylsulphuric acid, formaldehyde, and hydrogen chloride; from this it appears that the chloromethyl is more reactive than the methyl group. Hence it was to be expected that the employment of chloromethyl sulphate as a methylating agent would lead to the formation of chloromethyl derivatives. This has been realised in the case of the three aminobenzoic acids. Anthranilic acid and chloromethyl sulphate form the methosulphate of chloromethylanthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\text{Cl}\cdot\text{HMeSO}_4$, which readily loses hydrogen chloride, forming the methosulphate of methyleneanthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\cdot\text{HMeSO}_4$ (Mehner, *Abstr.*, 1901, i, 470; 1902, i, 676). The methyleneanthranilic acid, when liberated, rapidly polymerises, hence the yield of cyanomethylanthranilic acid formed from it by the action of potassium cyanide and hydrogen chloride is the less the longer the methylene acid has been in the free state. *m*- and *p*-Aminobenzoic acids behave in the same manner as the *o*-amino-acid.

The action of chloromethyl sulphate on methylantranilic acid leads to the formation of a substance, which is probably *methylenebis-methyldiantranilic acid*, $\text{CH}_2(\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$, and must be formed by loss of hydrogen chloride from a mol. of methyl chloromethylanthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CH}_2\text{Cl}$, and a mol. of unchanged methylantranilic acid, $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$.

The action of chloromethyl sulphate on ammonia and substituted ammonias has also been studied. Whilst the action of chloromethyl sulphate on ammonia leads to the formation of methylamine hydrochloride, hexamethylenetetramine, and ammonium sulphate, diethylamine yields tetraethylmethylenediamine or, under special conditions, chloromethyldiethylamine. Primary and secondary aromatic amines react similarly, forming derivatives of methylenediamine.

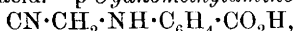
The following substances are new:

Methyleneanthranilic acid, $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2)_n$, is obtained as a golden-yellow powder, which darkens at 190° , m. p. 210° , is soluble in acids or alkalis, and yields a green *copper*, white *ferrous*, and dark

brown *ferric* salt. When treated with concentrated alcoholic hydrogen chloride, the acid yields an unstable *product*, which may be its hydrochloride or chloromethylanthranilic acid.

Chloromethyl sulphate and methyl anthranilate yield a *substance*, which is probably the methyl ester of the polymeric methylene-anthranilic acid, and on reduction with zinc and hydrochloric acid forms polymeric methyleneanthranilic acid together with traces of methylanthranilic acid.

p-Methyleneaminobenzoic acid, $(C_8H_7O_2N)_n$, is obtained as a white precipitate, darkening at 220° , decomp. 250° , and absorbs hydrogen chloride, forming a brown, deliquescent *acid*, which may be *p*-chloromethylaminobenzoic acid.

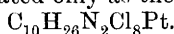


prepared together with a small amount of a *substance*, crystallising in white needles, m. p. 225° , from *p*-aminobenzoic acid, formaldehyde, and hydrogen cyanide, or in small amounts by adding potassium cyanide to *p*-methyleneaminobenzoic acid dissolved in dilute hydrochloric acid, forms a white, crystalline powder, m. p. 177° (decomp.).

m-Methyleneaminobenzoic acid, $(C_8H_7O_2N)_n$, is obtained as a yellowish-brown powder, decomp. 260° , which absorbs hydrogen chloride, forming an unstable, reddish-brown *product*.

m-Cyanomethylaminobenzoic acid, $C_9H_8O_2N_2$, prepared from *m*-aminobenzoic acid, crystallises in yellowish-brown leaflets, m. p. 193° . The *product*, obtained in small amount by the action of potassium cyanide and hydrochloric acid on *m*-methyleneaminobenzoic acid, has m. p. 182° .

Chloromethyl diethylamine, $NEt_2 \cdot CH_2Cl$, prepared by the action of chloromethyl sulphate on diethylamine at low temperatures, is unstable and can be isolated only as the *platinichloride*,



Tetraphenylmethylenediamine, $C_{25}H_{22}N_2$, prepared from chloromethyl sulphate and diphenylamine, forms an unstable, white, crystalline mass, m. p. $82-85^\circ$, is soluble in concentrated acids, and gives with nitrous acid a green oil dissolving to a bluish-green solution in ether.

s-Diphenyldiethylmethylenediamine, $CH_2(NPhEt)_2$, prepared from ethylaniline, crystallises from acetone in leaflets, m. p. 145° .

Di-p-bromo-s-diphenylmethylenediamine, $CH_2(NH \cdot C_6H_4Br)_2$, from *p*-bromo aniline, crystallises in white leaflets, m. p. 181° (decomp.); the sulphate, $C_{13}H_{14}N_2Br_2SO_4$, rhombic plates.

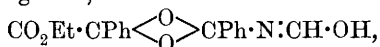
The *di-m-bromo* compound forms leaflets, m. p. 135° . 2:2'-Dinitro-*s-di-p-tolylmethylenediamine* $CH_2(NH \cdot C_6H_3Me \cdot NO_2)_2$, from 2-nitro-*p*-toluidine, crystallises in brown needles, m. p. 207° ; the sulphate forms yellowish-white needles. These derivatives of methylenediamine, when heated with sulphuric acid, yield formaldehyde and the corresponding amines.

G. Y.

Separation of Hippuric Acid from Urine. HERBERT E. ROAF (*Bio.-Chem. J.*, 1908, 3, 185-187).—To each litre of herbivorous urine, 250 grams of ammonium sulphate and 15 c.c. of concentrated sulphuric acid are added. The hippuric acid then crystallises out readily, and with a comparatively small amount of adherent urinary

pigment. This can be removed by recrystallisation after boiling with animal charcoal. W. D. H.

Bisbenzoyl Cyanide. OTTO DIELS and ALBERT PILLOW (*Ber.*, 1908, 41, 1893—1901).—A substance having the composition of benzoyl cyanide, but not identical with it or with trisbenzoyl cyanide, which was obtained by Wache (*Abstr.*, 1889, 684) by the action of sodium on benzoyl cyanide, and by Claisen (*Abstr.*, 1898, i, 423) by treating benzoyl chloride with hydrogen cyanide in presence of pyridine, is now found to be bisbenzoyl cyanide. It is considered to have the constitution $\text{CN} \cdot \text{CPh} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CPh} \cdot \text{NC}$, because (1) it does not give ketone reactions. (2) When treated with alcoholic hydrogen chloride, it forms an additive compound with 1 mol. of water, whilst at the same time one cyanogen group is converted into a carbethoxy-group; the resulting *ester*, which is formulated as



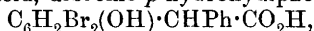
crystallises in prisms, m. p. 143—144°, forms with phenylcarbimide an *additive* compound, $\text{C}_{25}\text{H}_{22}\text{O}_6\text{N}_2$, crystallising in short prisms, m. p. 163—164°, and when treated with alkalis is hydrolysed, yielding benzoylformic acid, benzamide, formic acid, and ethyl alcohol. (3) Treatment of bisbenzoyl cyanide with hydriodic acid leads to the formation of an *amide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{CPh} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CPh} \cdot \text{NC}$, which crystallises in rhombic prisms, m. p. 174—177° (decomp.), cannot be converted into the preceding ester by treatment with alcoholic hydrogen chloride, and is hydrolysed by alkalis, yielding benzoylformamide, benzoic acid, and hydrogen cyanide; and (4) bisbenzoyl cyanide forms an *amidoxime*, $\text{OH} \cdot \text{N} : \text{C}(\text{NH}_2) \cdot \text{CPh} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CPh} \cdot \text{NC}$, which crystallises in rectangular prisms, m. p. 181° (decomp.), and on hydrolysis yields benzoic acid, hydrogen cyanide, and *benzoylformamidoxime*, $\text{COPh} \cdot \text{C}(\text{NH}_2) : \text{N} \cdot \text{OH}$, crystallising in quadratic prisms, m. p. 133—134°. When treated successively with phosphorus pentachloride in ethereal solution and with ice, this undergoes Beckmann's transformation, yielding benzoyl-carbamide. G. Y.

Synthesis of Polypeptides. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Ber.*, 1908, 41, 1991).—In the paper XV on the derivatives of 2 : 5-di-iodo-*L*-tyrosine (this vol., i, 420), the figures should be 3 : 5 in place of 2 : 5 throughout. C. S.

Liberation of Carbon Monoxide from Secondary and Primary Carboxylic Acids. AUGUSTIN BISTRZYCKI and B. VON SIEMIRADZKI (*Ber.*, 1908, 41, 1665—1672. Compare Oechsner de Coninck and Raynaud, *Abstr.*, 1903, i, 457, 458).—In continuation of the work previously published (*Abstr.*, 1906, i, 135), the liberation of carbon monoxide from various secondary and primary carboxylic acids when heated with concentrated sulphuric acid has been investigated. Most of the secondary acids studied, when heated with sulphuric acid, evolve roughly two-thirds to three-quarters of the theoretical amount

of carbon monoxide, whilst the primary acids yield relatively far less carbon monoxide. As a rule, the stability of the normal primary acids decreases with an increase in the number of methylene groups, whilst the normal acids are more stable than their isomerides with side-chains.

The secondary acids investigated were diphenylacetic acid, tetra-nitrodiphenylacetic acid, dibromo-*p*-hydroxydiphenylacetic acid,

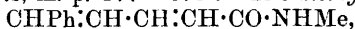


2 : 5-dimethylhydratropic acid, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, hexahydrobenzoic acid, quinic acid, and sulphocamphylic acid. The last acid is very stable towards sulphuric acid; when camphoric acid is heated with sulphuric acid at 200° , only slightly more than 1 mol. of carbon monoxide is evolved from 1 mol. of the acid, showing that the introduction of a sulphonic group into the acid radicle prevents the evolution of carbon monoxide. The primary acids studied were butyric acid, *isobutyric* acid, α -ethylbutyric acid, valeric acid, *isovaleric* acid, hexoic acid, and γ -methylvaleric acid.

W. H. G.

Action of Ammonia and Amines on Cinnamerylacrylic [Cinnamylideneacetic] Acid and its Methyl Ester. ADOLF RIEDEL (*Annalen*, 1908, 361, 96—108).—Hinrichsen observed (Abstr., 1904, i, 1012) that cinnamylideneacetic acid and its salts do not react with phosphorus pentachloride. This is in agreement with Meyer's observation (Abstr., 1901, i, 407) that acids with conjugated double linkings, if containing a second negative group in the δ -position to the carboxyl, are, in general, incapable of forming acid chlorides. The present author has found that methyl cinnamylideneacetate does not react with phosphorus pentachloride, but has obtained the amide in about an 8% yield by heating the methyl ester with alcoholic ammonia at 140 — 160° . Primary aliphatic amines, and to a very small extent secondary amines, such as diethylamine and piperidine, react with methyl cinnamylideneacetate in the same manner as does ammonia. Primary aromatic amines, on the other hand, do not react with the ester when boiled in a reflux apparatus, whilst at higher temperatures complete decomposition takes place. When heated with cinnamylideneacetic acid, aniline and *o*-toluidine form salts.

Cinnamylideneacetamide, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in yellow leaflets, m. p. 185° , decolorises bromine and permanganate solutions, and when heated with acetic anhydride in benzene solution yields the *acetyl* derivative, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHAc}$, crystallising in yellow leaflets, m. p. 177 — 178° . The *methylamide*,



crystallises in white needles, m. p. 157° ; the *ethylamide*, $\text{C}_{13}\text{H}_{15}\text{ON}$, white needles, m. p. 143 — 144° ; the *propylamide*, $\text{C}_{14}\text{H}_{17}\text{ON}$, white needles, m. p. 133° ; the *butylamide*, $\text{C}_{15}\text{H}_{19}\text{ON}$, white crystals, m. p. 119 — 120° ; the *diethylamide*, $\text{C}_{15}\text{H}_{19}\text{ON}$, white crystals, m. p. 106° ; the *piperidide*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NC}_5\text{H}_{10}$, colourless leaflets, m. p. 203° (decomp.).

The cinnamylideneacetates of the following bases are described; the temperatures are melting points. Methylamine, white needles, 142 — 143° ; ethylamine, white leaflets, 117 — 118° ; propylamine,

white leaflets, 140° (decomp.); butylamine, white leaflets, $107-108^{\circ}$; aniline, greenish-white needles, 184° ; *o*-toluidine, reddish-white needles; diethylamine, crystalline varnish, 80° ; piperidine, white prisms, 111° ; guanidine, yellowish-white leaflets, 220° . G. Y.

3:5-Dinitro-4-hydroxybenzoic Acid. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1908, [iv], 3, 591—593; *Arch. sci. phys. nat.*, 1908, 25, 474—478).—This acid, first prepared by Barth (*Zeit. Chem.*, 1866, 647) by nitration of *p*-hydroxybenzoic acid, was subsequently obtained by Salkowski from chrysanisic acid (*Abstr.*, 1872, 555), but the latter investigator expressed doubt as to the identity of the two acids. The results of the present work, undertaken to decide this point, show that the two are identical.

p-Hydroxybenzoic acid, nitrated by Barth's method, yields in addition to 3:5-dinitro-4-hydroxybenzoic acid, 3-nitro-4-hydroxybenzoic acid and 2:4-dinitrophenol. The ethyl ester of the dinitro-acid can be obtained by direct nitration of ethyl *p*-hydroxybenzoate. The methyl ester, m. p. $115-116^{\circ}$, similarly obtained, crystallises in colourless, prismatic needles, and is readily hydrolysed by ebullition with sodium carbonate solution. The dinitro-acid itself is best obtained by nitrating *p*-hydroxybenzoic acid dissolved in sulphuric acid and kept at 0° , with a mixture of equal parts of sulphuric acid and nitric acid (D 1.52). 3:5-Diamino-4-hydroxybenzoic acid, m. p. 205° , obtained by reducing the dinitro-acid with tin and hydrochloric acid, is readily oxidisable. The hydrochloride and sulphate are crystalline. T. A. H.

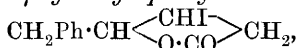
Action of Nascent Hypiodous Acid on Unsaturated Acids. Iodo-lactones. J. BOUGAULT (*Ann. Chim. Phys.*, 1908, [viii], 14, 145—183).—The first part of the paper contains an epitome of previous work (compare *Abstr.*, 1905, i, 9; 1906, i, 848; 1908, i, 179, 269). A number of new iodo-lactones are described; these have been obtained by the action of mercuric oxide and iodine on $\beta\gamma$ - or $\gamma\delta$ -unsaturated acids.

$\alpha\alpha$ -Dimethyl- Δ^{β} -pentenoic acid yields the lactone of β -iodo- γ -hydroxy- $\alpha\alpha$ -dimethylvaleric acid, $\text{CHI} \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CHMe} \end{smallmatrix} \text{O}$, m. p. 86° , a colourless, crystalline, neutral substance having a camphoraceous odour. $\alpha\alpha$ -Dimethylisocrotonic acid forms the lactone of β -iodo- γ -hydroxy- $\alpha\alpha$ -dimethylbutyric acid, $\text{CHI} \begin{smallmatrix} \text{CMe}_2 \\ \text{CH}_2 \cdot \text{O} \end{smallmatrix} \text{CO}$, a yellow liquid, which, like the preceding lactone, has a camphoraceous odour and is decomposed on boiling with aqueous sodium hydroxide.

The lactone of β -iodo- γ -hydroxyhexoic acid, $\text{CHI} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CHEt} \end{smallmatrix} \text{O}$, prepared from Δ^{α} -hydrosorbic acid, is a thick, yellow liquid, decomposing when distilled under atmospheric pressure. Fittig's α -hydropiperic acid furnishes the lactone of β -iodo- γ -hydroxy- δ -3:4-methylenedioxy-phenylvaleric acid, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CHI} \cdot \text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$, yellow crystals, m. p. 104° . Aqueous sodium hydroxide converts this into

the γ -ketonic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, whilst ammonium sulphite transforms it into the ammonium salt of a new sulphonic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{SO}_3\text{NH}_4)\\\text{O}\\\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$, which crystallises from hot water in glistening plates. The corresponding *barium* salt crystallises with $2\text{H}_2\text{O}$, and, when oxidised by potassium permanganate, furnishes piperonylic acid, homopiperonylic acid, and methylenedioxyphenylglyoxylic acid.

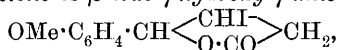
The lactone of β -iodo- γ -hydroxy- δ -phenylvaleric acid,



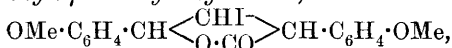
forms yellow crystals, m. p. 83° , and is prepared from hydrocinnamylidenecetic acid. Sodium hydroxide transforms it into the corresponding γ -ketonic acid, and in its behaviour with ammonium sulphite it resembles the preceding lactone. The *barium* salt has the composition $(\text{C}_{11}\text{H}_{11}\text{O}_3\text{SO}_3)_2\text{Ba}\cdot 3\text{H}_2\text{O}$. Phenylisocrotonic acid is the starting point for the preparation of the lactone of β -iodo- γ -hydroxy- γ -phenyl-

butyric acid, $\text{CHPh}\left\langle\begin{smallmatrix}\text{CHI}\\\text{O}\cdot\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$, m. p. 116° . This compound differs

from the two foregoing lactones in its behaviour towards sodium hydroxide and ammonium sulphite. The lactone of β -iodo- γ -hydroxy- α -*diphenylvaleric acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CHI}\\\text{O}\cdot\text{CO}\end{smallmatrix}\right\rangle\text{CHPh}$, yellow crystals, m. p. 106° , is obtained from Rebuffat's hydrophenylcinnamylidene acetic acid. The lactone of β -iodo- γ -hydroxy- γ -anisylvaleric acid,

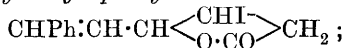


m. p. 125° , is prepared from anisylisocrotonic acid. The lactone of β -iodo- γ -hydroxy- α -*dianisylbutyric acid*,



yellow crystals, m. p. 115° , is obtained from Fittig's dianisylpentenoic acid.

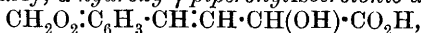
The two following iodo-lactones are obtained from unsaturated acids of the general formula $\text{CHR}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The lactone of γ -iodo- δ -hydroxyvaleric acid, $\text{CHI}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\\text{CH}_2-\text{O}\end{smallmatrix}\right\rangle\text{CO}$, is a liquid, becoming brown on exposure and decomposing when distilled. The lactone of γ -iodo- δ -hydroxy- δ -phenylvaleric acid, $\text{CHI}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2\\\text{CHPh}\cdot\text{O}\end{smallmatrix}\right\rangle\text{CO}$, forms yellow crystals, m. p. 90° . Cinnamenylisocrotonic acid yields the lactone of β -iodo- γ -hydroxy- ϵ -phenyl- Δ^8 -hexenoic acid,



this is sparingly soluble in alcohol and has m. p. 125° .

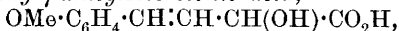
Anisylpyruvic acid, on partial reduction with sodium amalgam, gives α -hydroxy- γ -phenylisocrotonic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$. This was not isolated, but on treating an aqueous solution of its sodium salt with iodine the lactone of β -iodo- α -*dihydroxy- γ -phenylbutyric acid*, $\text{CHI}\left\langle\begin{smallmatrix}\text{CH}(\text{OH})\\\text{CHPh}\cdot\text{O}\end{smallmatrix}\right\rangle\text{CO}$, was formed. This occurs as yellow crystals, which darken at 125° and melt with decomposition at 132° . It

is much more soluble in the ordinary media than the preceding lactones. Similarly, *α*-hydroxy-γ-piperonylisocrotonic acid,



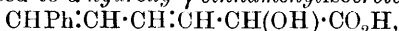
m. p. 143°, furnishes the lactone of β-iodo-αγ-dihydroxy-γ-methylenedioxy-butyric acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}$ $\left\langle \begin{smallmatrix} \text{CHI} \\ \text{O}\cdot\text{CO} \end{smallmatrix} \right\rangle \text{CH}\cdot\text{OH}$, small, yellow needles,

m. p. 150°. When anisylidenepyruvic acid is partly reduced by sodium amalgam, *α*-hydroxy-γ-anisylisocrotonic acid,



m. p. 145°, is obtained together with *α*-hydroxy-γ-anisylbutyric acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 116–117°. The former acid readily yields the lactone of β-iodo-αγ-dihydroxy-γ-anisylbutyric acid,

$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}$ $\left\langle \begin{smallmatrix} \text{CHI} \\ \text{O}\cdot\text{CO} \end{smallmatrix} \right\rangle \text{CH}\cdot\text{OH}$, m. p. 122°. Cinnamylidenepyruvic acid can be reduced to *α*-hydroxy-γ-cinnamenylisocrotonic acid,



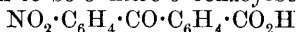
the sodium salt of which reacts readily with iodine to form yellow crystals of the lactone of β-iodo-αγ-dihydroxy-ε-phenyl-Δ^δ-hexenoic acid,

$\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}$ $\left\langle \begin{smallmatrix} \text{CHI} \\ \text{O}\cdot\text{CO} \end{smallmatrix} \right\rangle \text{CH}\cdot\text{OH}$, m. p. 122°.

The following βγ-unsaturated acids having a ketonic group in the α-position cannot be made to yield iodo-lactones: *piperonylidene-pyruvic acid*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 161°; *anisylidenepyruvic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 131°; *furfurylidene-pyruvic acid*, $\text{C}_4\text{H}_4\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 111°; *p-methoxyhydratropylidenepyruvic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 180°.

W. O. W.

Nitrobenzoylbenzoic Acids. J. RAINER (*Monatsh.*, 1908, 29, 177–180).—The compound obtained by Lang (*Abstr.*, 1905, i, 895) by adding *o*-benzoylbenzoic acid to nitric acid (1·52), and described as being identical with Kliegl's *p*-nitro-*o*-benzoylbenzoic acid (*Abstr.*, 1905, i, 187), is shown to be 3'-nitro-*o*-benzoylbenzoic acid,

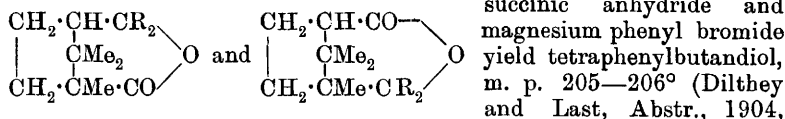


(compare Basler Chemische Fabrik, *Abstr.*, 1904, i, 512). A compound was obtained in the preparation of *p*-nitro-*o*-benzoylbenzoic acid by Kliegl's method which is probably *m*-nitro-*o*-benzoylbenzoic acid, $\text{COPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}_2\text{H}$; it crystallises in rectangular leaflets, m. p. 212°.

W. H. G.

Reactions of Dicarboxylic Anhydrides with Magnesium Organic Compounds. JOSEF HOUBEN and ARNOLD HAHN (*Ber.*, 1908, 41, 1580–1588).—The authors have studied the action of magnesium organic compounds on camphoric anhydride. As this reaction takes place less simply (Komppa, this vol., i, 352) than that with the anhydrides of monocarboxylic acids or with phthalic anhydride, the study has been extended to other dicarboxylic anhydrides. It is found that, whilst phthalic, naphthalic, camphoric, and citraconic anhydrides react readily, the last with almost explosive violence, with magnesium organic compounds, succinic anhydride reacts with great difficulty, and to an almost complete extent only in boiling toluene solution. With succinic anhydride, the reaction leads to the formation of products, $\text{C}_2\text{H}_4(\text{CR}_2\cdot\text{OH})_2$, in which the two

carbonyl oxygen atoms are displaced each by two alkyl groups. Thus



succinic anhydride and magnesium phenyl bromide yield tetraphenylbutandiol, m. p. 205—206° (Dilthey and Last, Abstr., 1904, i, 667). Camphoric anhydride, on the other hand, forms isomeric campholides (annexed formulæ), two alkyl groups being substituted for only one of the two carbonyl oxygen atoms.

ααδδ-Tetrabenzylbutan-αδ-diol, $\text{OH} \cdot \text{C}(\text{C}_7\text{H}_7)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7)_2 \cdot \text{OH}$, prepared from succinic anhydride and magnesium benzyl chloride, crystallises in needles, m. p. 129°, and gives a red coloration with concentrated sulphuric acid. The by-products of the reaction are probably unsaturated hydrocarbons or benzylated hydrofurans.

The action of magnesium ethyl bromide on succinic anhydride leads to the formation of *tetraethylhydrofuran*, $\text{C}_{12}\text{H}_{24}\text{O}$, which is obtained as an oil, b. p. about 80—120°/11 mm.

Camphoric anhydride and magnesium benzyl chloride form two dibenzylcampholides, $\text{C}_8\text{H}_{14} \left\langle \begin{array}{c} \text{C}(\text{C}_7\text{H}_7)_2 \\ \text{CO} \end{array} \right\rangle \text{O}$, which are separated by means of the sodium salts of the corresponding hydroxycampholic acids.

a-Dibenzylhydroxycampholic acid, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{C}(\text{C}_7\text{H}_7)_2 \cdot \text{OH}$, crystallises in needles containing alcohol of crystallisation, m. p. 177—178°, and is electrified when dried and rubbed. The sodium salt is sparingly soluble; the barium salt was analysed. *a-Dibenzylcampholide* is best prepared by boiling the acid with acetyl chloride, or by distillation of the acid in a vacuum; it forms prisms, m. p. 118°.

b-Dibenzylhydroxycampholic acid crystallises in needles, m. p. 145°. *b-Dibenzylcampholide* crystallises in needles, m. p. 114°. A mixture of the two dibenzylcampholides has m. p. about 50°. The allocation of the two constitutions requires further investigation. G. Y.

Preparation of Benzoic Acid. HANS VON LIEBIG (*Ber.*, 1908, 41, 1644—1645).—A 90—95% yield of this acid, free from benzoic acid, and therefore much better than that ordinarily obtained, results when 100 grams of benzil are boiled with a 50% aqueous solution of 100 grams of potassium hydroxide and 200 grams of alcohol for ten to twelve minutes; the mass is then left for several hours before collecting the salt, which is well washed with alcohol, then dissolved in cold water, heated to boiling, and the benzoic acid precipitated with sulphuric acid. W. R.

Tritancarboxylic Acids. HANS VON LIEBIG (*Ber.*, 1908, 41, 1645—1648. Compare Abstr., 1905, i, 781; 1907, i, 45, 930—1045; this vol., i, 445).—Cooled sulphuric acid gives in the condensation of benzil with hydroxybenzenes fairly good yields of *p*-hydroxytritanic acids, but poor yields of the ortho-acids. In order to obtain these acids in better yields, benzoic acid has been substituted, and experiments carried out by heating the molten acid with the phenol, the fusion treated twice with boiling water and then twice with 5% sodium carbonate to remove the free hydroxytritanic acid; the residue consists of lactone.

Resorcinol gives an almost quantitative yield of 2:4-dihydroxytritanolactone (1905, *loc. cit.*), and phenol an 80—90% yield of *p*-hydroxytritanic acid (Bistrzycki and Nowakowski, Abstr., 1901, i, 716) and 10—20% of *o*-hydroxytritanolactone (1907, *loc. cit.*).

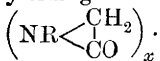
o-Cresol leads to the formation of 2-hydroxy-3-methyltritanolactone, $C_{21}H_{16}O_2$, which crystallises from alcohol in stout needles, m. p. 136—137°, and 4-phenoxy-3-methyltritanic acid, which sinters at 130°, froths at 140—143°, and is thereby converted into the anhydride, $C_{42}H_{34}O_5$, m. p. 215°. *m*-Cresol gives 4-hydroxy-2-methyltritanic acid and 2-hydroxy-4-methyltritanolactone (Bistrzycki and Nowakowski, *loc. cit.*). *p*-Cresol, in addition to the lactone (m. p. 132°: Bistrzycki gives 130°) and the *p*-acid, gives the 5:5'-ether of 4:4'-dihydroxy-2:2'-dimethyltritanic acid, $C_{42}H_{34}O_5$, which crystallises from benzene in needles, m. p. 245°.

Thymol yields the *p*-hydroxy-acid (Geipert, Abstr., 1904, i, 319) and a small quantity of 2-hydroxy-3-methyl-6-isopropyltritanolactone, crystallising in leaflets, m. p. 124°. Quinol gives 2:5-dihydroxytritanolactone (m. p. 200—201°: Tarczynsky, Diss., Freiburg, gives 194°). Methyl 2:5-dimethoxytritanate, $C_{23}H_{22}O_4$, crystallises in glistening leaflets from alcohol, m. p. 133°. Catechol gives 2:3-dihydroxytritanolactone, which separates from alcohol in fine crystals, m. p. 136°.

Guaiacol gives a mixture, one constituent of which is probably 4-hydroxy-3-methoxytritanic acid, $C_{21}H_{18}O_4$, crystals, m. p. 194°. Orcinol leads to the formation of 2:4-dihydroxy-6-methyltritanolactone, $C_{21}H_{16}O_3$, the crystals of which contain benzene of crystallisation, m. p. 177°, after warming, and pyrogallol yields 2:3:4-trihydroxytritanolactone, $C_{20}H_{14}O_3$, large crystals from benzene, m. p. 184°.

W. R.

Anhydrides of α -Amino-*N*-carboxylic Acids and of α -Amino-acids. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1908, 41, 1721—1726. Compare Abstr., 1906, i, 236; 1907, i, 770).—Anhydrides have been obtained by the action of thionyl chloride on the carbomethoxy-derivatives of *C*-phenylaminoacetic acid, phenylalanine, and leucine. The anhydrides crystallise well, and have low melting points. They are readily decomposed by water or absolute alcohol, yielding carbon dioxide and amorphous compounds of the type



N-Carbomethoxy-*C*-phenylglycine, $\text{CO}_2\text{Me} \cdot \text{NH} \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$, crystallises from water or benzene in needles, m. p. 87—88°. The anhydride,

$\text{CHPh} \begin{array}{c} \text{NH} \cdot \text{CO} \\ | \\ \text{CO} - \text{O} \end{array}$, crystallises from benzene or chloroform in prisms,

m. p. 99—100° (decomp.), and when boiled with absolute alcohol, yields phenylglycine anhydride, $\left(\text{CHPh} \begin{array}{c} \text{NH} \\ | \\ \text{CO} \end{array} \right)_x$, as an amorphous powder insoluble in all ordinary solvents.

N-Carbomethoxyphenylalanine, $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO}_2\text{Me}$, is a syrup, and the corresponding phenylalanine-*N*-carboxylic anhydride,

$\text{CH}_2\text{Ph}\cdot\text{CH}\begin{matrix} \text{NH}\cdot\text{CO} \\ \text{CO}\text{--}\text{O} \end{matrix}$, crystallises from cold ethyl acetate in colourless, glistening, rectangular plates, m. p. 127—128°.

N-Carbomethoxy*leucine* is a viscid oil, and *leucine-N-carboxylic anhydride*, $\text{C}_7\text{H}_{11}\text{O}_3\text{N}$, crystallises from benzene in colourless prisms, m. p. 48—50°. At above 80°, it loses carbon dioxide. J. J. S.

Amide Acids of Phenylsuccinic Acid. RICHARD ANSCHÜTZ and PAUL WALTER (*Annalen*, 1908, 361, 73—78).—It was found previously (Abstr., 1907, i, 766) that the action of ammonia or of substituted ammonias on phenylsuccinic anhydride leads to the formation of phenylsuccin- β -amic acids, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHR}$, the basic group combining with the carbonyl of the more feebly acid carboxyl. Lüttgen, on the other hand, on treating phenylsuccinic anhydride with ammonia, converting the resulting acid into the silver salt, and heating this with ethyl iodide, obtained small amounts of β -ethyl phenylsuccin- α -amate, $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which he prepared also by the action of potassium cyanide on ethyl benzylidene-malonate and distillation of the resulting ethyl hydrogen β -carbamyl-benzylmalonate, $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}_2\text{H}$ (*Diss.*, Bonn, 1899). The comparison of these results made it appear probable that the action of ammonia on phenylsuccinic anhydride leads to the formation of a mixture of phenylsuccinamic acids, the β -amic acid being the chief product, and that Lüttgen's esterification product was a mixture of esters, from which he isolated only the more sparingly soluble isomeride. These views have now been confirmed.

β -Ethyl phenylsuccin- α -amate, prepared by the action of concentrated sulphuric acid on ethyl β -cyano- β -phenylpropionate, has m. p. 173° (167°: Lüttgen, *loc. cit.*).

When converted into the silver salt and heated with ethyl iodide at 50—60°, the product of the action of ammonia on phenylsuccinic anhydride yields chiefly α -ethyl phenylsuccin- β -amate together with small amounts of the β -ethyl α -amate. By converting the mixed amic acids into the corresponding methyl esters, which can be readily separated quantitatively, it is shown that only about 5% of the reaction product is the α -amic acid, the reaction of the anhydride with ammonia taking place to the extent of 95% according to the rule previously laid down. G. Y.

Wandering of Alkyl Groups During the Distillation of Ether Acids. JACQUES POLLAK and H. FELDCHAREK (*Monatsh.*, 1908, 29, 139—155).—Nitro-2 : 3 : 4-trimethoxybenzoic acid when distilled was found by Pollak and Goldstein (Abstr., 1907, i, 320) to be converted into the methyl ester of the acid. The object of this investigation was to ascertain whether the esterification of the acid depends on the presence of the nitro-group, and to what extent the change is influenced by the number and positions of the methoxy- and nitro-groups. The following substances were distilled under the ordinary and under reduced pressure: nitro-3 : 4 : 5 trimethoxybenzoic

acid, dinitroanisic acid, nitroanisic acid, 3 : 4 : 5-trimethoxybenzoic acid, *o*-methoxybenzoic acid, *m*-methoxybenzoic acid, and anisic acid. The results obtained may be summarised as follows: (1) The presence of a nitro-group in the molecule decreases the stability of the acid and favours the formation of the ester; thus, nitro-3 : 4 : 5-trimethoxybenzoic acid and dinitroanisic acid are largely converted into their methyl esters when distilled in a vacuum. (2) An increase in the number of nitro-groups is accompanied by a marked decrease in stability; thus, dinitroanisic acid decomposes with the formation of the methyl ester when distilled under a pressure of 12 mm., whilst nitroanisic acid is only partly converted into its ester when slowly distilled under a pressure of 40 mm. (3) The methoxy-acids which do not contain a nitro-group may be distilled in a vacuum without undergoing decomposition. *o*-Methoxybenzoic acid, when distilled under the ordinary pressure, decomposes, yielding a mixture of methyl salicylate and methyl *o*-methoxybenzoate. Anisic acid and, more especially, *m*-methoxybenzoic acid are far more stable than the ortho-compound. However, the methyl esters of these acids are also formed on heating them for several hours at 180—270°. (4) Since *o*-methoxybenzoic acid decomposes far more readily than 3 : 4 : 5-trimethoxybenzoic acid, it follows that the ortho-position of the groups has a greater influence on the stability of the compound than the presence of a large number of methoxy-groups not ortho to the carboxyl group. 3 : 4 : 5-Trimethoxybenzoic acid is, however, far less stable than either anisic or *m*-methoxybenzoic acid.

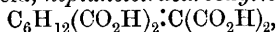
Ethyl 3 : 4 : 5-trimethoxybenzoate, $C_6H_2(OMe)_3 \cdot CO_2Et$, prepared by the action of methyl sulphate and potassium hydroxide on ethyl gallate, crystallises in white leaflets, m. p. 53—57°; the *nitro*-derivative, $NO_2 \cdot C_6H(OMe)_3 \cdot CO_2Et$, forms yellow crystals, m. p. 68—70°, and yields, on hydrolysis, the *acid*, $NO_2 \cdot C_6H(OMe)_3 \cdot CO_2H$, m. p. 164°.

W. H. G.

Santoninic Acid. ANGELO ANGELI and LUIGI MARINO (*Mem. R. Accad. Lincei*, 1908, [v], 6, 385—401. Compare Abstr., 1907, i, 321).—The following oxidation products of santonin have been obtained by the authors.

Dioxysantonin, $C_{15}H_{18}O_6$, obtained by oxidising santonin in sodium hydroxide solution by means of permanganate, separates from benzene in crystals, m. p. 261°, reacts with phenylhydrazine or hydroxylamine, and is the lactone of a dioxysantoninic acid.

A syrupy *ketonic acid*, $CO_2H \cdot CO \cdot C_{10}H_{14}(CO_2H)(COMe) \cdot OH$, obtained in the same way as the preceding compound, yields a crystalline *phenylhydrazone*, $C_{15}H_{20}O_5(N_2HPh)_2$, m. p. about 100°, which behaves as a dibasic acid. When treated with lead dioxide, this ketonic acid loses carbon dioxide and yields another *ketonic acid*, which forms a *phenylhydrazone*, $C_{14}H_{20}O_5(N_2HPh)_2$, m. p. 114—116° (decomp.). Under the action of alkaline permanganate solution, the syrupy ketonic acid, $C_{15}H_{20}O_7$, gives oxalic, formic, and acetic acids, together with an unstable acid, which readily loses two carbon atoms and forms a saturated aliphatic acid, *heptanetetra-carboxylic acid*,



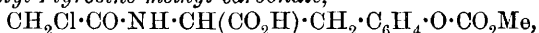
m. p. 165° (decomp.). When the latter is heated, it loses water and carbon dioxide, yielding the *anhydride*, $C_7H_{13}(C_2O_3) \cdot CO_2H$, m. p. 145° , of a heptanetricarboxylic acid. With water, this anhydride gives an *acid*, $C_{10}H_{16}O_6$, softening at about 88° , and then melting; with sodium hydroxide, the anhydride yields a *heptanetricarboxylic acid*, $C_{10}H_{16}O_6$, m. p. 127° . When the anhydride $C_{10}H_{14}O_5$ is oxidised with chromic and sulphuric acids, it yields succinic acid and a *pentanetricarboxylic acid*, $C_5H_9(CO_2H)_3$, m. p. about 110° , which may be identical with the acid prepared by Emery (Abstr., 1891, 547) and by Perkin (Trans., 1896, 69, 1510).

On heating a crude sample of the heptanetetracarboxylic acid, an *anhydride*, $C_{10}H_{14}O_5$, m. p. 141° , was obtained, which, when boiled with water, yields an *acid*, $C_{10}H_{16}O_6$, m. p. 141° . T. H. P.

The Synthesis of Polypeptides. EMIL FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 542—553).—The methods employed in the synthesis of polypeptides from amino-acids are not directly applicable when it is required to combine aminohydroxy-acids, owing to the action of phosphorus pentachloride on the hydroxyl group. It is found that the introduction of the carbomethoxyl group gives the necessary protection, the group being afterwards readily removed by hydrolysis. The products are, however, optically inactive.

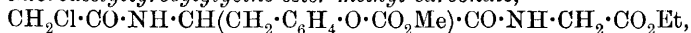
The reduction of polypeptides with sodium amalgam (this vol., i, 323) gives poor yields, but derivatives of acetals are readily prepared by condensing aminoacetal with chloroacetyl chlorides and treated the products with ammonia.

Chloroacetyl-L-tyrosine methyl carbonate,

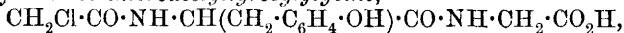


from chloroacetyl-L-tyrosine and methyl chlorocarbonate, separates from hot water as an oil, which slowly crystallises in thin, colourless, microscopic leaflets, m. p. 116° (corr.), $[\alpha]_D^{20} + 48.7^{\circ}$. It is readily hydrolysed by alkali.

With acetyl chloride and phosphorus pentachloride, it yields *chloroacetyltyrosyl chloride methyl carbonate*, which may be crystallised, but is best condensed, without previous isolation, with glycine ester, yielding *chloroacetyltyrosylglycine ester methyl carbonate*,



m. p. 130° (corr.), to a clear liquid, after sintering at 125° . The solutions in alcohol or chloroform are optically inactive. Sodium hydroxide hydrolyses it to *chloroacetyltyrosylglycine*,



which crystallises from hot water in small, quadrangular plates, m. p. $188-190^{\circ}$ (corr.) (decomp.).

Glycyltyrosylglycine, obtained by the action of ammonia on the above, separates from alcohol in microscopic crystals, m. p. 221° (corr.) (decomp.).

Glycylaminoacetal, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2$, prepared from aminoacetal and chloroacetyl chloride and heating the chloro-compound thus obtained with aqueous ammonia at 100° or dissolving it in liquid ammonia, separates from light petroleum in deliquescent, colourless crystals, m. p. 45° . The base is strongly alkaline, and does

not reduce Fehling's solution. The *hydrochloride* forms microscopic leaflets, m. p. 119° (corr.) (decomp.). The *hydrogen oxalate*, prepared by precipitation in alcoholic solution, has m. p. about 150° (decomp.); the *picrate* crystallises from ethyl acetate in yellow needles. Cold hydrochloric acid converts glycyaminoacetal into glycyglycinaldehyde.

A form of capillary polarimeter tube is described, having a capacity of only 0.1 c.c., and a pycnometer of about the same capacity. It has been found possible to make satisfactory determinations of the rotatory power and density with 0.01—0.02 gram of the substance.

C. H. D.

Condensation Reactions of $\alpha\beta$ -Unsaturated Aldehydes. II.

HANS MEERWIN (*Annalen*, 1908, 360, 323—347. Compare this vol., i, 89).—Vorländer (Abstr., 1898, i, 27; 1905, i, 792) found that cinnamaldehyde and crotonaldehyde react readily with methyl sodiomalonate, whilst, on the other hand, Bechert (Abstr., 1894, i, 488) and Hinrichsen (Abstr., 1905, i, 132) prepared cyanocinnamylideneacetic esters and cinnamylidenemalononitrile by condensation of cinnamaldehyde with cyanoacetic esters and malononitrile respectively in presence of sodium ethoxide; hence it was to be expected that $\alpha\beta$ -unsaturated aldehydes would condense with methyl malonate in presence of sodium ethoxide to form products of the type $\text{CHR}:\text{CH}:\text{CH}:\text{C}(\text{CO}_2\text{Me})_2$. It is now found, however, that, in the presence of sodium ethoxide, methyl malonate reacts with 3 mols. of $\alpha\beta$ -unsaturated aldehyde, the product having the constitution



The mechanism of this reaction is discussed, and the conclusion is drawn that the first product is $\text{CH}(\text{CO}_2\text{Me})_2 \cdot \text{CHR} \cdot \text{CH}:\text{CH}:\text{CH}(\text{CO}_2\text{Me})_2$, which, in presence of the alkali, may undergo transformation into $\text{CH}(\text{CO}_2\text{Me})_2 \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CH}:\text{C}(\text{CO}_2\text{Me})_2$. The present paper contains an account chiefly of the derivatives of cinnamaldehyde.

Pentamethyl hydrogen α -phenylpropane- $\alpha\gamma\gamma$ -trimalonate, $\text{C}_{23}\text{H}_{28}\text{O}_{12}$, prepared from cinnamaldehyde and methyl malonate, crystallises in flat needles, m. p. 119 — 120° , loses 1 mol. of carbon dioxide at 140 — 150° , and slowly decolorises permanganate, but not bromine. The *polycarboxylic acid*, obtained on hydrolysis of the ester with dilute sodium hydroxide, is an oil. *Methyl α -phenylpropane- $\alpha\gamma\gamma$ -trimalonate*, $\text{C}_{24}\text{H}_{30}\text{O}_{12}$, prepared from methyl cinnamylidenemalonate and methyl malonate, or by esterification of the pentamethyl hydrogen ester by means of methyl alcohol and hydrogen chloride, crystallises in monoclinic prisms, m. p. 86 — 87° .

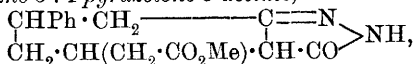
Knoevenagel and Herz's supposed methyl cinnamylidenemalonate (Abstr., 1905, i, 63), prepared by the action of cinnamaldehyde on methyl malonate in piperidine solution, is now found to be methyl cinnamylidenemalonate, m. p. 67° (Thiele and Meisenheimer, Abstr., 1899, i, 603).

β -Phenylpimelic- δ acetic acid,



is formed together with smaller amounts of 1-phenylcyclohexane-3-one-5-acetic acid when the pentamethyl hydrogen ester is boiled with

bromine in aqueous solution until the evolution of carbon dioxide and methyl bromide has ceased. It separates from water in crystalline crusts, m. p. 141—142°, and is not attacked by permanganate or bromine. The *methyl ester*, $C_{18}H_{24}O_6$, is a colourless oil. When boiled with sodium and small amounts of alcohol in toluene solution, this ester is converted into *methyl 1-phenylcyclohexane-3-one-4-carboxylate-5-acetate*, $CH_2 \begin{matrix} \text{CO} \cdot \text{CH}(\text{CO}_2\text{Me}) \\ \text{CHPh} \text{---} \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, which crystallises in white needles, m. p. 139—140°, and does not give a coloration with alcoholic ferric chloride. When heated above its m. p., or on prolonged boiling in alcoholic solution, the keto-ester is transformed into the *enolic modification*, which is crystalline, gives a bluish-violet coloration with ferric chloride, and is unstable, decomposing partly and changing into the keto-ester when brought into contact with water. The *phenylhydrazone* of the keto-ester, $C_{23}H_{26}O_4N_2$, crystallises in yellow needles, m. p. 142—144° (decomp.). When heated with hydrazine hydrate and methyl alcohol, the keto-ester is converted into *methyl 1-phenylcyclohexane-3:4-pyrazolone-5-acetate*,



which crystallises in white needles, m. p. 230—231° (decomp.), gives an intense brownish-red coloration with alcoholic ferric chloride, and is soluble in dilute alkalis.

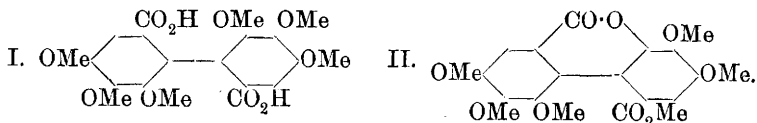
1-Phenylcyclohexan-3-one-5-acetic acid, $C_{14}H_{16}O_3$, formed by hydrolysis of methyl 1-phenylcyclohexan-3-one-4-carboxylate-5-acetate with acids, crystallises in white needles, m. p. 118—119°, and is identical with the by-product of the hydrolysis of pentamethyl hydrogen diphenylpropane- $\alpha\gamma\gamma$ -trimalonate. The *sodium, silver, and copper salts* are described. The *phenylhydrazone* crystallises in yellow needles, m. p. 166—167° (decomp.). The *methyl ester*, $C_{15}H_{18}O_3$, transparent needles, m. p. 81°. The action of bromine on the acid leads to the formation of hydrogen bromide and a white, crystalline *substance*, m. p. 174° (decomp.), which contains bromine.

Methyl benzylidenedimalonate, $\text{CHPh}[\text{CH}(\text{CO}_2\text{Me})_2]_2$, prepared by condensation of benzaldehyde with methyl malonate in presence of sodium ethoxide (compare Hinrichsen, *loc. cit.*; Staudinger, Abstr., 1905, i, 736), forms prismatic crystals, m. p. 64—65°, and, when hydrolysed with concentrated hydrobromic acid, yields β -phenylglutaric acid, m. p. 142—143° (138°: Vorländer, Abstr., 1902, i, 309; 139.5°: Staudinger, *loc. cit.*).

Methyl o-nitrobenzylidenedimalonate, prepared from *o*-nitrobenzaldehyde and methyl malonate, forms white crystals, m. p. 94—95°, and, on hydrolysis with concentrated hydrobromic acid, yields β -*o*-nitrophenylglutaric acid (Abstr., 1907, i, 534). G. Y.

Constitution of Ellagic Acid. JOSEF HERZIG and JULIUS POLAK (*Monatsh.*, 1908, 29, 263—280).—The correctness of Graebe's formula for ellagic acid (Abstr., 1903, i, 262) is further emphasised by the preparation of the following compounds from ellagic acid: 2:3:4:4':5':6'-hexamethoxydiphenyl-6:2'-dicarboxylic acid (I), its

methyl ester, and the lactone of methyl 2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylate (II):



In carrying out methoxyl determinations with these substances, it was found necessary to add repeatedly small portions of strong hydriodic acid, and to boil until methyl iodide ceased to be evolved; this often required seven to fourteen hours.

Tetramethylellagic acid is readily prepared by acting on ellagic acid with an ethereal solution of diazomethane (compare Goldschmiedt, *Abstr.*, 1905, i, 900). It is converted into a mixture of methyl 2:3:4:4':5':6'-hexamethoxydiphenyl-6:2'-dicarboxylate and of the lactone of methyl 2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylate when boiled for sixteen hours with methyl iodide and potassium hydroxide in alcoholic solution.

Methyl 2:3:4:4':5':6'-hexamethoxydiphenyl-6:2'-dicarboxylate, $C_{12}H_2(OMe)_6(CO_2Me)_2$, crystallises in two forms: small, coarse crystals, m. p. 109—111°, and slender, white needles, m. p. 90—95°. It is hydrolysed when boiled with an alcoholic solution of potassium hydroxide, yielding the *ether acid*, $C_{12}H_2(OMe)_6(CO_2H)_2$, m. p. 240°. Both the ether acid and its methyl ester are converted by hydriodic acid into ellagic acid.

The *lactone of methyl 2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylate*, $C_{13}H_2O_2(OMe)_5 \cdot CO_2Me$, m. p. 109—111°, when hydrolysed with alcoholic potassium hydroxide, is converted into *2-hydroxy-3:4:4':5':6'-pentamethoxydiphenyl-6:2'-dicarboxylic acid*, $OH \cdot C_{12}H_2(OMe)_5(CO_2H)_2$, m. p. 200—203° (decomp.). The latter compound, when treated with diazomethane, yields the above mentioned methyl hexamethoxydiphenyldicarboxylate.

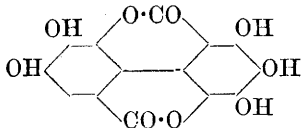
Preparation of Ellagic Acid [with MARIANNE VON BRONNECK].—The accuracy of Ernst and Zwenger's statement (*Annalen*, 1869, 159, 32) that ellagic acid is formed on treating ethyl gallate with sodium carbonate or ammonia in the presence of air seemed doubtful, since gallic acid when treated with potassium hydroxide yields galloflavin; their work was therefore repeated, and found to be correct. Ellagic acid is also formed from methyl gallate in the same way. Details are given for obtaining the best yield of ellagic acid from ethyl gallate.

W. H. G.

Resoflavin and its Analogue from Gallic Acid. JOSEF HERZIG and RUDOLF TSCHERNE (*Monatsh.*, 1908, 29, 281—294. Compare Perkin and Nierenstein, *Trans.*, 1904, 87, 1412).—A continuation of work previously published (*Abstr.*, 1907, i, 421). When the ether ester, $C_{14}H_3O_2(OMe)_7$, obtained from resoflavin is heated with a dilute potassium hydroxide solution, it is converted into the ether acid, $CO_2H \cdot C_{12}H_3(OMe)_5 \cdot CO_2Me$ (*loc. cit.*), but when heated with strong aqueous potassium hydroxide it yields the ether acid, $C_{12}H_3(OMe)_5(CO_2H)_2$.

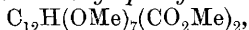
Since resoflavin when heated with zinc dust yields fluorene, it is evidently a derivative of diphenyldimetholide; two of the hydroxyl groups probably occupy positions 4 and 4' in the diphenyl nucleus, but the position of the third is still uncertain.

The analogue of resoflavin obtained from gallic acid by oxidation with ammonium persulphate is shown to be a monohydroxyellagic acid having the annexed constitution, since it is converted into the ether ester, $C_{14}H_3O_2(OMe)_9$, when treated with potassium hydroxide and methyl iodide; the ether ester on hydrolysis yields the ether acid, $C_{12}H(OMe)_7(CO_2H)_2$.



[With S. EPSTEIN.]—The ether ester, $C_{14}H_3O_2(OMe)_7$ (Herzig and Tscherne, *loc. cit.*), when boiled with a strong solution of potassium hydroxide in dilute alcohol, is converted into 3 (or 5) : 2 : 4 : 4' : 6'-*penta-methoxydiphenyl-6 : 2'-dicarboxylic acid*, $C_{12}H_3(OMe)_5(CO_2H)_2$, crystallising in white needles, m. p. 247—249°.

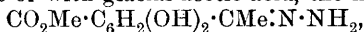
[With MARIANNE VON BRONNECK.]—The product obtained by the oxidation of gallic acid with persulphate (flavellagic acid) is converted by diazomethane into the *ether ester*, $C_{14}H_3O_4(OMe)_5$, m. p. 245°. It is converted by methyl iodide and potassium hydroxide into *methyl 3 : 4 : 5 : 6 : 2' : 3' : 4'-heptamethoxydiphenyl-2 : 6'-dicarboxylate*,



m. p. 83—87°, which, on hydrolysis with potassium hydroxide, yields the *acid*, $C_{12}H(OMe)_7(CO_2H)_2$, m. p. 163—167°; it crystallises with $1H_2O$, and then has m. p. 95—100° (decomp.). W. H. G.

Glaucohydroellagic Acid. MAXIMILIAN NIERENSTEIN (*Ber.*, 1908, 41, 1649—1650).—With the object of ascertaining whether ellagic acid on reduction behaves like tannin (compare Nierenstein, this vol., i, 90), the formation of glaucohydroellagic acid from ellagic acid has been investigated (compare Rembold, this Journ., 1876, i, 592). It is found that glaucohydroellagic acid is identical with pentahydroxydiphenylmethylolide, described by A. G. Perkin and Nierenstein (*Trans.*, 1905, 87, 1420). W. H. G.

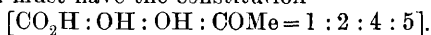
Xanthophanic Acid. IV. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1908, 41, 1607—1619. Compare *Abstr.*, 1906, i, 556; 1907, i, 889).—It was shown previously that the bromophenylhydrazone prepared from the “transformation product” of xanthophanic acid is a derivative, not of this, but of methyl resacetophenone-carboxylate. This is now found to be the case also with the hydrazone formed by the action of hydrazine on the “transformation product.” When heated alone or with glacial acetic acid, the hydrazone,



yields hydrazine and a lemon-yellow compound, which must have the constitution $N_2[CMe \cdot C_6H_2(OH)_2 \cdot CO_2Me]_2$, as when boiled with dilute sulphuric acid it forms hydrazine, methyl alcohol, and resacetophenone. These substances have now been prepared synthetically.

Resorcinol dimethyl ether is converted by means of hydrogen cyanide and hydrochloric acid into β -resorcyraldehyde dimethyl ether.

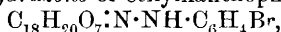
which is oxidised by potassium permanganate, forming β -resorecylic acid dimethyl ether, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$ [$\text{CO}_2\text{H}:\text{OMe}:\text{OMe}=1:2:4$]. An acetyl group is introduced into this by means of acetyl chloride and aluminium chloride, and finally the methyl groups are removed by treatment with hydriodic acid. This series of changes has been carried out also, starting from resorcinol diethyl ether. The resulting acid is identical with resacetophenonecarboxylic acid, which is obtained from the "transformation product" of xanthophanic acid methyl or ethyl ether, and must have the constitution



The methyl ester of the synthetical acid yields a *p*-bromophenylhydrazone identical with that obtained from the "transformation product." On the other hand, the hydrazone obtained from the synthetical methyl ester differs from that prepared from the "transformation product" both in its m. p. and in its solubility. It is considered that these hydrazones may be stereoisomerides, the more that the lemon-yellow products obtained on heating the hydrazones are identical.

When heated with ethyl ethoxymethyleneacetoacetate and small amounts of sodium ethoxide in alcoholic solution, ethyl resacetophenonecarboxylate yields traces of xanthophanic and glaucophanic acids, but the chief product is an acid, $\text{C}_{18}\text{H}_{14}\text{O}_7$, which crystallises in needles, m. p. 164—165°.

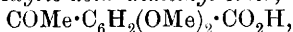
The *p*-bromophenylhydrazone of ethylxanthophanic acid,



prepared from ethylxanthophanic acid and *p*-bromophenylhydrazine in benzene solution, crystallises in red needles, m. p. 180—181°, decomposes on prolonged boiling with alcohol, and gives a yellowish-green fluorescence with concentrated sulphuric acid.

The products of each stage of the synthesis of resacetophenonecarboxylic acid were isolated and are described. The following are new.

Resacetophenonecarboxylic acid dimethyl ether,



crystallises in prisms, m. p. 231—233°. The *diethyl ether*, m. p. 190—202°, was obtained mixed with the *monoethyl ether*.

Methyl resacetophenonecarboxylate crystallises in needles, m. p. 124°. The *ethyl ester*, colourless needles, m. p. 94°. The *p*-bromophenylhydrazone of the methyl ester, m. p. 227—228° (224°: *loc. cit.*).

The *hydrazone*, prepared by the action of hydrazine on the "transformation product" of ethylxanthophanic acid, crystallises in white needles, m. p. 138°, decomp. 150—160°, forming the lemon-yellow *azine*, $\text{C}_{20}\text{H}_{20}\text{O}_8\text{N}_2$, m. p. 327°. The *hydrazone*, obtained from the synthetical methyl ester, forms yellowish-green crystals, m. p. 170°, changing into the lemon-yellow *azine*, m. p. 327°. G. Y.

Condensation of *o*-Nitrobenzaldehyde with Aromatic Hydrocarbons in Presence of Concentrated Sulphuric Acid. ALFRED KLIEGL (*Ber.*, 1908, 41, 1845—1851. Compare this vol., i, 82).—*m*- and *p*-Nitrobenzaldehyde condense with benzene in presence of concentrated sulphuric acid to form *m*- and *p*-nitrotriphenylmethane (Baeyer and

Tchacher, Abstr., 1887, 44; 1888, 373; 1890, 1141), but the author finds that the reaction proceeds quite differently when *o*-nitrobenzaldehyde is used, *o*-nitrophenyl *p*-tolyl ketone and *p*-tolylanthroxan being obtained from toluene, and phenylanthroxan with but a trace of *o*-nitrobenzophenone (in one experiment) from benzene. To confirm these results, *o*-nitrophenyl *p*-tolyl ketone was synthesised by oxidising *o*-nitrophenyl-*p*-tolylmethane (yellow oil, b. p. 195—198°/12 mm., prepared from *o*-nitrobenzyl chloride and toluene in presence of aluminium chloride) with sodium dichromate and glacial acetic acid. It forms thin, colourless prisms, m. p. 155°. On oxidation, it yields 2'-nitro-4-benzoylbenzoic acid, shining plates, m. p. 235·5—236°, and on reduction with tin and glacial acetic acid, *p*-tolylanthroxan, $C_{14}H_{11}ON$, yellow crystals, m. p. 95·5°.

J. C. C.

The Reaction between Potassium Cyanide and *o*-Nitrobenzaldehyde. JOAN POPOVICI (*Ber.*, 1908, 41, 1851—1853).—By the interaction of potassium cyanide and *o*-nitrobenzaldehyde, the author obtained (Abstr., 1907, i, 628) 2:2'-dinitrobenzoin, but Ekecrantz and Ahlquist (this vol., i, 347) stated that the product of the reaction was a mixture of *o*-nitrosobenzoic acid and *o*-azoxybenzoic acid. The author has now repeated the experiment under the same conditions, and confirms the former result. 2:2'-Dinitrobenzoin has m. p. 161—162° (corr.), and not 155·5° (corr.) as previously given. J. C. C.

Synthesis of Pulenone Derivatives from *o*-Cresol. KARL AUWERS and MAX HESSENLAND (*Ber.*, 1908, 41, 1790—1816).—The product, $C_9H_{12}OCl_2$ (Abstr., 1906, i, 947), obtained by the action of magnesium methyl iodide on 2-keto-1-methyl-1-dichloromethyl- $\Delta^{2,3}$ -cyclohexadiene, is shown to be a ketone, although it gives none of the characteristic reactions of ketones, probably owing to the inhibiting effect of the $-CHCl_2$ group. When reduced for several days with acetic acid and zinc dust, it yields the ketone, $C_9H_{14}O$, in the form of a liquid, b. p. 63—65°/16 mm. or 172—174°/757 mm., with an odour of peppermint.

The corresponding semicarbazone, $C_{10}H_{17}ON_3$, crystallises from a mixture of benzene and light petroleum in glistening needles, m. p. 129°. The ketonic nature of these products indicates that the magnesium methyl iodide has added itself to the double bond, and not to the carbonyl group, so that the original condensation product is 1:4-dimethyl-4-dichloromethyl- Δ^5 -cyclohexen-3-one, and the reduction product, 1:4:4-trimethyl- Δ^5 -cyclohexen-3-one or $\beta\gamma$ -pulenone, $CH \begin{smallmatrix} \diagup CH \\ \diagdown CHMe \end{smallmatrix} - CMe_2 > CO$ (compare Wallach, 1904, i, 74).

The optical properties of the compounds are in complete harmony with these formulæ. When reduced with sodium and alcohol, $\beta\gamma$ -pulenone yields an unsaturated alcohol, $\beta\gamma$ -pulenol, $C_9H_{16}O$, as a clear, mobile liquid, b. p. 82—85°/15 mm. or 189°/754 mm. It has $D_4^{18.5}$ 0.9209 and $n_D^{18.5}$ 1.47398, and when oxidised with chromic anhydride yields $\beta\gamma$ -pulenone.

The product obtained by the action of concentrated sulphuric acid on dichloro- $\beta\gamma$ -pulenone is the isomeric dichloro- $\alpha\beta$ -pulenone,

$\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}(\text{CHCl}_2) \\ \text{CMe} \text{---} \text{CH} \end{smallmatrix} > \text{CO}$ (compare Abstr., 1906, i, 947), and when reduced with acetic acid and zinc dust yields $\alpha\beta$ -pulenone as an oil, b. p. 86—88°/15 mm. or 208°/753 mm. It has D_4^{16} 0.9317 and n_D^{16} 1.47958. Its semicarbazone crystallises from methyl alcohol in flat, glistening prisms, m. p. 200—201°. When reduced, the $\alpha\beta$ -ketone yields a saturated alcohol, pulenol, probably identical with Wallach's pulenol, as when oxidised it yields pulenone. The formation of this saturated alcohol is in harmony with the view that $\alpha\beta$ -pulenone has the ethylene linking in the $\alpha\beta$ -position with respect to the carbonyl group. An examination of the oxidation products also supports this view. When oxidised with permanganate at 0—10°, $\alpha\beta$ -pulenone yields a mixture of Wallach's $\alpha\alpha$ -dimethyl- γ -acetylbutyric acid, the semicarbazone of which has m. p. 169° (Wallach: 163°), and $\alpha\alpha\delta$ -trimethyl- δ -hydroxyadipic acid, m. p. 145—148°, which is insoluble in benzene. A bimolecular reduction product, $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Cl}_4$, is obtained when dichloro- $\alpha\beta$ -pulenone is reduced with sodium amalgam, alcohol, and dilute acetic acid; a small amount is also formed during the reduction with zinc dust and acetic acid. It crystallises from alcohol, and has m. p. 215—225°.

Dichloro- $\alpha\beta$ -pulenone reacts with magnesium methyl iodide, yielding 1:1:4-trimethyl-4-dichloromethylcyclohexan-3-one, $\text{C}_{10}\text{H}_{16}\text{OCl}_2$, which has b. p. 135—145°/17—18 mm., m. p. 73°.

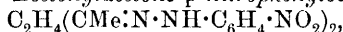
Dihydroxydichloropulenone (1:2-dihydroxy-1:4-dimethyl-4-dichloromethylcyclohexan-3-one), $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CMe}(\text{CHCl}_2) \\ \text{CMe}(\text{OH}) \cdot \text{CH}(\text{OH}) \end{smallmatrix} > \text{CO}$, is formed when dichloro- $\alpha\beta$ -pulenone is oxidised with a dilute aqueous acetone solution of permanganate in the presence of acid. It crystallises from water in compact prisms containing $1\text{H}_2\text{O}$; it melts at 70°, then solidifies, and melts again at 113°. Its monobenzoyl derivative, $\text{C}_{16}\text{H}_{18}\text{O}_4\text{Cl}_2$, has m. p. 182—183°. J. J. S.

Conversion of Dichloro- $\alpha\beta$ -pulenone into $\Delta^{1:3}$ -Dihydro-*p*-xylene. KARL AUWERS and MAX HESSENLAND (*Ber.*, 1908, 41, 1816—1827).—When dichloro- $\alpha\beta$ -pulenone (preceding abstract) is warmed with alcoholic potash, the chief products are a monobasic unsaturated acid, $\text{C}_9\text{H}_{13}\text{O}_2\text{Cl}$, an unsaturated acid, $\text{C}_9\text{H}_{12}\text{O}_2$, and a hydrocarbon, C_8H_{12} . The chlorinated acid is formed in small quantities only, probably according to the equation $\text{C}_9\text{H}_{12}\text{OCl}_2 + \text{H}_2\text{O} \rightarrow \text{C}_9\text{H}_{13}\text{O}_2\text{Cl} + \text{HCl}$; it crystallises from light petroleum, has m. p. 141.5°, and is probably 3-chloro-1:4-dimethyl- Δ^1 -cyclohexene-2-carboxylic acid. The acid $\text{C}_9\text{H}_{12}\text{O}_2$ can be obtained in larger quantity, and is 1:4-dimethyl- $\Delta^{1:3}$ -cyclohexadiene-2-carboxylic acid. It is best purified by conversion into the methyl ester and subsequent hydrolysis with alcoholic potassium hydroxide. The acid crystallises from dilute methyl alcohol or from light petroleum in glistening, flat plates, m. p. 40—42°. It is volatile with steam, but when heated alone to 155—175°, or when boiled with oxalic acid solution or with alkalis, carbon dioxide is eliminated and the hydrocarbon C_8H_{12} formed. The acid combines with bromine, and the dibromide when heated with alcoholic potassium hydroxide yields 2:5-dimethylbenzoic acid. The

methyl ester, $C_{10}H_{14}O_2$, has b. p. $79-81^\circ/10\text{ mm.}$, $D_4^{20} 0.997$, $n_D^{18} 1.47643$, and it is only slowly polymerised.

$\Delta^{1,3}$ -*Dihydro-p-xylene* (1:4-dimethyl- $\Delta^{1,3}$ -cyclohexadiene) is a clear, mobile liquid with an ethereal odour. It has $D_4^{20} 0.832$, $n_D^{19} 1.478$.

The hydrocarbon yields a dibromide, m. p. $240-247^\circ$, and when nitrated yields trinitro-*p*-xylene. The constitution of the hydrocarbon follows from the formation of this nitro-derivative, and from the fact that acetylacetone and acetone are found among its products of oxidation. The two ketones were isolated in the form of their *p*-nitrophenylhydrazones. *Acetylacetone p-nitrophenylhydrazone*,

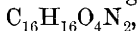


crystallises from glacial acetic acid or boiling amyl alcohol, and has m. p. $210-212^\circ$. J. J. S.

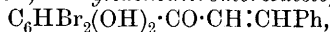
Derivatives of Resacetophenone. WILLY DANSE (*Ber.*, 1908, 41, 1619—1625).—The compounds described were prepared in order to compare them with the resacetophenone derivatives obtained from xanthophanic acid (compare this vol., i, 548). *Resacetophenonehydrazone*,



$OH\langle \text{Cyclohexadiene ring} \rangle CMe:N\cdot NH_2$, obtained by the action of hydrazine hydrate on the ketone in absolute alcohol, crystallises in white needles; on boiling with glacial acetic acid or heating at 125° , the *azine*,



is formed, crystallising from nitrobenzene in yellow needles, m. p. 307° . Resacetophenone gives only a monoacetate on boiling with sodium acetate and acetic anhydride (m. p. $72-73^\circ$, Nencki and Sieber, *Abstr.*, 1881, 591), the *phenylhydrazone*, $C_{16}H_{16}O_3N_2$, of which forms golden-yellow needles, m. p. 130° . Bromination of resacetophenone gives 3:5-dibromoresacetophenone, $C_6HBr_2(OH)_2\cdot COMe$, crystallising in needles, m. p. $173-174^\circ$; the *hydrazone*, $C_8H_8O_2N_2Br_2$, forms glistening, white needles, and at 145° or on heating with glacial acetic acid passes into the *azine*, $C_{16}H_{12}O_4N_2Br_4$, yellow needles, m. p. 340° ; the *phenylhydrazone*, $C_{14}H_{12}O_2N_2Br_2$, crystallises in white needles, m. p. 162° . Benzylidene derivatives are obtained on heating the dibromoresacetophenone with the aldehyde and concentrated sulphuric acid at 100° ; *benzylidenedibromoresacetophenone*,

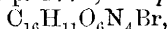


forms greenish-yellow needles, m. p. 165° ; the *m*- and *p*-nitrobenzylidene derivatives, $C_{15}H_9O_5NBr_2$, are greenish-yellow, and have m. p. 236° (decomp.) and 228° respectively.

Dibromoresacetophenone diacetate, $C_{12}H_{16}O_5Br_2$, crystallises from alcohol in needles, m. p. $104-105^\circ$, and on oxidation with chromic acid in acetic acid gives 3:5-dibromo-2:4-dihydroxybenzoic acid (Zehenter, *Abstr.*, 1882, 193), a result which establishes the position of the bromine atoms in dibromoresacetophenone.

Bromodinitrodihydroxybenzoic acid, $C_6Br(NO_2)_2(OH)_2\cdot CO_2H$, obtained when dibromoresacetophenone is warmed with three times its weight of nitric acid (D 1.4), crystallises from water in yellow needles, m. p. 187° ; the *silver salt*, $C_7H_2O_8N_2BrAg$, is an unstable, orange-yellow powder; the *methyl ester*, $C_8H_5O_8N_2Br$, forms white needles, m. p. 100° .

When, however, the dibromoresacetophenone is kept cool during nitration, *bromodinitroresacetophenone*, $C_8H_5O_7N_2Br$, is formed, which crystallises in yellowish-white needles, m. p. 148° ; the *potassium* and *sodium* salts are golden-yellow; the *diacetate*, $C_{12}H_9O_9N_2Br$, crystallises in white needles, m. p. 177° ; the *phenylhydrazone*,



in red needles, m. p. 236° ; the *hydrazone*, $C_8H_7O_6N_4Br$, in brown needles, decomp. 161° ; the *azine*, $C_{16}H_{10}O_{12}N_6Br_2$, is yellow, m. p. 320° .
W. R.

1 : 5-Diketones. III. PAUL RABE (*Annalen*, 1908, 360, 265—288. Compare Abstr., 1904, i, 747).—The author has continued his work on the synthesis of dicyclic keto-alcohols containing a bridged linking by transformation of semi-cyclic 1 : 5-diketones.

Transformation of Ethyl γ -Benzoyl- α -acetyl- β - γ -diphenylbutyrate into a Cyclic Keto-alcohol [With RICHARD EHRENSTEIN].—When deoxybenzoin is condensed with ethyl benzylideneacetoacetate in presence of sodium ethoxide, the sodium compound of *ethyl γ -benzoyl- α -acetyl- β - γ -diphenylbutyrate* is obtained, which, on treatment with ice-cold dilute sulphuric acid, yields the *ester* as a pale yellow, viscous oil, giving a violet coloration with alcoholic ferric chloride. This, slowly when alone, or more rapidly by treatment with alcohol, is transformed into ethyl 1 : 2 : 3-triphenylcyclohexan-1-ol-5-one-4-carboxylate, m. p. 123° , alcoholic solutions of which, when freshly prepared, do not give a reaction with ferric chloride, but when boiled for some time give a violet coloration. The substance therefore, on boiling, is partly converted into an *enolic* modification; this is obtained as a viscous oil by treating the sodium derivative with dilute sulphuric acid. It is quickly converted into the ketonic form in presence of alcohol. *Ethyl 2 : 3 : 4-triphenyl-1 : 6-dimethyl-1 : 4-dihydropyridine-5-carboxylate*, obtained by mixing the sodium compound of ethyl γ -benzoyl- α -acetyl- β - γ -diphenylbutyrate with methylamine hydrochloride in alcoholic methylamine solution, has m. p. 88° . *Ethyl 5-methylimino-1 : 2 : 3-triphenylcyclohexan-1-ol-4-carboxylate*, m. p. 108° , results on mixing ethyl 1 : 2 : 3-triphenylcyclohexan-1-ol-5-one-4-carboxylate with alcoholic methylamine.

Dicyclic Alcohols with Bridged Linkings [With MAX JAHR].—Methylcyclo-nonanolone (Abstr., 1904, i, 509), on treatment with hydroxylamine, furnishes two stereoisomeric oximes. The α -oxime, which separates on pouring the mixture on to ice, has m. p. 201° , and contains benzene of crystallisation when crystallised from this solvent. On reduction with sodium and alcohol, it yields the corresponding α -amine, m. p. 202 — 204° . The β -oxime, isolated from the mother liquor, has m. p. 145° , and on reduction furnishes the β -amine, m. p.

86 — 87° . Both these amines have the common position of a 7-amino-1-methyldicyclo-[1 : 3 : 3]-nonan-5-ol (annexed formula). The β -amine forms a *hydrochloride*, m. p. 272 — 275° (decomp.), a yellow *picrate*, decomp. 238° , a *picrolonate*, decomp. 285 — 286° , and a *methiodide*, decomp. 278° .

1:3-Dimethyldicyclo-[1:3:3]-nonan-5-ol-7-one, obtained by condensing dimethylcyclohexenone and ethyl acetoacetate in presence of sodium ethoxide, has m. p. 85°, and b. p. 160—170°/9—10 mm. On reduction with sodium and alcohol, it gives 1:3-dimethyldicyclo-[1:3:3]-nonan-5:7-diol, m. p. 195°, and on treatment with hydriodic acid and phosphorus, 1:3-dimethyldicyclo-[1:3:3]-nonane, a colourless, volatile liquid, b. p. 195—200°/750 mm. Dimethyldicyclononanone forms an α -oxime, m. p. 186—187°, and a β -oxime, m. p. 140—141°. The former gives the corresponding α -amine, m. p. 203—204°, and the latter the β -amine, m. p. 155°. The hydrochloride, decomp. at 265—268°, the picrate, m. p. 225—227° (decomp.), the picrolonate, decomp. at 274—275°, and the methiodide, decomp. at 220—223°, of the latter were prepared. J. C. C.

Method for the Determination of the Configuration of α -Dioximes. LEO TSCHUGAEFF (*Ber.*, 1908, 41, 1678—1684. Compare Abstr., 1905, i, 743).—The fact that, of the various stereoisomerides of an α -dioxime, the *syn*-modification alone yields complex metallic dioximines is utilised for the determination of the configuration of dioximes. Stierlin's α -anisildioxime (Abstr., 1889, 512), Hoffmann's α -cuminildioxime (Abstr., 1890, 1143), and α -furildioxime (m. p. 166—168°) are thus shown to possess the *syn*-configuration, whilst Werner and Bloch's two stereoisomeric *o*:*o'*-dichlorobenzildioximes (Abstr., 1899, i, 753), which do not form coloured complex metallic derivatives, must be the *amphi*- and the *anti*-modifications.

An interesting illustration of the method is given by Boeris' stereoisomeric methylanisylglyoxaldioximes (Abstr., 1894, i, 72). The modification, m. p. 125°, obtained by Angeli's method of reducing the corresponding peroxide, is probably the *amphi*-dioxime, and, in accordance with the rule, does not form dioximines. By heating, it is transformed into an isomeride, m. p. 207°, which does yield dioximines, and has consequently the *syn*-configuration, although Angeli's researches on purely aromatic peroxides show that the *amphi*-dioximes obtained by reduction are converted into *anti*-dioximes by heat. An explanation is offered of the abnormal behaviour of the preceding aliphatic aromatic dioxime. The nickel and the ferrodipyrrodine dioximines of α -anisildioxime and of α -furildioxime are described shortly. C. S.

Diethoxybenzoquinone. JACQUES POLLAK and J. GOLDSTEIN (*Monatsh.*, 1908, 29, 135—138).—Will has stated (Abstr., 1888, 457) that some dimethoxybenzoquinone is formed on adding pyrogallol trimethyl ether to concentrated nitric acid, whilst according to Schiffer (Abstr., 1892, 715) pyrogallol triethyl ether is not converted into diethoxybenzoquinone when added to nitric acid in glacial acetic acid.

This difference in the behaviour of the two ethers has been further investigated. Schiffer's work has been repeated and confirmed; when, however, the trimethyl ether is treated in the same way, it is partly converted into dimethoxybenzoquinone. It is also found that if the mixture of nitric and glacial acetic acids is added to a solution of pyrogallol triethyl ether in glacial acetic acid, some diethoxybenzoquinone is formed. The latter compound crystallises in wide

needles, m. p. 124—126° (compare Weidel and Pollak, Abstr., 1900, i, 290).
W. H. G.

Bornyl Palmitate. O. VON SOBBE (*J. pr. Chem.*, 1908, [ii], 77, 510—512).—Bornyl palmitate is best prepared by the action of palmityl chloride, which has been distilled over sodium, on the sodium derivative of borneol in boiling ethereal solution. The borneol should first be freed from *isoborneol* by the alcohol-sulphuric acid method. The ester crystallises in glistening, white scales, m. p. 67—68°.

G. Y.

Preparation of Acetals by Claisen's Method. ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 637—652).—Part of this paper has been already published (Abstr., 1907, i, 749).

The action of ethyl orthoformate on menthone or pulegone in presence of sulphuric acid yields the unstable acetal of menthone or pulegone, which, under the conditions of experiment, decomposes, giving ordinary alcohol and the ether corresponding with an unsaturated alcohol. Thus menthone yields the *ether*, $C_{10}H_{17}\cdot OEt$, b. p. 83—84°/9 mm., D_0^{20} 0.8749, and pulegone the *ether*, $C_{10}H_{15}\cdot OEt$, b. p. 97—97.5°/12 mm., D_0^{20} 0.9047.

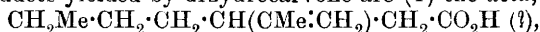
Camphoracetal, $C_{10}H_{16}(OEt)_2$, prepared by the action of ethyl orthoformate on camphor in presence of sulphuric acid, is an almost colourless liquid, b. p. 119—120°/16.5 mm., D_0^0 0.9632, D_0^{22} 0.9462. Besides camphoracetal, this reaction gives a *compound*, b. p. 82—83°/15 mm., which contains C, 72.73% and H, 10.62%, and is probably a compound of camphor and alcohol analogous with the so-called chloral alcoholate.

Methylmenthone, $C_{11}H_{22}O$, prepared by the action of magnesium methyl iodide on menthone, is a colourless, pleasant-smelling liquid, b. p. 103°/17 mm., 215.5°/749.6 mm., D_0^0 0.9121, D_0^{19} 0.8970.

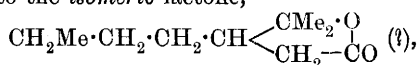
T. H. P.

Chemical Action of Light. XII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 576—582; *Ber.*, 1908, 41, 1928—1935. Compare Abstr., 1907, i, 537; this vol., i, 277).—When dissolved in aqueous alcohol and subjected to the prolonged action of light, dihydrocarvone, like other *cycloketones* (*loc. cit.*), yields an aliphatic acid and an aldehyde, whilst carvone is almost completely converted into an isomeric compound under the same conditions.

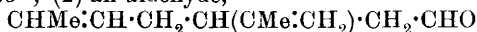
The products yielded by dihydrocarvone are (1) the *acid*,



which is an oily liquid, b. p. 135—137°/12 mm., 254.5°/758 mm., and, when boiled with sulphuric acid diluted with its own volume of water, is transformed into the *isomeric* lactone,



b. p. 264—265°; (2) an aldehyde,



which was not separated, but was converted into the corresponding hydroxamic acid, and this, by boiling with aqueous sulphuric acid, into the lactone, $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe}_2 \cdot \text{O} \\ \text{CH}_2 - \text{CO} \end{smallmatrix}$, b. p. 266—267°.

Curvone yields (1) an isomeric compound (annexed formula), m. p. 100°, b. p. 206·5°, which has the normal molecular weight in freezing acetic acid and (?) closely resembles camphor in odour and appearance; its oxime, $\text{C}_{10}\text{H}_{11} \cdot \text{NOH}$, m. p. 126—128°, separates from light petroleum in large, monoclinic crystals [BOERIS: $a : b : c = 1 \cdot 1057 : 1 : 0 \cdot 6233$; $\beta = 67^\circ 36'$], and its semicarbazone, $\text{C}_{11}\text{H}_{17} \cdot \text{ON}_3$, crystallises from alcohol in large prisms, m. p. 239°; (2) a small proportion of an oily compound, $\text{C}_{10}\text{H}_{16}\text{O}$ or $\text{C}_{10}\text{H}_{18}\text{O}$, b. p. 218—223°, which has an odour resembling that of roses. T. H. P.

Action of Magnesium Methyl Iodide on Carvenone and Pulegone. HANS RUPE and F. EMMERICH (*Ber.*, 1908, 41, 1750—1754).—The action of magnesium methyl iodide on carvenone, $\text{CHMe} \begin{smallmatrix} \text{CO} - \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPr}^\beta$, leads to the formation of an unstable, tertiary alcohol, which loses water, forming an unsaturated hydrocarbon, which must be 2-methylcarvenene, $\text{CMe} \begin{smallmatrix} \text{CMe} - \text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPr}^\beta$, since its molecular refraction is considerably higher than the calculated, as is also that of carvenone. It has been shown by other authors (Wallach, *Abstr.*, 1895, i, 672; 1904, i, 752; 1905, i, 450; Knoevenagel, *Abstr.*, 1897, i, 606) that in regard to their molecular refractions, $\alpha\beta$ -unsaturated ketones resemble alcohols with two ethylene linkings. The high molecular refraction of the unsaturated hydrocarbon agrees with the presence of two conjugated ethylene linkings. The hydrocarbons obtained in the same manner from carvone, dihydrocarvone, pulegone, and isopulegone (this vol., i, 433), which contain an ethylene linking in the 4(8)- or (8)(9)-position, have normal refractions, and hence cannot contain conjugated ethylene linkings.

The hydrocarbon obtained by the action of methyl iodide on pulegone, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CMe}_2$, must be 3-methyl- $\Delta^{4(8)}$ -menthadiene, $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CMe}_2$, and not 3-methylene- $\Delta^{4(8)}$ -terpene, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{C}(\text{CH}_2) \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CMe}_2$, as stated by Grignard (*Abstr.*, 1901, i, 679).

2-Methylcarvenene, $\text{C}_{11}\text{H}_{18}$, is a colourless, mobile oil, b. p. 86—87°/10 mm., $D_{20}^{20} 0 \cdot 8563$, $n_D^{20} 1 \cdot 49613$, $[\alpha]_D + 0 \cdot 67^\circ$, has a sweet flavour, and is not reduced by sodium and boiling amyl alcohol. As the hydrocarbon does not contain an asymmetric carbon atom, the small rotatory power must result from the presence of an impurity.

3-Methyl- $\Delta^{4(8)}$ -menthadiene, $\text{C}_{11}\text{H}_{18}$, is a colourless, mobile oil, b. p.

71—73°/10 mm., D^{20}_D 0.8402, n^{20}_D 1.47252, $[\alpha]^{20}_D$ -81.41°, -96.89°, is not reduced by sodium and amyl alcohol, and when oxidised by potassium permanganate yields acetone and an acid, which crystallises in white prisms, m. p. 153—154°. A mixture of this acid with adipic acid, m. p. 149—150°, had m. p. 120—127°. G. Y.

Isomerisation Phenomena during the Preparation of Cadinene. NICOLAUS LEFESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 698—699).—In order to investigate the genetic relations of the sesquiterpenes obtained from oleum cadinum, the author has studied the actions of hydrogen chloride and acetic acid on cadinene.

Cadinene dihydrochloride decomposes on heating, yielding cadinene exhibiting the following constants: b. p. 148—149°/20 mm., D^{20}_4 0.9172, n_D 1.5107, $[\alpha]_D$ -111.28°. But on prolonged heating in a sealed tube at 180—200°, cadinene dihydrochloride undergoes isomeric change into an unstable chloride, which yields a sesquiterpene having b. p. 145—148°/20 mm., D^{20}_4 0.9061, n^{20}_D 1.5041, and $[\alpha]_D$ -2.80°; this sesquiterpene is probably identical with the one obtained by Schindelmeiser (this vol., i, 353), and is isomeric with the one previously obtained by the author (this vol., i, 278) by the action of hydriodic acid on the sesquiterpene having $[\alpha]_D$ -14.12°.

When cadinene is heated with acetic acid at 180—200°, its rotation falls from -111.28° to -8°; the products formed have not been investigated.

The purest cadinene prepared by the author was obtained by the action of sodium ethoxide on the dihydrochloride, and has the following constants: b. p. 149°/20 mm. and 271—272° at ordinary pressure, D^{20}_4 0.9183, n^{20}_D 1.5073, and $[\alpha]_D$ -110.96°. T. H. P.

Constituents of Essential Oils. Elemicin, a High-boiling Constituent of Elemi Oil, and the Displacement of Alkyloxy-groups in the Benzene Nucleus by Hydrogen. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 1768—1775).—The author has investigated the composition of the fraction of crude elemi oil which has the highest boiling point. The specimen studied had D^{20} 1.031, n_D 1.5188, and on analysis gave figures pointing to the presence of a benzene derivative, accompanied by small amounts of a sesquiterpene alcohol. A fraction, b. p. 150—156°/10 mm., obtained on further distillation over sodium, had D^{20} 1.036, n_D 1.54193, was slightly levorotatory, and is considered to consist of *elemicin*, $\text{CHMe}:\text{CH}:\text{C} \begin{smallmatrix} \text{CH}:\text{C}(\text{OMe}) \\ \text{CH}:\text{C}(\text{OMe}) \end{smallmatrix} \text{C}:\text{OMe}$ (?). The propenyl group may be formed by intramolecular change of an allyl group during the distillation over sodium. When reduced with sodium and alcohol, elemicin yields an optically inactive product, $\text{C}_{12}\text{H}_{18}\text{O}_2$ (?), b. p. 125.5°/10 mm., D^{20} 0.994, n_D 1.51200. Oxidation of elemicin by means of potassium permanganate in acetone solution leads to the formation of 3:4:5-trimethoxybenzoic acid. When treated with sodium and alcohol, this acid is reduced to *m*-methoxybenzoic acid. *o*-Methoxybenzoic, veratric, asaronic, and myristic acids, on the other hand, are not reduced by sodium and alcohol. G. Y.

Constituents of Essential Oils. Elemicin and isoElemicin. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 1918—1921. Compare preceding abstract).—When treated with ozone in moist benzene solution, elemicin, which has not been distilled over sodium, yields trimethylhomogallaldehyde and trimethylhomogallic acid, but after distillation over sodium it yields trimethylgallaldehyde. Elemicin therefore contains an ethylene linking in the $\beta\gamma$ -position in the side-chain, and, when distilled over sodium, undergoes isomerisation into isoelemicin, which has the ethylene linking in the $\alpha\beta$ -position.

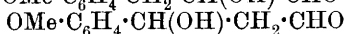
Trimethylhomogallaldehyde, $C_{11}H_{14}O_4$, b. p. 162—165°/10 mm., forms a semicarbazone, m. p. 188°. *Trimethylhomogallic acid*, $C_{11}H_{14}O_5$, m. p. 119—120°, forms a methyl ester, b. p. 172—182°/10 mm., D^{20}_D 1.153.

Trimethylgallaldehyde (3:4:5-trimethoxybenzaldehyde), $C_{10}H_{12}O_4$, m. p. 75°, b. p. 163—165°/10 mm., forms a semicarbazone, $C_{11}H_{15}O_4N_3$, m. p. 218°, and the aldoxime, $C_{10}H_{12}O_3 \cdot NOH$, m. p. 82—84°, b. p. 198—200°/10 mm. When heated with acetic anhydride, the aldoxime is converted into 3:4:5-trimethoxybenzonitrile, $C_{10}H_{11}O_3N$, m. p. 93°, b. p. 180—185°/10 mm., which on hydrolysis yields trimethoxybenzoic acid. G. Y.

Ethereal Oils, Material for the Investigation of. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1908, i, 464—465; from *Wiss. indust. Ber. Roure-Bertrand Fils*, 1907, [2], 6, 15—32).—Oil from Sandal Wood.—A yield of 3.8% oil, $[\alpha]_D + 47.07^\circ$, D^{15}_D 0.9799, found to contain 0.4% ester and 44.1% alcohol calculated as linalyl acetate and linalool. Oil from Linaloe Seeds.— $[\alpha]_D + 1.5^\circ$, after acetylation $[\alpha]_D - 3.2^\circ$, D^{15}_D 0.8883, saponification number 29.2, 10.2% ester calculated as linalyl acetate, saponification number after acetylation 164.5, 51.6% alcohol calculated as linalool. Oil of Sage from Grasse.—Two samples examined, $[\alpha]_D + 6.13^\circ$, $+ 6.45^\circ$, D^{15}_D 0.915, 0.916, saponification number 13.4, after acetylation 53.7. Climate and soil are stated to influence the physical and chemical constants of this oil. Oil from *Tetranthera polyantha* var. *citrata*.—(1) *From the bark*: $[\alpha]_D + 20.5^\circ$, after acetylation $+ 8.77^\circ$, D^{15}_D 0.8673, saponification number 252.3; contains 8% citral, 10% citronellal, 56.5% alcohols, and 2.4% esters. (2) *From the leaves*: $[\alpha]_D - 15.5^\circ$, after acetylation $- 4.3^\circ$, D^{15}_D 0.9013, saponification number [after acetylation 104.7; contains 6% citral, 21.2% cineol, and 31.3% alcohols. (3) *From the fruit*: $[\alpha]_D + 12.7^\circ$, after acetylation $+ 10.2^\circ$, D^{15}_D 0.8872, saponification number after acetylation 172.5; contains 64% citral, 19.4% alcohols, and 2% esters. Oil from *Magnolia Kobus* D. C.— $[\alpha]_D - 1.33^\circ$, D^{15}_D 0.9432; contains about 15% citral and a small quantity of anethole and estragole (?). J. V. E.

Lævorotatory Component of Tarragon Oil. MAURICE DAUFRESNE and FLAMENT (*Bull. Soc. chim.*, 1908, [iv], 3, 656—658. Compare this vol., i, 19).—The lævorotation of the higher boiling fractions of tarragon oil is shown to be due to the presence of an unstable aldehyde, which on heating loses water and resinifies. It has already been suggested that the source of the *p*-methoxycinnam-

aldehyde noted as a constituent of the oil may be an aldehyde-alcohol of the constitution $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$ or



(*Bull. Soc. chim.*, 1908, [iv], 3, 330).

T. A. H.

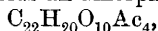
Congo-Copal and (White) Benguela-Copal. A. ENGEL (*Arch. Pharm.*, 1908, 246, 293—305).—The portion of Congo-copal soluble in ether yields to sodium carbonate *Congocopallic acid*, $\text{C}_{19}\text{H}_{30}\text{O}_2$, m. p. 115—118° (48—50%), *α-Congocopaloresen* (5—6%), and an ethereal oil (3—4%); the residue, soluble in alcohol and ether, yields *Congocopalolic acid*, $\text{C}_{22}\text{H}_{34}\text{O}$, m. p. 108—110° (22%), and *β-Congocopaloresen*, m. p. 175—178° (12%); impurities and ash, 4—5%. For Benguela-copal the corresponding results are: *Bengucopallic acid*, $\text{C}_{19}\text{H}_{30}\text{O}_2$, m. p. 134—136° (43—45%), *α-Bengucopaloresen* (4—5%), ethereal oil (3—4%), *Bengucopalolic acid*, $\text{C}_{21}\text{H}_{32}\text{O}_3$, m. p. 114—116° (a lower homologue of Congo-copalolic acid), 22%, and *β-Bengucopaloresen*, $\text{C}_{22}\text{H}_{36}\text{O}_2$, m. p. 192—196°. All these substances are amorphous. G. B.

Fagopyrum-Rutin. A. WUNDERLICH (*Arch. Pharm.*, 1908, 246, 241—256).—The glucoside from the flowers of buckwheat (*Polygonum fagopyrum*) is identical with rutin from rue and with violaquercitrin (viola-rutin); it has the formula $\text{C}_{27}\text{H}_{30}\text{O}_{16} \cdot 3\text{H}_2\text{O}$.

The quercetin trimethyl ether of Wallaschko (Abstr., 1904, i, 760), m. p. 154°, is hydrolysed by alcoholic potassium hydroxide to methylphloroglucinol and veratric acid; since hydroxyl groups in the ortho-position to the carbonyl groups are not directly methylated, this substance must be 1-hydroxy-3:3':4'-trimethoxyflavanol. It yields on acetylation *diacetylquercetin trimethyl ether*, $\text{C}_{15}\text{H}_5\text{O}_7\text{Me}_3\text{Ac}_2$, m. p. 170—171°. The yellow substance, m. p. 240°, obtained by Wallaschko (*loc. cit.*) is *quercetin methyl ether*, $\text{C}_{15}\text{H}_9\text{O}_7\text{Me}$, and yields *tetra-acetylquercetin methyl ether*, $\text{C}_{15}\text{H}_5\text{O}_7\text{MeAc}_4$, m. p. 156—157°; this methyl ether differs from the three known quercetin monomethyl ethers. Acetylruin, m. p. 114—116°, amorphous, probably contains nine acetyl groups, and would then have the composition $\text{C}_{27}\text{H}_{21}\text{O}_{16}\text{Ac}_9$. G. B.

Rhamnosides from Capparis spinosa and Globularia alypum. A. WUNDERLICH (*Arch. Pharm.*, 1908, 246, 256—259).—The above rhamnosides are identical with rutin (compare preceding abstract). G. B.

Sakuranin, a New Glucoside from the Bark of Prunus Pseudo-Cerasus var. Sieboldi. Y. ASAHINA (*Arch. Pharm.*, 1908, 246, 259—272).—*Sakuranin*, $\text{C}_{22}\text{H}_{24}\text{O}_{10} \cdot 4\text{H}_2\text{O}$, is extracted by water from the bark of the Japanese cherry tree, and is obtained crystalline after precipitation of impurities by basic aluminium acetate solution. Crystallised from alcohol or ethyl acetate, it forms white needles, m. p. 210—212°, has a bitter taste and dissolves in alkalis with an intense yellow colour; it yields an amorphous *acetyl* derivative,



and a crystalline *benzoyl* derivative, $\text{C}_{22}\text{H}_{20}\text{O}_{10}\text{Bz}_4$, m. p. 227°. On hydrolysis, sakuranin yields equal molecules of dextrose and *sakuranetin*, $\text{C}_{16}\text{H}_{14}\text{O}_5$, crystals from ether or benzene, m. p. 150°. The latter

substance contains one methoxyl group, absorbs bromine, and, when fused with potassium hydroxide, yields phloroglucinol, acetic and *p*-hydroxybenzoic acids. Sakuranin is physiologically inert, and does not produce glycosuria (like phloridzin). G. B.

New Reduction Products of Artemisin. PASQUALE BERTOLO (*Gazzetta*, 1908, 38, i, 554—559).—According to Rimini (*Soc. Chim. Roma*, Jan. 12, 1908), santonin and artemisin contain the same fundamental nucleus, the latter compound containing a hydroxyl group in place of a hydrogen atom of the former: santonin, $\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot$, artemisin, $\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{CMe}\cdot$. The author points out that artemisin cannot contain a hydroxyl group, since it does not yield an acetyl or benzoyl derivative, and, on reduction with zinc dust and acetic acid, forms a dehydropinacone, artemisone (compare Bertolo and Ranfaldi, *Abstr.*, 1905, i, 897). The formation of the latter compound, which may be regarded as an oxysantanone, indicates the presence in the molecule of a carbonyl group adjacent to a methylene group, $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}\cdot$.

The action of various reducing agents on artemisin has been studied, the results being as follows.

Reduction of artemisin with hydriodic acid and red phosphorus gives a good yield of a compound, m. p. 98—99°, crystallising from water in shining needles and somewhat resembling artemisic acid (compare *Abstr.*, 1904, i, 177). Reduction with sodium amalgam gives an almost quantitative yield of an acid, m. p. 170°, of which the ethyl ester was prepared. Reduction by means of chromous hydroxide yields a small proportion of a substance which retains the lactonic linking and a ketonic carbonyl group, and has the same m. p., 170°, as santonin and, like the latter, turns yellow in the light and gives a violet coloration with sulphuric acid and ferric chloride; this substance is also obtained by reducing artemisin with ferrous hydroxide. Reduction of the hydrazone of artemisin with sodium amalgam gives an acid, m. p. 116°, which contains nitrogen. T. H. P.

Nearest Acid Derivatives of the Chlorophyllins. LEON MARCHLEWSKI (*Ber.*, 1908, 41, 1858—1860. Compare Marchlewski and Schunck, *Trans.*, 1900, 77, 1080).—Polemical. A criticism of Tsvet's recent communication (this vol., i, 440). W. H. G.

Tetrahydropyrone Compounds. PAVEL PETRENKO-KRITSCHENKO and L. DEMENTYEFF (*Ber.*, 1908, 41, 1696—1697).—Ethyl 2:6-diphenyltetrahydropyrone-3:5-dicarboxylate in cold alcoholic solution reacts with concentrated alcoholic potassium hydroxide to form the salt, $\text{O} \begin{array}{c} \diagup \text{CHPh} \text{---} \text{C}(\text{CO}_2\text{Et}) \\ \diagdown \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Et}) \end{array} \text{C}\cdot\text{OK}$, whilst from the boiling solution cinnamic, benzylidenemalonic, and malonic acids have been isolated, and benzaldehyde detected by its odour. C. S.

Oxidation Products of Aconine. HEINRICH SCHULZE (*Arch. Pharm.*, 1908, 246, 281—292. Compare *Abstr.*, 1906, i, 599).—By the oxidation of aconine, ($\text{C}_{25}\text{H}_{41}\text{O}_9\text{N}$), with chromic acid, two substances,

$C_{24}H_{35}O_8N$ and $C_{24}H_{33}O_9N$, are formed, of which the former has basic and the latter both acid and basic properties; they appear to be an amino-alcohol and the corresponding amino-acid, and the acid has also been obtained by oxidation of the alcohol.

To the description of the base previously published, the following should be added. From analyses of the hydrochloride, the base has undoubtedly the formula $C_{24}H_{35}O_8N$, and the alternative formula $C_{24}H_{37}O_8N$, previously suggested, is now definitely excluded. The hydrochloride has $[\alpha]_D^{20} + 54.37^\circ$; the free base, m. p. $157-160^\circ$, its *sulphate*, and its *aurichloride* are all amorphous; the *hydriodide*, $C_{24}H_{35}O_8N \cdot HI \cdot 3H_2O$, forms fine needles, m. p. $220-230^\circ$ (decomp.). On acetylation, a crystalline *tetra-acetyl* derivative, m. p. 233° (decomp.), is formed, and, as the substance was previously shown to contain three methoxy-groups, seven of the eight oxygen atoms are thus accounted for, and the formula of the acetyl derivative may be written $C_{20}H_{19}O_5Ac_4(OMe)_3NMe$. The *aurichloride* of the acetyl derivative was also analysed.

Besides having one methoxy-group less, the base, $C_{24}H_{35}O_8N$, differs from aconine in reducing acid potassium permanganate, and also in forming a *methiodide*. The latter forms needles from alcohol, m. p. 222° (decomp.), and has the composition $C_{25}H_{33}O_8NI$. The only product which could be isolated on further oxidation of the base, $C_{24}H_{35}O_9N$, was a minute quantity of the hydrochloride of the under-mentioned amino-acid.

The *amino-acid*, $C_{24}H_{33}O_9N$, is formed from aconine in larger quantity than the alcohol if much chromic acid is used. Its *hydrochloride* forms glassy plates and short prisms, soluble in water with acid reaction, of the composition $C_{20}H_{21}O_6(OMe)_3NMe \cdot HCl \cdot \frac{1}{2}H_2O$ (decomp. above 250°). The crystalline *barium* salt, $C_{48}H_{66}O_{18}N_2Ba \cdot 10H_2O$, and the crystalline *hydrochloride* of the amorphous *methyl* ester,

$C_{19}H_{20}O_4(OMe)_3(NMe) \cdot CO_2Me \cdot HCl$,
m. p. $215-220^\circ$ (decomp.), have also been analysed.

G. B.

Carnine and Inosic Acid. FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1908, 29, 157—175. Compare Neuberg and Brahm, *Abstr.*, 1907, i, 1097; Bauer, *Abstr.*, 1907, i, 1098).—Carnine, originally obtained from meat extract by Weidel (*Abstr.*, 1871, 716), is shown to be an approximately equal molecular mixture of hypoxanthine and a new substance, inosine, so named because it is evidently closely related to, and is probably derived from, the same parent substance as inosic acid. By slightly modifying the method of Weidel (*loc. cit.*), the authors have obtained about 5—6 grams each of carnine and inosic acid from one pound of fresh meat extract.

Inosine, $C_{10}H_{12}O_5N_4$, may be separated from carnine by repeated extraction with small quantities of water, in which it is fairly soluble, or by treating carnine with acetic anhydride and sodium acetate, when it is obtained in the form of an *acetate*, $C_{10}H_9O_2N_4(OAc)_3$ or $C_{20}H_{16}O_3N_8(OAc)_6$, crystallising in glistening, silky needles or rhomboidal plates, m. p. 236° (decomp.). Inosine crystallises in slender, silky needles, m. p. 215° (decomp.); $[\alpha]_D^{18} - 49.2^\circ$; $[M]_D^{18} - 131.8^\circ$ (in water); 100 c.c. of the saturated solution in water at 20° contains

1.615 grams of inosine; the *silver* salt, obtained as a gelatinous precipitate, is soluble in ammonia. Inosine is hydrolysed when boiled with dilute sulphuric acid, yielding hypoxanthine and a *pentose*, the *osazone* of which, $C_5H_8O_3(N \cdot NHPh)_2$, crystallises in microscopic, pale yellow needles, m. p. 163° (decomp.).

Hypoxanthine aurichloride, $C_5H_4ON_4, HAuCl_4$, crystallises in glistening, prismatic needles. W. H. G.

True Tannates of Quinine. II. PIETRO BIGINELLI (*Gazzetta*, 1908, 38, i, 559—582. Compare Abstr., 1907, i, 955).—The author has prepared a number of true and false tannates of quinine and has studied their behaviour towards various reagents, the results obtained differing in some instances from those of Muraro (this vol., i, 451).

Hydrochloric acid acts on true tannates of quinine in the same way as dilute sulphuric acid, first displacing the tannic acid from its combination with quinine and then, as quinine salt, combining with the displaced tannic acid. Both the undissolved and dissolved portions represent pseudo-tannates, the nature of the former being independent of that of the true tannate employed; the dissolved false tannate, being, however, derived from quinine dihydrochloride, varies with the particular true tannate used.

In the action of tannic acid on quinine, several tannates of quinine are obtained, certain of them being formed in preference to the others according to the proportions of the components and the experimental conditions.

All the pseudo-tannates of quinine described in the various pharmacopœias are prepared from quinine sulphate or disulphate. They may be distinguished from the true tannates of quinine by the following methods: (1) 0.2—0.3 gram of the tannate is treated with a little moderately concentrated hydrochloric acid for a few minutes, after which 2—3 c.c. of water are added, and in a short time the acid decanted away. The yellow residue is treated with about 20 c.c. of water, with which it is shaken three or four times at intervals. If the residue dissolves completely, the original tannate is a true tannate of quinine, whilst, if there remains an undissolved residue, the compound examined is a pseudo-tannate derived from quinine sulphate or disulphate; (2) 0.2—0.3 gram of the tannate is treated with 2—3 c.c. of concentrated nitric acid, which is afterwards removed by heating on a water-bath. After cooling, the residue is treated with 20—30 c.c. of water and filtered, the filtrate being heated to 70° with a few drops of barium nitrate solution and then left. The gradual deposition of barium sulphate indicates a pseudo-tannate.

The following represent the compositions of the true tannates of quinine described by the author, the percentages of quinine present being indicated in brackets: $5C_{20}H_{24}O_2N_2, 5C_{14}H_{10}O_9$ (50.15);

$4C_{20}H_{24}O_2N_2, 5C_{14}H_{10}O_9$ (44.59); $2C_{20}H_{24}O_2N_2, 3C_{14}H_{10}O_9$ (40.14);

$2C_{20}H_{24}O_2N_2, 4C_{14}H_{10}O_9$ (33.47); $2C_{20}H_{24}O_2N_2, 5C_{14}H_{10}O_9$ (28.70);

$2C_{20}H_{24}O_2N_2, 6C_{14}H_{10}O_9$ (25.11); $2C_{20}H_{24}O_2N_2, 7C_{14}H_{10}O_9$ (22.32);

T. H. P.

Cytisine. EMIL MAASS (*Ber.*, 1908, 41, 1635—1637).—The conclusion that one of the nitrogen atoms of cytisine is secondary, the other being tertiary, is supported by the preparation of *cytisine cytisinyldithiocarbamate*, $C_{11}H_{13}ON_2 \cdot CS \cdot SH, NH : C_{11}H_{13}ON$, from carbon disulphide; it forms a white powder, m. p. 197—198°, decomp. 200°. Hydrochloric acid regenerates cytisine and carbon disulphide; copper acetate, mercuric chloride, and silver nitrate give reddish-brown, white crystalline, and white, flocculent precipitates respectively.

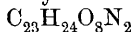
Benzoylcytisine, $C_{18}H_{18}O_2N_2$, prepared by the Schotten-Baumann method, is difficult to purify; it forms prisms, m. p. 116°.

W. R.

Sparteine. XII. CHARLES MOUREU and AMAND VALEUR (*Bull. Soc. chim.*, 1908, [iv], 3, 674—678. Compare Scholtz, *Abstr.*, 1906, i, 379).—Further results of work on the α and α' -sparteine methiodides (*Abstr.*, 1905, i, 608, 609, 659) are given. The two isomerides may be separated by crystallisation from alcohol. When pure, the α' -methiodide has $[\alpha]_D - 47.2^\circ$, solubility in water 8% at 15°, and furnishes a hydriodide having $[\alpha]_D - 40.32^\circ$ in water, which, when heated, yields the same sparteine hydriodide as is obtained from the hydriodide of the α -isomeride (*loc. cit.*). Sparteine dihydriodide, $C_{15}H_{26}N_2 \cdot 2HI, H_2O$, $[\alpha]_D - 15.91^\circ$, does not react with methyl iodide even when heated with it in a closed tube at 140—150°.

T. A. H.

Strychnos Alkaloids. I. New Method of Oxidising Brucine and Strychnine. HERMANN LEUCHS (*Ber.*, 1908, 41, 1711—1720).—When brucine and strychnine are oxidised with permanganate in acetone solution, 25% yields of crystalline acids, brucinonic acid,



and strychninonic acid, $C_{21}H_{20}O_6N_2$, are formed respectively. These acids contain four atoms of oxygen more and two atoms of hydrogen less than the corresponding alkaloids, and it is suggested that they are formed by the rupture of an ethylene linking with the production of two carboxyl groups and at the same time the oxidation of a secondary alcoholic to a carbonyl group. The acids are thus regarded as ketonic dibasic acids. In addition to these acids, small amounts of dihydrobrucinonic acid, $C_{23}H_{26}O_8N_2$, and dihydrostrychninonic acid, $C_{21}H_{22}O_6N_2$, are also formed; these are probably the secondary alcohols corresponding with the ketonic acid.

Brucinonic acid crystallises from water in colourless prisms containing H_2O , and has m. p. 178—183° (corr.), but when anhydrous sinters at 225° and melts at 266° (corr., decomp.); $[\alpha]_D^{20} - 48.5^\circ$. It dissolves readily in sodium carbonate solution, and behaves as a monobasic acid towards phenolphthalein or litmus. Solutions of its sodium salt yield precipitates with cupric sulphate, ferric chloride, silver nitrate, and lead acetate. The *monoethyl ester*, $C_{25}H_{28}O_8N_2$, obtained by the Fischer-Speyer method, crystallises from absolute alcohol in colourless prisms, m. p. 132°, or from glacial acetic acid in prisms, m. p. 161—163°.

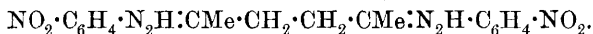
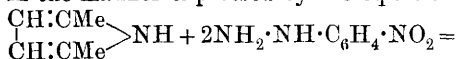
Dihydrobrucinonic acid crystallises from hot glacial acetic acid in

minute needles; it is lævorotatory in concentrated solution, but dextro-rotatory in more dilute solution.

Strychninonic acid crystallises from hot water in colourless prisms containing $2\text{H}_2\text{O}$. When anhydrous, it melts and decomposes at $265\text{--}267^\circ$ (corr.), and has $[\alpha]_{\text{D}}^{20} - 43.3^\circ$. *Dihydrostrychninonic acid* crystallises in rectangular plates, decomposes at about 315° (corr.), and has $[\alpha]_{\text{D}}^{20} + 4.3^\circ$ in 3.5% solution. The acids are not poisonous.

J. J. S.

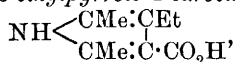
A Transformation of Dimethylpyrrole. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 485—486. Compare this vol., i, 207).—The interaction of ethyl formate and 2:5-dimethylpyrrole yields a mixture which, with *p*-nitrophenylhydrazine, gives a small quantity of a hydrazone, which is probably acetonylacetone-*p*-nitrophenylhydrazone. This compound, which is also obtained when 2:5-dimethylpyrrole is treated with *p*-nitrophenylhydrazine, is formed by the opening of the pyrrole ring in the manner expressed by the equation:



The hydrazines are hence able to convert dimethylpyrrole into ketohydrazones in the same way as hydroxylamine. T. H. P.

Synthesis of Ethyl 2:5-Dimethyl-3-ethylpyrrole-4-carboxylate. GEORG KORSCHUN (*Bull. Soc. chim.*, 1908, [iv], 3, 593—595. Compare Abstr., 1905, i, 373).—A continuation of work on the synthesis of similar esters by Hantzsch's method (Abstr., 1890, i, 1155).

Ethyl 2:5-dimethyl-3-ethylpyrrole-4-carboxylate,



m. p. $74\text{--}75^\circ$, could not be prepared by treating a mixture of ethyl acetoacetate and methyl α -chloropropyl ketone with ammonia, but a yield of about 27% of the theoretical was eventually obtained by the replacement of ethyl acetoacetate by ethyl β -aminocrotonate. The ester is difficult to purify by recrystallisation, and recourse was had to treating the crude product with a boiling solution of potassium hydroxide in methyl alcohol, which attacks the associated impurities, but has no action on the pyrrole ester. The latter was finally obtained in colourless, brilliant, bulky crystals from dilute methyl alcohol.

T. A. H.

Condensation of Acetonedicarboxylic Esters with Aldehydes under the Influence of Ammonia and Amines. III. PAVEL PETRENKO-KRITSCHENKO and W. PETROFF (*Ber.*, 1908, 41, 1692—1695. Compare Abstr., 1906, i, 452; 1907, i, 708).—The substances described previously as the nitrosoamines of the esters of 2:6-diphenylpiperidone-3:5-dicarboxylic acid and its *N*-methyl homologue are in reality the nitrites, since the bases are liberated by ammonium hydroxide in the cold.

The piperidone structure of the condensation products of ethyl acetonedicarboxylate with aldehydes has been proved by oxidising ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate with chromic and acetic acids, whereby a substance, $C_{23}H_{21}O_5N$, m. p. 195° , is obtained, which receives the constitution $NH < \begin{smallmatrix} CPh:C(CO_2Et) \\ CPh:C(CO_2Et) \end{smallmatrix} > CO$, because it does not give a coloration with ferric chloride, and is hydrolysed without fission by concentrated boiling alcoholic potassium hydroxide, yielding the acid, $C_{19}H_{13}O_5N$, m. p. 258° (decomp.).

The piperidone bases in benzene solution form salts with mineral acids which are insoluble in water. When, however, an alcoholic solution of the base is treated with a mineral acid, excepting nitric, the salts are not precipitated by the addition of water; from the solutions, ammonium hydroxide and platinum tetrachloride precipitate the unchanged bases and the platinichlorides respectively. The nitrites and nitrates, however, do not exist in the soluble forms, and are precipitated by the addition of these acids to the solutions of the salts. The nitrate of ethyl diphenylpiperidonedicarboxylate, $C_{23}H_{25}O_5N \cdot HNO_3$, m. p. $154-157^\circ$, has been prepared in this way.

C. S.

Decomposition of 3-Methyl 2-Hydrogen Quinoline. ALFRED KIRPAL (*Monatsh.*, 1908, 29, 227—234. Compare Abstr., 1907, i, 722).—It has been proved that the compound obtained as a by-product in the preparation of 2-methyl 3-hydrogen quinoline by the action of methyl alcohol on the anhydride of the acid is 3-methyl 2-hydrogen quinoline (Abstr., 1906, i, 697). The ammonium quinolinamate derived from the ester is converted by the action of alkaline hypobromite into a compound which must be 3-aminopicolinic acid, since, when heated above its melting point, it liberates carbon dioxide, yielding 3-aminopyridine (compare Pollak, Abstr., 1895, i, 391).

The quinolinamate is also converted through the diazo-compound into a substance which must be 3-hydroxypicolinic acid, for it yields 3-hydroxypyridine on distillation.

3-Aminopicolinic acid, $2NH_2 \cdot C_5H_3N \cdot CO_2H \cdot H_2O$, crystallises in faintly coloured plates, m. p. 210° (decomp.).

3-Hydroxypicolinic acid, $OH \cdot C_5H_3N \cdot CO_2H$, crystallises in colourless prisms or small, triangular plates, m. p. 215° . W. H. G.

Nitration of Quinoline and its Mononitro-derivatives. II. ADOLF KAUFMANN and HANS HÜSSY (*Ber.*, 1908, 41, 1735—1742. Compare Abstr., 1906, i, 984).—Quinoline when nitrated yields a mixture of equal amounts of 5- and 8-nitroquinolines. The 5-nitro-derivative on further nitration yields 5:7-dinitro-, and the 8-mononitro- yields 6:8-dinitro-quinoline (Claus and Hartmann's 5:8-dinitro-quinoline). 6-Nitroquinoline yields a mixture of 5:6- and 6:8-dinitroquinolines, and 7-nitroquinoline yields a mixture of the 5:7- and 7:8-dinitro-compounds.

The 6:7-dinitroquinoline cannot be obtained by direct nitration or by synthesis.

6:8-Dinitroquinoline is obtained free from the isomeric 5:6-compound when 6-nitroquinoline is added gradually to a mixture of sulphur trioxide and concentrated nitric acid, and the temperature allowed to rise gradually to 100° while the mixture is stirred. The constitution of the dinitroquinolines has been established by their syntheses from substituted anilines by Skraup's method, using either arsenic or picric acid as oxidising agent.

The melting points are 5:7, 180°; 5:6, 185°; 7:8, 221—223°. The 5:7-dinitro-compound dissolves in aqueous sodium hydroxide, yielding a red solution, whereas the 7:8-compound yields a yellow solution. The dinitro-compounds do not combine directly with methyl iodide; the 5:6-derivative, however, combines with methyl sulphate, and from this sulphate a *methiodide*, $C_9H_5O_4N_2 \cdot MeI$, can be obtained by double decomposition. It crystallises from water in brilliant dark red plates, and decomposes at 125—126°. J. J. S.

Fixation of Aromatic Amines on Vinyl Ketones. 4-Alkylquinolines. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 658—667).—The authors have studied the condensation of aromatic amines with vinyl ketones. In absence of water, the action of aniline on the β -chloro-ketones gives rise to the formation of 4-alkylquinolines. This is a general method of synthesis, and gives pure compounds, although the yield is not very good.

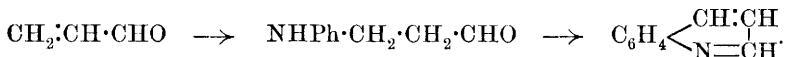
β -Anilinoethyl ethyl ketone, $NHPh \cdot C_2H_4 \cdot COEt$, is obtained by heating a mixture of aniline, water, and ethyl chloroethyl ketone on the water-bath, and crystallises from ether in plates, m. p. 55.5°. The *semicarbazone* has m. p. 130° (decomp.), and the *phenylcarbamide*, m. p. 76—77°. β -Anilinoethyl propyl ketone, $NHPh \cdot C_2H_4 \cdot COPr^a$, prepared from chloroethyl propyl ketone, separates from alcohol in pale yellow leaflets, m. p. 60°. The *phenylcarbamide* has m. p. 107—108°. β -Methylanilinoethyl ethyl ketone, $NPhMe \cdot C_2H_4 \cdot COEt$, has b. p. 164°/15 mm.; the *semicarbazone* has m. p. 163°, and the *picrate*, m. p. 110°. β -2-Carboxyanilinoethyl ethyl ketone, $CO_2H \cdot C_6H_4 \cdot NH \cdot C_2H_4 \cdot COEt$, has m. p. 106°.

4-Ethylquinoline (see following abstract) is obtained by heating on the water-bath a mixture of aniline (2 mols.), aniline hydrochloride (1 mol.), ethyl β -chloroethyl ketone (1 mol.), and an amount of absolute alcohol equal to the weight of the aniline hydrochloride. β -Anilinoethyl ethyl ketone is an intermediate product in this reaction, for it yields 4-ethylquinoline when heated with aniline hydrochloride.

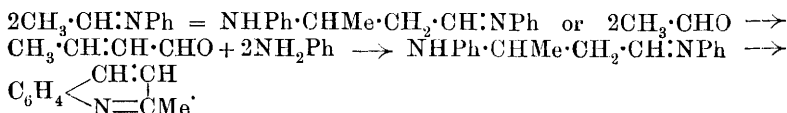
J. C. C.

4-Alkylquinolines. Mechanism of the Reactions of Skraup and of Doebner and Miller. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 667—674).—In view of the light thrown on the mechanism of the formation of quinolines (see preceding abstract), the authors consider that both Skraup's reaction and that due to Doebner and Miller can be explained in the same way. Skraup's reaction is to be regarded as (1) formation of an acraldehyde; (2) fixation of a mol. of aniline on the double linking, and (3) ring

formation by elimination of water and loss of two atoms of hydrogen, thus:



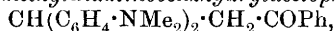
In the case of Doebner and Miller's reaction, the mechanism is:



4-Ethylquinoline (preceding abstract) has b. p. $134^\circ/9$ mm. The following salts are described: *picrate*, canary-yellow needles, m. p. 192° (decomp.), *dichromate*, brown needles, m. p. 94° , *platinichloride*, orange crystals, m. p. 208° (decomp.), *aurichloride*, yellow needles, m. p. 156° , *mercurichloride*, needles, m. p. 161° , *cadmiobromide*, needles, m. p. 204° , *methiodide-di-iodide*, brown crystals, m. p. $120-121^\circ$. On oxidation with chromic acid, 4-ethylquinoline yields cinchoninic acid.

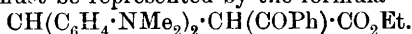
4-Propylquinoline (Koenigs, Abstr., 1899, i, 75), prepared from aniline and β -chloroethyl propyl ketone, has b. p. $159^\circ/16$ mm.; the *picrate*, m. p. 204° , the *platinichloride*, m. p. 198° (decomp.), the *mercurichloride*, m. p. 148° , the *cadmiobromide*, m. p. 148° . J. C. C.

Constitution of the Compounds of Tetramethyldiaminobenzhydrol with some Methylenic Derivatives. ROBERT FOSSE (*Compt. rend.*, 1908, 146, 1039—1042. Compare Abstr., 1907, i, 414). —The condensation of this alcohol with methylene compounds can be most simply represented thus: $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{OH} + \text{HCHXY} = \text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CHXY} + \text{H}_2\text{O}$. But the fact that all the compounds produced, when treated with dimethylamine in the presence of acetic acid, regenerate the methylene compound and give the leuco-base of crystal-violet suggests that the combination occurs through the oxygen atom, thus: $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{OH} + \text{HO}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} = \text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$. From the behaviour of the condensation compounds, however, the author concludes that in neutral or alkaline solution they have the constitution first suggested. Thus ethyl tetramethyldiaminobenzhydrylacetylacetate, $\text{C}_{23}\text{H}_{30}\text{O}_5\text{N}_2$, must have the constitution $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}(\text{COMe})\cdot\text{CO}_2\text{Et}$, since it forms an *oxime*, crystalline needles, m. p. 205° , and on hydrolysis loses carbon dioxide, giving a new ketone, *pp-tetramethyldiaminobenzhydrylpropanone*, $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{CH}_2\cdot\text{COMe}$, needles, m. p. 110° , which forms an *oxime*, m. p. $136-137^\circ$, a *semicarbazone*, m. p. 185° (decomp.), a *dihydrochloride*, and a *platinichloride*. As ethyl tetramethyldiaminobenzhydrylbenzoylacetate, $\text{C}_{28}\text{H}_{32}\text{O}_5\text{N}_2$, on hydrolysis loses carbon dioxide, giving *tetramethyldiaminobenzhydrylacetophenone*,



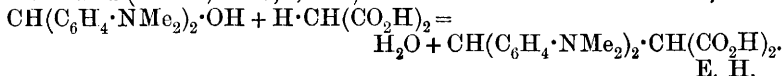
fine brilliant needles, m. p. 145° , which forms an *oxime* and a *platinichloride*, whilst, when treated with concentrated alcoholic potash, it undergoes simultaneously both "acid" and "ketone" hydrolysis, giving benzoic and tetramethyldiaminobenzhydrylacetic acids, tetra-

methyl-diaminobenzhydrylaceto-phenone, carbon dioxide, and alcohol, its constitution must be represented by the formula

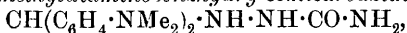


Similarly, tetramethyl-diaminobenzhydrylacetylacetone should be represented by $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CH}(\text{COMe})_2$, since alcoholic potash transforms it into potassium acetate and the substituted propanone described above. Again, alcoholic potash converts tetramethyl-diaminobenzhydrylbenzoylaceto-phenone into a mixture of the two mono-ketones, tetramethyl-diaminobenzhydrylaceto-phenone and tetramethyl-diaminobenzhydrylaceto-phenone, and therefore $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CH}(\text{COMe}) \cdot \text{COPh}$ must be the formula of the diketone.

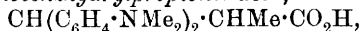
The oxide formula is inapplicable to tetramethyl-diaminobenzhydrylmalonic acid and its derivatives, which must have the constitution $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$. This acid can be prepared from the ethyl ester or it can be obtained directly. When malonic acid reacts with the hydrol, there is formed either tetramethyl-diaminobenzhydrylacetic acid (Abstr., 1907, i, 136) or the substituted malonic acid, thus:



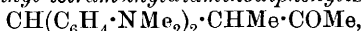
Constitution of the Methylene Derivatives of Tetramethyl-diaminodiphenylmethane. Replacement of Hydroxyl in Michler's Carbinol by the Alkylmethylene Radicle. ROBERT FOSSE (*Compt. rend.*, 1908, 146, 1277—1280. Compare preceding abstract).—The author has extended his work on the condensation of tetramethyl-diaminobenzhydryl. The constitution of the methylene derivatives described in the present paper is not in accord with Weil's ketonic formula (Abstr., 1894, i, 419) for the carbinol. The compounds have the constitution $(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \text{CH} \cdot \text{CX} \cdot \text{YR}$, and give a colourless solution with cold acetic acid, which becomes intensely blue on heating. They are decomposed in acetic acid solution in presence of dimethylaniline into the methylenic constituent and the leuco-base of crystal-violet. *Methyl tetramethyl-diaminobenzhydrylmethylacetate*, $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{CMeAc} \cdot \text{CO}_2\text{Me}$, has m. p. 113—114°. Under the influence of semicarbazide, it yields methyl methylacetate and *tetramethyl-diaminobenzhydrylsemicarbazide*,



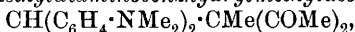
m. p. 185—187°, and when treated with alcoholic potash furnishes *α-tetramethyl-diaminobenzhydrylpropionic acid*,



sintering at 170°, m. p. 190°, the *ethyl* ester of which has m. p. 103—104°, and *methyl tetramethyl-diaminodiphenylisopropyl ketone*,



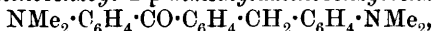
m. p. 144—145°; the *semicarbazone* sinters at 200°, m. p. 215—216° (decomp.). *Tetramethyl-diaminobenzhydrylmethylacetylacetone*,



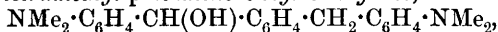
has m. p. 140—143°. With alcoholic potash, it gives methyl tetramethyl-diaminodiphenylisopropyl ketone.

J. C. C.

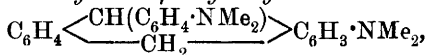
Amino-derivatives of *o*-Dibenzoylbenzene. ALFRED GUYOT and P. PIGNET (*Compt. rend.*, 1908, 146, 984—987. Compare Guyot and Catel, *Abstr.*, 1905, i, 226, 516, 540; 1906, i, 761; 1907, i, 76). —*p*-Dimethylaminobenzoyl-2-*p*-dimethylaminobenzylbenzene,



m. p. 133°, prepared by the condensation of dimethylaniline with *p*-dimethylaminobenzylbenzoyl chloride in the presence of aluminium chloride, forms pale yellow needles, and does not yield condensation products with hydrazine, phenylhydrazine, hydroxylamine, or semicarbazide; it forms a *trinitro*-derivative, $\text{C}_{24}\text{H}_{23}\text{O}_7\text{N}_5$, m. p. 174°, crystallising in brilliant yellow prisms; it is reduced by sodium amalgam to *tetramethyl-p*-diaminobenzylbenzhydrol,



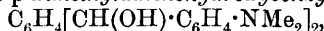
colourless prisms, m. p. 98°, which on further reduction yields 1 : 2-*di-p*-dimethylaminobenzylbenzene, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, m. p. 90°. When tetramethyldiaminobenzylbenzhydrol is mixed with concentrated sulphuric acid, it loses H_2O and forms an anthracene derivative, 2-*dimethylamino*-9-*p*-*dimethylaminophenyldihydroanthracene*,



m. p. 168°, which on oxidation with chloranil loses H_2 and is converted into 2-*dimethylamino*-9-*p*-*dimethylaminophenylan*thracene, $\text{C}_{24}\text{H}_{24}\text{N}_2$, m. p. 184°. 1 : 2-*Di-p*-dimethylaminobenzoylbenzene,



m. p. 207°, obtained as pale yellow prisms by the oxidising action of chloranil on *p*-dimethylaminobenzoyl-2-*p*-dimethylaminobenzylbenzene, yields a *monophenylhydrazone*, $\text{C}_{30}\text{H}_{30}\text{ON}_4$, m. p. 194°, a *dioxime*, $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_4$, m. p. 230°, and a *phthalazine*, $\text{C}_{24}\text{H}_{24}\text{N}_4$, m. p. 281°; it yields on reduction 1 : 2-*di-p*-dimethylaminohydroxybenzylbenzene,

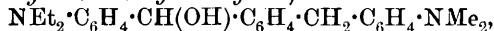


m. p. 124°, which loses H_2O by the action of phosphoryl chloride and is converted into 1 : 2-*p*-dimethylaminophenyl-1 : 2-*dihydroisobenzofuran*, $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \\ \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \end{array} \right\rangle \text{O}$, m. p. 145°.

The diethyl homologues of the above compounds have also been prepared: *p*-diethylaminobenzoyl-2-*p*-dimethylaminobenzylbenzene,



m. p. 104°, and *trinitro*-derivative, $\text{C}_{26}\text{H}_{27}\text{O}_7\text{N}_5$, m. p. 125°; *p*-diethylamino-*p*-dimethylaminobenzylbenzhydrol,



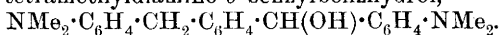
highly refractive, colourless crystals, m. p. 73°; 1-*p*-diethylaminobenzyl-2-*p*-dimethylaminobenzylbenzene, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 57°; the *dihydroanthracene* derivative, $\text{C}_{26}\text{H}_{30}\text{N}_2$, m. p. 113 the *anthracene* derivative, $\text{C}_{26}\text{H}_{28}\text{N}_2$, m. p. 132°; 1-*p*-diethylaminobenzoyl-2-*p*-dimethylaminobenzoylbenzene, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 110°, and its *phthalazine*, $\text{C}_{26}\text{H}_{28}\text{N}_4$, m. p. 189°, and *phenylhydrazone*, $\text{C}_{32}\text{H}_{34}\text{ON}_4$, m. p. 170°. M. A. W.

Some *o*-Benzylated Dyes from Triphenylmethane. ALFRED GUYOT and P. PIGNET (*Compt. rend.*, 1908, 146, 1043—1045).—The

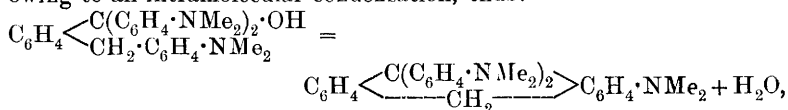
stability towards alkalis conferred on dyes of the type of malachite-green by substituting groups in the ortho-position to the methane carbon atom is usually explained by a steric protection by these groups. On this hypothesis, it would be expected that groups of higher molecular weight would have a proportionally greater effect, and it has been found, in fact, that the benzyl group has a protective action of the same order as the sulphonic group when substituted in the ortho-position. The tetra-alkyldiamino-*o*-benzoylbenzylbenzenes,

$C_6H_4 \begin{smallmatrix} \diagup CO \cdot C_6H_4 \cdot NR_2 (1) \\ \diagdown CH_2 \cdot C_6H_4 \cdot NR_2 (2) \end{smallmatrix}$, and the tetra-alkyldiamino-*o*-benzylbenz-

hydrols, $C_6H_4 \begin{smallmatrix} \diagup CH(OH) \cdot C_6H_4 \cdot NR_2 (1) \\ \diagdown CH_2 \cdot C_6H_4 \cdot NR_2 (2) \end{smallmatrix}$ (preceding abstract), readily condense with various amines, giving *o*-benzylated malachite-greens or their leuco-derivatives. Thus dimethylaniline in the presence of phosphoryl chloride reacts with tetramethyldiamino-*o*-benzoylbenzylbenzene, giving *o*-dimethylaminobenzylphenyltetramethyldiaminodiphenylcarbinol, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot OH$, which can be isolated in the form of small, reddish-brown crystals of the *zincchloride*, $C_{32}H_{36}N_3Cl_3Zn$. The dye also forms a double *nitrate* with potassium, $C_{32}H_{36}O_6N_5K$, beautiful crystals having a coppery reflex, and a similar *sodium salt*. The *leuco-base*, $C_{32}H_{37}N_3$, fine white needles, m. p. 162° , is easily obtained by reducing the dye with zinc and hydrochloric acid, or by the direct condensation of dimethylaniline with tetramethyldiamino-*o*-benzylbenzhydrol,



This dye, like all the amido-dyes derived from triphenylmethane, dissolves in concentrated sulphuric acid with an orange-red coloration; in this instance, however, the liquid is rapidly decolorised, owing to an intramolecular condensation, thus:



giving 2:13:13'-hexamethyltriamino-9:9-diphenyldihydroanthracene, a white, crystalline powder, m. p. 175° , giving colourless solutions in dilute mineral acids.

By using diethylaniline in place of the methyl derivative, the homologue of the above dye is obtained, and can be isolated in the form of the *zincchloride*, $C_{34}H_{40}Cl_3N_3Zn$, and the double *nitrates* with *sodium* and *potassium*, $C_{34}H_{40}O_6N_5Na$ and $C_{34}H_{40}O_6N_5K$. The *leuco-base*, $C_{31}H_{41}N_3$, has m. m. 107° .

When *o*-dimethylaminobenzyl-diethylaminobenzoylbenzene is similarly condensed with diethylaniline, an *o*-dimethylaminobenzyl derivative in the form of a brilliant green is produced. This gives the double *nitrates* $C_{36}H_{41}O_6N_5K$ with *potassium*, and $C_{36}H_{41}O_6N_5Na$ with *sodium*, and a *leuco-derivative*, $C_{36}H_{45}N_3$, m. p. 118° . E. H.

Striking Fluorescence Phenomena in Picryl Compounds. HEINRICH LEY [in part F. MÜLLER and P. KRAFFT] (*Ber.*, 1908, 41, 1637—1644).—It has already been noted that $\alpha\beta$ -diphenyl- γ -benzylhydroxyamidine picrate and analogous compounds (Abstr., 1901, i,

759) are strongly fluorescent, a result in direct contradiction to the generalisation that the introduction of nitro-groups depresses the fluorescence. The same phenomenon is observed with the picryl compounds of diguanidine, guanylfornamidide, and diformamidide. Ley and Müller have likewise shown that abnormally coloured and very stable salts are given by analogous amidides (Abstr., 1907, i, 730), and the fluorescence may be explained in a similar way, the supplementary valencies of the picryl radicle acting on a basic group, :NPh for example.

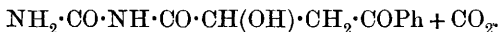
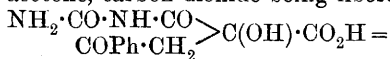
Whereas the free diphenylbenzylhydroxyamidine has only a shallow band, and picryl chloride no absorption in the ultra-violet, yet the picryl derivative has two well-defined bands, one in the greenish-violet and the other in the ultra-violet. The fluorescent spectrum has also a broad band in the visible spectrum, but no rays could be detected in the ultra-violet, a result in partial harmony with the conclusion drawn by Stark and Meyer that there is a parallelism between the absorption and fluorescent spectra (Abstr., 1907, ii, 418; compare, also, ii, 147). The results are not in harmony with Hewitt's theory (Abstr., 1900, ii, 318), but may be explained by Stark's (this vol., ii, 138) or by Collie and Baly's oscillation hypothesis (Trans., 1905, 87, 1332).

The fluorescence diminishes in the order of the following solvents: ethyl acetate, chloroform, benzene, carbon tetrachloride, acetone, carbon disulphide, amyl alcohol, ethyl alcohol, methyl alcohol.

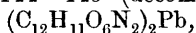
The dark orange picryl- $\alpha\beta$ -diphenyl- γ -benzylhydroxyamidine crystallises from a mixture of chloroform and light petroleum in yellow crystals, which are composed of 13 or 14 mols. of amidine and 1 mol. of solvent, m. p. 110°.

Picrylphenyldiguanide, $\text{NH}\cdot\text{C}(\text{NHPh})\cdot\text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3]\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, obtained from the hydrochloride, picryl chloride, and sodium ethoxide, forms glistening, brownish-red crystals, m. p. 205°, and has a yellowish-green fluorescence in acetone. Neither diguanide nor β -diphenyl diguanide gives fluorescent picryl derivatives, but *picryl- $\beta\delta\epsilon$ -triphenyl-guanylamidide*, $\text{NH}\cdot\text{CPh}\cdot\text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3]\cdot\text{C}(\text{NHPh})\cdot\text{NPh}$, red needles, m. p. 182°, gives intense yellow, fluorescent solutions. W. R.

Phenacyl-dialuric Acid, tartronuric Acid, and isohydantoic Acid. OTTO KÜHLING (*Ber.*, 1908, 41, 1658—1664).—The compound obtained in the attempt to benzoylate phenacyldialuric acid by the Schotten-Baumann method, and previously described as phenacyl-alanturic acid (Abstr., 1905, i, 944), is now shown to be phenacyl*iso*-hydantoic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COPh}$, since it is obtained by boiling solutions of phenacyltartronuric acid in water or acetone, carbon dioxide being liberated, thus:



Phenacyltartronuric acid is obtained by treating phenacyldialuric acid with dilute aqueous sodium carbonate solution; it crystallises in microscopic needles, m. p. 144—145° (decomp.). The *lead* salt,



needle-shaped prisms, *silver* salt, $C_{12}H_{11}O_6N_2Ag$, a thick, gelatinous precipitate, and *sodium* salt, $C_{12}H_{10}O_6N_2Na_2$, a white, flocculent precipitate, were prepared and analysed.

Phenacylisohydantoic acid crystallises in concentrically grouped leaflets, m. p. $161-162^\circ$ (decomp.). W. H. G.

Some Methods of Preparation of Triazans. GUIDO GOLDSCHMIEDT (*Ber.*, 1908, 41, 1862—1864).—Polemical. The compound obtained by Michaelis (this vol., i, 471) from *as*-phenylbenzylhydrazine by various methods of preparation and supposed to be diphenyldibenzyltriazan is undoubtedly phenylbenzylbenzylidenehydrazone, a compound always present in old specimens of *as*-phenylbenzylhydrazine (compare Ofner, *Abstr.*, 1904, i, 818; Milrath, following abstract).

The compound described by Michaelis (*loc. cit.*) as triphenylbenzyltriazan is probably diphenylbenzylidenehydrazone. W. H. G.

Conditions of Formation of Phenylsemicarbazide and of Acetylphenylhydrazine. HUGO MILRATH (*Monatsh.*, 1908, 29, 337—350).—The author has repeated Jaffé's work on the production of phenylsemicarbazide from carbamide, phenylhydrazine, and acetic acid (*Abstr.*, 1897, ii, 575), and finds that either acetylphenylhydrazine or a mixture of this with phenylsemicarbazide is obtained in this reaction. For the exclusive formation of the latter, the transformation of carbamide into ammonium cyanate is necessary, as is also a high temperature, a long period of heating, and an increased concentration of carbamide. Acetylphenylhydrazine is largely formed by warming equal molecular quantities of phenylhydrazine and 7% acetic acid on the water-bath. Dog's and cat's urine, rich in carbamide, furnish phenylsemicarbazide only when warmed for four to five hours with phenylhydrazine and acetic acid; when normal human urine is used, the mixture must be warmed for at least five hours. J. C. C.

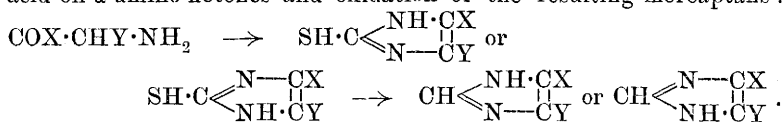
Condensation of Gallocyanin Dyes with Amino-compounds. EUGÈNE GRANDMOUGIN and ERNST BODMER (*J. pr. Chem.*, 1908, [ii], 77, 498—510. Compare *Abstr.*, 1907, i, 355).—It was shown previously (this vol., i, 289) that pruneanilide and correinanilide are formed by condensation of prune and correin with aniline. Details are now given of the preparation of similar condensation products of prune with *m*- and *p*-aminobenzoic acids, *o*-, *m*-, and *p*-nitroanilines, methylaniline, *p*-phenylenediamine, and benzidine. The substance obtained by condensation of prune with sulphanilic acid is not identical with the product of the sulphonation of pruneanilide. *Prune sulphate*, $C_{16}H_{14}O_5N_2 \cdot H_2SO_4$, olive leaflets, and *picrate*, $C_{16}H_{14}O_5N_2 \cdot C_6H_3O_7N_3$, green leaflets, were analysed.

Celestin-blue B (correin RR) forms a green, crystalline *picrate*, $C_{17}H_{17}O_4N_3 \cdot C_6H_3O_7N_3$. The condensation of the base with *o*-, *m*-, and *p*-aminobenzoic acids, *m*- and *p*-nitroanilines, and diethyl-*p*-phenylenediamine is described. G. Y.

Hydantoin and the Isomerism of the Methylhydantoins. CARL D. HARRIES (*Annalen*, 1908, 361, 69—72).—The *iso-ε*-methylhydantoin described by Harries and Weiss (*Abstr.*, 1903, i, 738) has now been found to be a mixture of *ε*-methylhydantoin and smaller amounts of another substance, which has not been completely separated; on repeated recrystallisation, fractions, m. p. 147—156° and m. p. 178°, were obtained.

When heated with alcoholic ammonia at 100°, ethyl hydantoate yields hydantoin, and not aminoacetamide as previously stated (*loc. cit.*). G. Y.

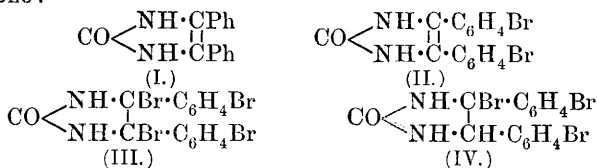
Tautomerism in the Iminazole Series. SIEGMUND GABRIEL (*Ber.*, 1908, 41, 1926—1928).—The virtual tautomerism of the benziminazoles having been demonstrated by Fischer, the present work was undertaken to determine if in the case of the simple monocyclic iminazoles, isomerides, such as $\text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CX} \\ \text{N} - \text{CY} \end{smallmatrix}$ and $\text{CH} \begin{smallmatrix} \text{N} - \text{CX} \\ \text{NH} \cdot \text{CY} \end{smallmatrix}$, are capable of separate existence, or if only one tautomeric substance is obtainable. It was shown previously (*Abstr.*, 1893, i, 734) that iminazoles are formed by the action of thiocyanic acid on α -amino-ketones and oxidation of the resulting mercaptans:



It is argued from the consideration of this scheme that, if the iminazoles be not tautomeric, the iminazole prepared in this manner from α -aminopropiophenone, $\text{COPh} \cdot \text{CHMe} \cdot \text{NH}_2$, must be isomeric with that derived from α -amino- α -phenylacetone, $\text{COMe} \cdot \text{CHPh} \cdot \text{NH}_2$. It is found, however, that the two amino-ketones yield the same 4-phenyl-5-methyl- or 5-phenyl-4-methyl-iminazolyl mercaptan (Behr-Bregowski, *Abstr.*, 1897, i, 458), which forms white leaflets, becoming rose-red at about 260°, sinter about 280°, m. p. 298—299°. Phenylmethyliminazole, formed by the oxidation of the mercaptan with nitric acid, crystallises in white leaflets, m. p. 185°, forming a brownish-violet liquid. G. Y.

Bromination of Diphenylglyoxalane. I. HEINRICH BILTZ and CHAIM RIMPEL (*Ber.*, 1908, 41, 1754—1760).—When boiled with bromine in chloroform solution and treated with water, diphenylglyoxalane (I) yields 4:5-di-*p*-bromodiphenylglyoxalane (II) together with small amounts of di-*p*-bromobenzil and di-*p*-bromodiphenylacetylenediureine. The main reaction is found to take place in several stages, the first, which is complete at the ordinary temperature, leading to the formation of 4:5-di-*p*-bromodiphenylglyoxalane dibromide (III). At higher temperatures, this is converted by the hydrogen bromide liberated during the first stage into 4-bromo-2-keto-4:5-di-*p*-bromodiphenyltetrahydroglyoxaline (IV), which when treated with

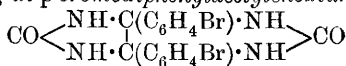
water loses hydrogen bromide and forms 4:5-di-*p*-bromodiphenylglyoxalone:



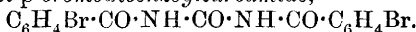
The intermediate substances (III) and (IV) are formed also by the action of bromine and hydrogen bromide respectively on di-*p*-bromodiphenylglyoxalone.

Di-p-bromodiphenylglyoxalone, $\text{C}_{15}\text{H}_{10}\text{ON}_2\text{Br}_2$, crystallises from alcohol in colourless, rectangular plates, m. p. 328° , or from glacial acetic acid in microscopic needles containing $\text{C}_2\text{H}_4\text{O}_2$, is soluble in alcoholic alkalis, and is oxidised by liquid nitrogen dioxide or concentrated nitric acid, forming *di-p-bromobenzil*, $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ (see following abstract). In the same manner, diphenylglyoxalone yields benzil when treated with nitric acid or sodium nitrite in concentrated sulphuric acid solution. The *diacetyl* derivative, $\text{C}_{15}\text{H}_8\text{ON}_2\text{Br}_2\text{Ac}_2$, crystallises in rhombic plates, m. p. $192\text{--}193^\circ$, and is readily hydrolysed by alcoholic potassium hydroxide.

Di-p-bromodiphenylglyoxalone dibromide, $\text{C}_{15}\text{H}_{10}\text{ON}_2\text{Br}_4$, prepared by the action of bromine on diphenylglyoxalone or di-*p*-bromodiphenylglyoxalone in glacial acetic acid, chloroform, or benzene solution, crystallises in yellow, rectangular plates and needles, reacts with carbamide, forming *di-p-bromodiphenylacetylenediureine*,

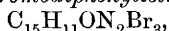


(see following abstract), and when heated with water is converted into the *glycol*, $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{C}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{OH} \\ | \\ \text{NH} \cdot \text{C}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{OH} \end{array}$, which decomposes into di-*p*-bromobenzil and carbamide, the latter reacting with unchanged dibromide to form di-*p*-bromodiphenylacetylenediureine. A similar decomposition takes place when the dibromide is treated with sodium hydroxide, but is accompanied by another reaction, leading to the formation of *s-di-p-bromodibenzoylcarbamide*,



When recrystallised from glacial acetic acid, di-*p*-bromodiphenylglyoxalone dibromide decomposes to the extent of about 33%, forming di-*p*-bromodiphenylglyoxalone, di-*p*-bromobenzil, and di-*p*-bromodiphenylacetylenediureine. In analogy to this, the same three end products are obtained, in varying proportions, when phenylglyoxalone is treated with bromine in concentrated sulphuric acid and the resulting dibromide precipitated by addition of ice, or when diphenylglyoxalone is allowed to remain in contact with bromine and water.

4-Bromo-2-keto-4:5-di-p-bromodiphenyltetrahydroglyoxalone,



prepared by the action of bromine and hydrogen bromide on di-*p*-bromodiphenylglyoxalone in chloroform solution, crystallises in light brown prisms, decomp. about 240° , and loses hydrogen bromide,

forming di-*p*-bromodiphenylglyoxalone when boiled with xylene, or more slowly when boiled with alcohol, glacial acetic acid, or ether.

4-Bromo-2-keto-4:5-diphenyltetrahydroglyoxaline, $\text{CO} \begin{array}{l} \text{NH} \cdot \text{CBrPh} \\ \text{NH} \cdot \text{CHPh} \end{array}$,

prepared by saturating a chloroform solution of diphenylglyoxalone with hydrogen bromide, crystallises in colourless prisms, and loses hydrogen bromide when treated with water.

s-Di-*p*-bromodibenzoylcarbamide, obtained on adding chromic anhydride to 4:5-di-*p*-bromodiphenylglyoxalone in boiling glacial acetic acid solution, or by oxidising the dibromo-compound with sodium hypobromite, crystallises in needles, m. p. 250° (decomp.) when quickly, or 245—247° (decomp.) when slowly, heated, forming *p*-bromobenzonitrile, is readily soluble in nitrobenzene, and on hydrolysis with alcoholic alkalis yields *p*-bromobenzoic acid.

When reduced with sodium and alcohol, di-*p*-bromodiphenylglyoxalone yields *diphenyldihydroglyoxalone*, m. p. 292—293°.

G. Y.

Bromination of Diphenylglyoxalone. II. HEINRICH BILTZ (*Ber.*, 1908, 41, 1761—1767. Compare preceding abstract).—The action of bromine on diphenylglyoxalone in boiling glacial acetic acid solution leads to the formation of di-*p*-bromobenzil, di-*p*-bromodiphenylacetylenediureine, and 5:5-di-*p*-bromodiphenylhydantoin (this vol., i, 462).

Di-*p*-bromobenzil, $\text{C}_{14}\text{H}_8\text{O}_2\text{Br}_2$, crystallises from benzene in flat needles, m. p. 228—229°, gives colour reactions with boiling alcoholic and aqueous alcoholic alkalis, and with alcoholic potassium hydroxide at the ordinary temperature forms a yellow solution which on acidification yields a slowly solidifying oil. Oxidation of di-*p*-bromobenzil with chromic anhydride in glacial acetic acid solution leads to the formation of *p*-bromobenzoic acid.

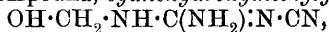
Di-*p*-bromodiphenylacetylenediureine, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4\text{Br}_2$, is formed by heating di-*p*-bromobenzil with carbamide, or by the action of bromine and carbamide on di-*p*-bromophenylglyoxalone, diphenylglyoxalone, or benzoin, in glacial acetic acid solution at the ordinary temperature. It crystallises in colourless threads or leaflets, decomp. about 360°, does not form an acetyl derivative (compare Biltz, this vol., i, 62), is stable towards concentrated sulphuric acid, sodium nitrite in concentrated sulphuric or glacial acetic acid solution, and bromine, and is only slightly attacked by aqueous or alcoholic potassium hydroxide, but is decomposed by fuming nitric acid.

Di-*p*-bromodiphenylglyoxalone forms small amounts of di-*p*-bromobenzil when heated with concentrated hydrochloric acid at 160—170°, but remains unchanged when boiled with hydrogen bromide in glacial acetic acid solution; when boiled with bromine, acetic acid, and water, on the other hand, it is rapidly decomposed, forming di-*p*-bromobenzil together with small amounts of di-*p*-bromodiphenylacetylenediureine and di-*p*-bromodiphenylhydantoin.

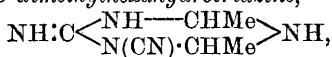
G. Y.

Dicyanodiamide. FRANZ POHL (*J. pr. Chem.*, 1908, [ii], 77, 533—548).—Although the object of numerous investigations, the constitution of dicyanodiamide has not hitherto been established with

certainty. Baumann (this Journ., 1873, 1025; 1874, 376) ascribed to dicyanodiamide the formula $\text{NH}\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}\text{C}\cdot\text{NH}$, whilst Klason (Abstr., 1886, 324) and Hofmann (Abstr., 1886, 41) preferred the form $\text{NH}_2\cdot\text{C}\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\text{C}\cdot\text{NH}_2$. Bamberger, on the other hand, considered the substance to be a cyanoguanidine, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CN}$ (Abstr., 1883, 907, 1090); in discussing this constitution, it is necessary to take into consideration the tautomeric form $\text{CN}\cdot\text{N}\cdot\text{C}(\text{NH}_2)_2$. The present author has found that, on treatment with sodium hypobromite solution, dicyanodiamide readily loses half its nitrogen, a behaviour which points to the presence of two amino-groups. When heated with 2 mols. of benzoic anhydride, dicyanodiamide forms benzoic acid, benzonitrile, carbon dioxide, dibenzoylcarbamide, and *dibenzoyldicyanodiamide*, $\text{CN}\cdot\text{N}\cdot\text{C}(\text{NHBz})_2$. With formaldehyde, dicyanodiamide forms an additive compound, *cyanohydroxymethylguanidine*,



but with acetaldehyde and ammonia a compound, which is probably 1-imino-6-cyano-3:5-dimethylhexahydrotriazine,



is formed, whilst with the sodio- β -keto-esters, dicyanodiamide forms 2-cyanoimino-4-alkyluracils, $\text{CN}\cdot\text{N}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{Calk} \\ \text{NH}---\text{CO} \end{smallmatrix}\text{CH}$, or 2-cyano-

amino-6-keto-4-alkylpyrimidines, $\text{CN}\cdot\text{NH}\cdot\text{C}\begin{smallmatrix} \text{N}---\text{Calk} \\ \text{N}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{CH}$. It is considered that these reactions show that dicyanodiamide reacts in both of the tautomeric forms of cyanoguanidine.

Dibenzoyldicyanodiamide, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4$, crystallises in needles, m. p. 225° (compare Gerlich, this Journ., 1876, ii, 196), is readily soluble in cold dilute alkalis, and when heated with hydrochloric acid under pressure yields benzoic acid.

If dicyanodiamide and benzoic anhydride are heated together in molecular proportions, the product contains benzonitrile, benzoic acid, and a substance, $\text{C}_9\text{H}_8\text{ON}_2$, white needles, m. p. $162\text{--}163^\circ$, but not dibenzoyldicyanodiamide.

Cyanohydroxymethylguanidine, $\text{C}_3\text{H}_6\text{ON}_4$, is obtained as a white, crystalline powder, m. p. 118° , yields formaldehyde and dicyanodiamide when heated with water, and forms unstable compounds with silver and mercuric salts and with platinum tetrachloride in hydrochloric acid solution.

1-Imino-6-cyano-3:5-dimethylhexahydrotriazine, $\text{C}_6\text{H}_{11}\text{N}_5$, crystallises in white needles, m. p. 190° , and is readily decomposed, forming ammonia, acetaldehyde, and dicyanodiamide when boiled with water, or more rapidly with dilute alkalis, or when heated with dilute hydrochloric acid at 40° for thirty minutes. The *picrate*, $\text{C}_{12}\text{H}_{16}\text{O}_8\text{N}_8$, was analysed. The *nitroso*-derivative, $\text{C}_6\text{H}_{10}\text{ON}_6$, forms yellow needles, m. p. 156° . The triazine reacts with aniline hydrochloride, forming ethylideneaniline, or with phenylhydrazine hydrochloride, forming phenylethylidenehydrazine.

2-Cyanoamino-6-hydroxy-4-methylpyrimidine, $\text{C}_6\text{H}_6\text{ON}_4$, prepared

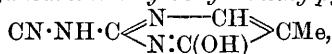
from dicyanodiamide and ethyl acetoacetate, separates from acetic acid in crystals, which become yellow at 240° , decomp. $280-285^{\circ}$. The sodium salt, $C_6H_5ON_4Na \cdot H_2O$, loses H_2O at $180-190^{\circ}$, decomp. 290° , and in aqueous solution gives characteristic precipitates with metallic salts. The silver salt, $C_6H_5ON_4Ag$, was analysed. When boiled with hydrochloric acid, the cyanoamino-compound is converted into 2-carbamido-6-hydroxy-4-methylpyrimidine, $NH_2 \cdot CO \cdot NH \cdot C \begin{smallmatrix} \text{N} \text{---} CMe \\ \text{N} : C(OH) \end{smallmatrix} CH$, which is obtained as a white, flocculent substance, sinters at 229° , m. p. $262-264^{\circ}$ becoming yellow. When heated with concentrated hydrochloric acid at 120° , the cyanoamino-compound is converted into iminomethyluracil.

2-Cyanoamino-6-hydroxy-4-phenylpyrimidine, $C_{11}H_8ON_4$, prepared from dicyanodiamide and ethyl benzoylacetate, crystallises in needles, which sinter at 230° , but do not melt. 2-Carbamido-6-hydroxy-4-phenylpyrimidine, $C_{11}H_{10}O_2N_4$, is a white, amorphous powder, m. p. 234° .

2-Cyanoamino-6-hydroxy-4:5-dimethylpyrimidine, $C_7H_8ON_4$, prepared from dicyanodiamide and ethyl methylacetoacetate, crystallises from boiling alcohol in leaflets, m. p. 280° (decomp.), yields iminodimethyluracil when heated with concentrated hydrochloric acid, and when boiled with dilute hydrochloric acid is converted into 2-carbamido-6-hydroxy-4:5-dimethylpyrimidine, m. p. 269° (decomp.).

2-Cyanoamino-6-hydroxy-4-methyl-5-ethylpyrimidine, prepared from ethyl ethylacetoacetate, is obtained as a crystalline powder, m. p. 257° (decomp.); the corresponding 2-carbamido-compound forms needles, m. p. 235° .

The action of dicyanodiamide on ethyl sodioformylpropionate leads to the formation of 2-cyanoamino-6-hydroxy-5-methylpyrimidine,



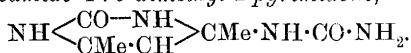
which crystallises from hot water in needles, becomes yellow, but does not melt, at 293° , when heated with fuming hydrochloric acid at 120° is hydrolysed to carbon dioxide, ammonia, formic acid, and propionic acid, and when boiled with dilute hydrochloric acid yields 2-carbamido-6-hydroxy-5-methylpyrimidine, crystallising in needles, m. p. 245° . G. Y.

Condensation of β -Diketones with Carbamide. T. DE HAAN (*Rec. trav. chim.*, 1908, 27, 162—191. Compare Evans, Abstr., 1893, i, 129; 1894, i, 111).—The compound obtained by Evans on condensing carbamide with acetylacetone crystallises with $2H_2O$ in monoclinic prisms. These are colourless when freshly prepared, but by warming in aqueous solution or on exposure to light are transformed without change of crystalline form into a yellow modification. The colourless compound is probably 4:6-dimethyl-2-pyrimidone, $CH \begin{smallmatrix} CMe = N \\ CMe \cdot NH \end{smallmatrix} CO$, whilst the yellow modification may possess the constitution originally ascribed to it by Evans, $CH_2 \begin{smallmatrix} CMe : N \\ CMe : N \end{smallmatrix} CO$. The potassium salt is colourless, and when treated with carbon dioxide

yields the colourless substance. The *nitrate* decomposes explosively at 245°. When acetylacetone is mixed with excess of carbamide in

aqueous solution, $\beta\delta$ -*pentanediureide*, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CMe} \cdot \text{NH} \\ > \text{CH}_2 \\ \text{NH} \cdot \text{CMe} \cdot \text{NH} \end{array} \text{CO}$, is

formed together with the diuriminoacetylacetone described by Combes (compare Abstr., 1893, i, 454). The former compound crystallises from water in lustrous plates containing $4\text{H}_2\text{O}$. The anhydrous substance has m. p. 290°. Cold nitric acid converts it into a *dinitrate*, but, on warming, this is decomposed into carbamide and 2-oxy-4:6-dimethylpyrimidine. The colourless modification of Combes' compound is probably 6-carbamido-4:6-dimethyl-2-pyrimidone,



A yellow form can also be obtained, and this is regarded as a derivative of the coloured variety of 4:6-dimethyl-2-pyrimidone.

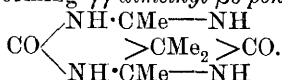
Methylacetylacetone and carbamide readily condense in aqueous solution, forming a mixture of (1) γ -methyl- $\beta\delta$ -*pentanediureide*,

$\text{CO} \begin{array}{c} \text{NH} - \text{CMe} - \text{NH} \\ > \text{CHMe} \\ \text{NH} - \text{CMe} - \text{NH} \end{array} \text{CO}$, which separates from water as brilliant

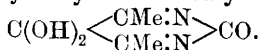
white, monoclinic crystals containing $2\text{H}_2\text{O}$ (the anhydrous substance darkens without melting at 316°), and (2) *carbamidobis*-4:5:6-*trimethyl*-2-pyrimidone, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CMe} \begin{array}{c} \text{NH} - \text{CO} \\ \text{CMe} : \text{CMe} \end{array} \text{NH} \end{array} \text{CO}$. This compound, distinguished from the foregoing diureide by its solubility in alcohol, forms white needles, m. p. 209—210° with effervescence. It separates with $2\text{H}_2\text{O}$ from aqueous solution.

A solution of either of the two preceding compounds in nitric acid evolves carbon dioxide and nitrous oxide, and deposits the yellow unstable 4:5:6-*trimethyl*-2-pyrimidone *nitrate*, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}, \text{HNO}_3$. The free base has the constitution $\text{CMe} \begin{array}{c} \text{CMe} = \text{N} \\ \text{CMe} : \text{NH} \end{array} \text{CO}$, and, when obtained by decomposing its *potassium* salt with carbon dioxide, forms colourless needles, which separate from water with $1\frac{1}{2}\text{H}_2\text{O}$.

Dimethylacetylacetone and carbamide condense when heated together at 140—160°, forming $\gamma\gamma$ -*dimethyl*- $\beta\delta$ -*pentanediureide*,



This separates from water in colourless crystals, m. p. 270°, which contain $2\text{H}_2\text{O}$. Nitric acid converts it into a substance, m. p. 266°. This is probably 5:5-dihydroxy-4:6-dimethyl-2-pyrimidone,



W. O. W.

Action of Hydrazine on Ethyl Phenacylacetoacetate. CARL BÜLOW AND HANS FILCHNER (*Ber.*, 1908, 41, 1886—1889).—Paal and Kühn (this vol., i, 57) have studied the action of hydrazine on ethyl phenacylbenzoylacetate, and the present authors now describe experi-

ments with ethyl phenacylacetate, which gives rise to a similar condensation product.

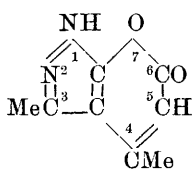
Ethyl 6-phenyl-3-methyl-4 : 5-dihydropyridazine-4-carboxylate,



obtained by adding hydrazine hydrate to ethyl phenacylacetate below 0° , crystallises from light petroleum in aggregates of yellow needles, m. p. $90-91^\circ$. It is not attacked by nitrous acid.

J. C. C.

3 : 4-Dimethyl-1 : 2-pyrazo-6 : 7-pyrone (Lactone of 5-Hydroxy-3-methylpyrazole-4-isopropylencarboxylic Acid). CARL BÜLOW and FRITZ SCHAUB (*Ber.*, 1908, 41, 1945—1947).—The substance $\text{C}_8\text{H}_8\text{O}_2\text{N}_2$, m. p. $246-247^\circ$, which has been

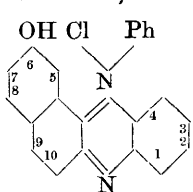


obtained in various ways (Knorr and Rosen-garten, *Abstr.*, 1894, i, 546; Wolff, *Abstr.*, 1905, i, 839; Bülow and Lobeck, *Abstr.*, 1907, i, 301), has been shown to have the annexed constitution by Stollé (*Abstr.*, 1905, i, 838) and Wolff (*loc. cit.* this vol., i, 291).

The formation of the lactone from ethyl oxalylbishydrazoneacetate at 187° (Bülow and Lobeck, *loc. cit.*), and from ethyl acetoacetate-benzoylhydrazone at 175° , leads the authors to the general statement that the action of heat under suitable conditions on ethyl acetoacetate-acylhydrazones results in the formation of a diacylhydrazine and 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone.

C. S.

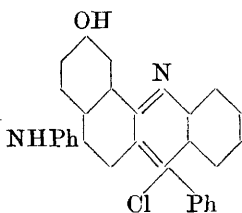
Azonium Compounds and Azines from 7-Hydroxy- β -naphthaquinone. FRIEDRICH KEHRMANN and R. BRUNEL (*Ber.*, 1908, 41, 1832—1837).—Azonium compounds containing a hydroxyl group in the meta- or para-position to the ammonium group are often converted into inner salts of a phenol-betaine character when the free bases are liberated from their salts. Thus the meta-series give *aposafranones*, *rosindones*, and *isorosindones*, and the para-series the *prasindones*.



The authors have now examined the behaviour of similar compounds containing a hydroxyl group in a different position, and find that in the case of 6-hydroxyphenylisonaphthaphenazonium chloride, annexed formula, the free base is a true ammonium base and does not form inner salts. 6-Hydroxyphenylisonaphthaphenazonium chloride, formed by condensing *o*-phenylenediamine and 7-hydroxy- β -naphthaquinone, is obtained in black, shining leaflets. The

platinichloride is brownish-violet. The base is formed by shaking the hydrochloride with silver hydroxide, but could not be isolated from the green solution. The *acetyl* derivative of the chloride is orange-red, and gives a *nitrate*, $\text{C}_{24}\text{H}_{17}\text{O}_2\text{N}_2 \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$, brownish-red needles, a *platinichloride*, scarlet, crystalline powder, and a *dichromate*, long needles. By treating 6-hydroxyphenylisonaphthaphenazonium chloride with aniline, 3-anilino-6-hydroxyphenylisonaphthaphenazonium

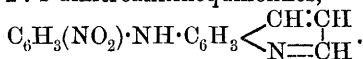
chloride, dark blue crystals with a coppery lustre, is obtained. The fact of this substance having a blue colour was crucial in deciding on the constitution of the parent substance, for from analogy the anilino-derivative of the isomeric 9-hydroxynaphthaphenazonium chloride, annexed formula, should be red. A small amount of this substance was contained in the mother liquor from the condensation, and was found to give a violet-red derivative with aniline.



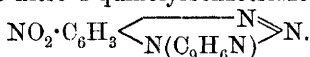
9-Hydroxynaphthaphenazonium chloride, steel-blue crystals, gives a *platinichloride*. The free base is bluish-green, and could only be obtained in solution.

9-Hydroxynaphthaphenazine, $\text{HO} \cdot \text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$, obtained from *o*-phenylenediamine hydrochloride and 7-hydroxy- β -naphthaquinone, crystallises from alcohol in yellow leaflets, m. p. 285°; the *hydrochloride* forms golden crystals. J. C. C.

Condensation Products of Chlorodinitrobenzene and Aminoquinolines. WILHELM MEIGEN, H. GARBS, W. MERKELBACH, and G. WICHERN (*J. pr. Chem.*, 1908, [ii], 77, 472—488).—1-Chloro-2:4-dinitrobenzene reacts with 6- and 7-aminoquinolines in boiling alcoholic solution, or with 5- and 8-aminoquinolines when fused, forming the corresponding 2:4-dinitroanilinoquinolines,



These, on reduction with ammonium sulphide, yield 4-nitro-2-aminoanilinoquinolines, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{C}_9\text{H}_6\text{N}$, which are converted by nitrous acid into 5-nitro-1-quinolybenzotriazoles,



Reduction of the dinitro-compounds with stannous chloride and hydrochloric acid leads to the formation of 2:4-diaminoanilinoquinolines, $\text{C}_6\text{H}_3(\text{NH}_2)_2 \cdot \text{NH} \cdot \text{C}_9\text{H}_6\text{N}$.

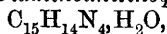
8-*op*-Dinitroanilinoquinoline crystallises in orange needles, m. p. 266°; the *platinichloride*, $(\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, brownish-yellow needles, m. p. 280°. 8-*p*-Nitro-*o*-aminoanilinoquinoline, brown needles, m. p. 231°; the *hydrochloride*, $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_4 \cdot \text{HCl}$, needles; the *platinichloride*, $(\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, brownish-yellow crystals, m. p. 276°; the *acetyl* derivative, $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_4$, yellow needles, m. p. 172°. 5-Nitro-1-*o*-quinolybenzotriazole, yellow needles, m. p. 274°, forms unstable salts. 8-*op*-Diaminoanilinoquinoline, $\text{C}_{15}\text{H}_{14}\text{N}_4 \cdot \text{H}_2\text{O}$, yellowish-green needles, m. p. 129°.

7-*op*-Dinitroanilinoquinoline forms brownish-yellow crystals, m. p. 204°. 7-*p*-Nitro-*o*-aminoanilinoquinoline, dark red needles, m. p. 215°. 5-Nitro-1-*m*-quinolybenzotriazole, m. p. 290°.

6-*op*-Dinitroanilinoquinoline crystallises in red needles, m. p. 217°; the *platinichloride* forms yellow leaflets. 6-*p*-Nitro-*o*-aminoanilinoquinoline is obtained as a red powder, m. p. 215°. 5-Nitro-1-

p-quinolylbenzotriazole, white needles, m. p. 274°. 6-*op*-Diaminoanilinoquinoline, silver-grey needles, m. p. 173°, forms yellow salts.

5-*op*-Dinitroanilinoquinoline crystallises from xylene in yellowish-red needles, m. p. 211°, and forms salts which are decomposed by water; the *hydrochloride* and *platinichloride* were analysed. The *methiodide*, $C_{15}H_{10}O_4N_4 \cdot MeI$, formed by heating the dinitro-base with methyl iodide at 100°, crystallises in yellow needles, m. p. 164°, and yields a dark violet *precipitate* when treated with an alkali. 5-*p*-Nitro-*o*-aminoanilinoquinoline, brown needles, m. p. 232°; the *platinichloride*, brown leaflets, m. p. 276°. The *acetyl* derivative, yellow crystals, m. p. 215°. 5-Nitro-1-ana-quinolylbenzotriazole, needles, m. p. 227°. 5-*op*-Diaminoanilinoquinoline,



yellowish-green needles, m. p. 191°.

G. Y.

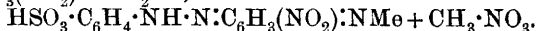
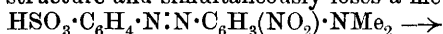
Action of *as*-Phenylbenzylhydrazine on Carbamide. HUGO MILRATH (*Ber.*, 1908, 41, 1865—1869).—Phenylbenzylsemicarbazide, obtained by heating carbamide with *as*-phenylbenzylhydrazine at 175°, or by warming equivalent quantities of the hydrazine hydrochloride and potassium cyanate in aqueous solution, has m. p. 139—140°; Michaelis (this vol., i, 471) gives m. p. 103°. The *diacetyl* derivative, $C_{17}H_{18}O_2N_2$, crystallises in glistening needles, m. p. 128°.

Diphenyldibenzylcarbazide, $(CH_2Ph \cdot NPh \cdot NH)_2CO$, m. p. 169°, is formed when *as*-phenylbenzylhydrazine (2 mol.) is heated with carbamide (1 mol.) at 175° or with phenylbenzylsemicarbazide at a temperature not above 180°. On the contrary, a *substance*, $C_{14}H_{12}ON_2$, m. p. 167—168°, is obtained when *as*-phenylbenzylhydrazine and carbamide are heated together at 270°; the *acetate* has m. p. 81—82°; the *benzoate* crystallises in broad, glassy needles, m. p. 82°; a crystalline *methyl* derivative was also prepared.

It is probable that the compound described by Michaelis (*loc. cit.*) as diphenylbenzylaminobiuret is identical with the substance, m. p. 167—168°.

W. H. G.

Action of Dilute Nitric Acid on Helianthin. JOHN J. FOX (*Ber.*, 1908, 41, 1989—1991).—When methyl-orange is mixed with dilute nitric acid at the ordinary temperature, the dye is decomposed with formation of 2:4-dinitromethylaniline, a methyl group being eliminated. If the mixture is kept cold, the presence of a diazo-compound can also be detected. The author considers that a mononitro-helianthin may be first formed, which then assumes the quinonoid structure and simultaneously loses a methyl group, thus:



The product is then decomposed with formation of dinitromethylaniline and diazobenzenesulphonic acid.

J. C. C.

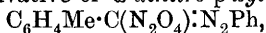
Aminoazo-compounds. JOHN T. HEWITT (*Ber.*, 1908, 41, 1986—1988).—A claim for priority. The theory of the constitution of the two forms of aminoazobenzenesulphonic acids recently put forward by Hantzsch (this vol., i, 469) had already been advanced by

the author (this vol., ii, 269). The decomposition of helianthin by dilute nitric acid (Fox, preceding abstract) can only be explained on the assumption of the quinonoid formula $O \begin{matrix} \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \\ \text{SO}_2 - \text{C}_6\text{H}_4 \cdot \text{NH} \end{matrix}$ for the free acid.

Benzeneazo-2:6-dibromoaniline has m. p. 168° (corr.), and not 191° (Hantzsch and Hilscher, this vol., i, 485). J. C. C.

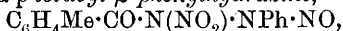
Action of Diazo-salts on Primary Dinitrohydrocarbons. GIACOMO PONZIO and G. CHARRIER (*Gazzetta*, 1908, 38, i, 526—532).—The reaction previously described (this vol., i, 482) for ω -dinitrotoluene is extended to ω -dinitro-*p*-xylene and *p*-methoxytoluene. In these cases, too, the diazobenzene derivatives, $\text{CR}(\text{N}_2\text{O}_4):\text{N}_2\text{Ph}$, readily undergo transformation into the isomeric α -nitro- β -nitroso- α -acyl- β -phenylhydrazines, $\text{R} \cdot \text{CO} \cdot \text{N}(\text{NO}_2) \cdot \text{NPh} \cdot \text{NO}$, and benzeneazodinitrohydrocarbons, $\text{N}_2\text{Ph} \cdot \text{CR}(\text{NO}_2)_2$.

The diazobenzene derivative of ω -dinitro-*p*-xylene.



m. p. 72° (decomp.), has a golden-yellow colour, dissolves in concentrated sulphuric acid, giving a green coloration, changes slowly into the isomeric red azo-compound, and gives off nitrogen when heated with alcohol.

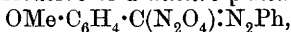
α -Nitro- β -nitroso- α -*p*-toluoyl- β -phenylhydrazine,



prepared by dissolving the diazobenzene derivative of ω -dinitro-*p*-xylene in anhydrous benzene, separates from the latter in unstable, white laminae, m. p. 97—98° (decomp.), gives a brown coloration with concentrated sulphuric acid and phenol, and dissolves in cold water, giving a solution which almost immediately deposits β -nitroso- α -*p*-toluoyl- β -phenylhydrazine, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh} \cdot \text{NO}$, in the form of faintly yellow laminae, m. p. 115—116° (decomp.).

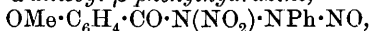
ω -Dinitro- ω -benzeneazo-*p*-xylene, $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_4\text{Me}$, prepared from the diazobenzene derivative of ω -dinitro-*p*-xylene by heating it with alcohol or dissolving it in aqueous ether, crystallises from alcohol in orange-red prisms, m. p. 130—135° (decomp.).

The diazobenzene derivative of ω -dinitro-*p*-methoxytoluene,



is an unstable, yellow compound, m. p. 85° (decomp.), and dissolves in concentrated sulphuric acid, giving an emerald-green solution.

α -Nitro- β -nitroso- α -anisoyl- β -phenylhydrazine,



separates rapidly from an ice-cold anhydrous benzene solution of the diazobenzene derivative of ω -dinitro-*p*-methoxytoluene in unstable, yellow laminae, m. p. 123—124° (decomp.), and gives an emerald-green coloration with concentrated sulphuric acid and phenol; it dissolves in cold water, which rapidly transforms it into nitric acid and β -nitroso- α -anisoyl- β -phenylhydrazine (compare Bamberger and Pemsel, *Abstr.*, 1903, i, 286). Boiling water converts the latter into α -anisoyl- β -phenylhydrazine, with evolution of nitrous vapours and partial resinification.

ω-Dinitro-*ω*-benzeneazo-*p*-methoxytoluene, $\text{NPh} \cdot \text{N} \cdot \text{C}(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is formed spontaneously from the diazobenzene derivative of *ω*-dinitro-*p*-methoxytoluene, or, more rapidly, in alcoholic, ethereal, or chloroform solution, or by shaking the benzene solution with water. It separates in blood-red, flattened needles, m. p. 141—148° (decomp.), and is moderately stable. T. H. P.

Primary Bisazo-compounds of Benzylethyl-*m*-aminophenol. CARL BÜLOW and THEODOR SPROESSER (*Ber.*, 1908, 41, 1684—1692. Compare Bülow and Wolfs, *Abstr.*, 1898, i, 308; 1899, i, 135; Bülow and Sproesser, this vol., i, 272).—The authors find that two isomeric bisazo-compounds can be obtained at will from benzylethyl-*m*-aminophenol under suitable conditions. If the substituted *m*-aminophenol in an aqueous solution slightly acidified with hydrochloric acid is treated with an equivalent quantity of a diazo-salt, $\text{RN}_2 \cdot \text{X}$, the

monoazo-compound, $\text{RN}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NET} \cdot \text{CH}_2\text{Ph}$, is obtained, which reacts in an alcoholic alkaline solution with another equivalent of a diazo-salt,

$\text{R}'\text{N}_2 \cdot \text{X}$, to yield the bisazo-compound $\text{RN}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NET} \cdot \text{CH}_2\text{Ph}$.

Conversely, benzylethyl-*m*-aminophenol can be coupled in alkaline solution with an equivalent quantity of $\text{RN}_2 \cdot \text{X}$, yielding

$\text{C}_6\text{H}_3(\text{OH}) \cdot \text{NET} \cdot \text{CH}_2\text{Ph}$, which can then unite with $\text{R}'\text{N}_2 \cdot \text{X}$ in acetic acid

solution, forming $\text{R}'\text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NET} \cdot \text{CH}_2\text{Ph}$. The following compounds

are described.

5-Benzylethylamino-2-benzeneazophenol,

$\text{N}_2\text{Ph} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NET} \cdot \text{CH}_2\text{Ph}$,

m. p. 117°, red crystals with blue reflex. **5-Benzylethylamino-2-*p*-tolueneazophenol**, $\text{C}_{22}\text{H}_{23}\text{ON}_3$, m. p. 110°, orange-red crystals. **5-Benzylethylamino-2-*α*-naphthaleneazophenol**, $\text{C}_{25}\text{H}_{23}\text{ON}_3$, m. p. 110°, greenish-black crystals. **5-Benzylethylamino-2-benzeneazophenetole**, $\text{C}_{23}\text{H}_{25}\text{ON}_3$, m. p. 103·5°, orange-red leaflets. **5-Benzylethylamino-2-*p*-sulphobenzeneazophenol**, $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}_3\text{S}$, m. p. 230°, small, red crystals; the sodium salt contains $2\text{H}_2\text{O}$, and has m. p. 258—268° (decomp.).

5-Benzylethylamino-2:4-bisbenzeneazophenol, $\text{C}_{27}\text{H}_{25}\text{ON}_5$, m. p. 129°, greenish-black crystals with a metallic lustre, which dissolve in concentrated sulphuric acid with a green colour, becoming red on dilution. **5-Benzylethylamino-2:4-bis-*p*-tolueneazophenol**, $\text{C}_{29}\text{H}_{29}\text{ON}_5$, m. p. 154°, green prisms. **5-Benzylethylamino-2-benzeneazo-4-*p*-tolueneazophenol**, $\text{C}_{28}\text{H}_{27}\text{ON}_5$, m. p. 116°, highly refractive, green crystals, red by transmitted light. C. S.

Deaminoproteins. ZDENKO H. SKRAUP (*Biochem. Zeitsch.*, 1908, 10, 245—248. Compare Abstr., 1906, i, 913; 1907, i, 367, 739).—Deaminoproteins, obtained by the action of nitrous acid, generally contain slightly less nitrogen than the proteins from which they are derived. This diminution in the nitrogen content is apparently connected with a considerable reduction of the amount of histidine and arginine, and a complete disappearance of lysine among the products of hydrolysis. G. B.

The So-called Amidic Nitrogen of the Proteins. ZDENKO H. SKRAUP and EMIL R. VON HARDT-STREMAYR (*Monatsh.*, 1908, 29, 255—262).—In the investigations hitherto recorded on the quantities of ammonia formed on the hydrolysis of proteins with hydrochloric acid, the protein has been boiled for some hours with concentrated hydrochloric acid (compare Hausmann, Abstr., 1899, i, 653; 1900, i, 317; Kutscher, Abstr., 1901, i, 107). The present communication contains the results of several determinations of the quantities of ammonia formed by boiling various proteins with both strong and dilute hydrochloric acid for from five minutes to five hours. The substances examined and the maximum amounts of ammonia they yield when boiled with hydrochloric acid are as follows: casein, 1.6%; edestin, 1.6%; serum-globulin, 1.0%; crystallised egg-albumin, 1.1%; sodium hysalbinat, 0.7%, and sodium protalbinat, 1.0%. Gelatin was also examined, but, contrary to the statement of Hart (Abstr., 1901, i, 783), was found to contain no amidic nitrogen.

The maximum of amidic nitrogen is obtained by boiling with the strong acid for about five hours, but about two-thirds of the total amidic nitrogen is eliminated during the first five minutes when strong hydrochloric acid is used, and in fifteen minutes when dilute acid (1 : 1) is employed. The conclusion is drawn therefore that the greater part of the amidic nitrogen is eliminated during the transformation of the protein into the albumose, and that consequently the formation of the albumose from the protein is not simply a hydrolytic process, but is accompanied by the liberation of ammonia.

Ammonia is also probably evolved during the further dissociation of the albumose (compare Henderson, Abstr., 1900, i, 265).

W. H. G.

Protoplasmic Hydrolysis. ALÉXANDRE ÉTARD and ANTONY VILA (*Compt. rend.*, 1908, 146, 1155—1156).—The author discusses the conditions required for the hydrolysis of protoplasmides and the means of separating the products, pointing out important objections to the use of phosphotungstic acid. The fact is emphasised that in protoplasmic hydrolysis the true weight of the initial organic matter is never known, owing to the impossibility of completely drying it. The conclusions are drawn that the nitrogenous compounds resulting from the breaking down of protoplasmides are produced in very small quantities, that the high yields proceed from calculations of nitrogen based on hypothesis and not on experience, and that precipitates of high molecular weight give an inexact idea of the true amount of organic matter that they contain. E. H.

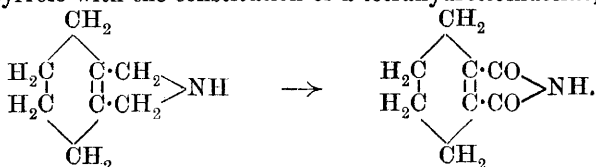
Action of Certain Oxidising Agents on Blood Pigments.

JOHN A. MACWILLIAM (*Bio.-Chem. J.*, 1908, 3, 155—164).—If strong solutions of chlorates are added to blood, there is beyond the phase of methæmoglobin a jellying effect. The jelly is firm, and its formation is accelerated by acidification or by warmth (30—40°), and retarded by alkalis. The red colour in time gives place to a deep green as seen by reflected light, although thin slices appear brownish-red by transmitted light. The green colour gradually changes to yellow. Sometimes the jelly contracts, squeezing out a clear fluid rich in protein, but free from iron. If the blood is diluted beyond a certain point, jellying fails, and a coloured precipitate is formed when a chlorate is added; this rapidly becomes green if acid is added. Bromates produce similar effects, but iodates produce a red precipitate with different properties. Chlorates and bromates produce the same effects with hæmoglobin solutions, but not with stromata, serum, plasma, or egg-albumin. Solutions of hæmatin fail to give the results also. The altered hæmoglobin is very insoluble; it, however, dissolves in alkali, dries to a dark powder, and microscopically polygonal flakes are seen. It shows no absorption bands. The product is probably due to oxidation, and is not a halogen compound.

The substance retains all the iron of the hæmoglobin in very firm combination. It is digestible by peptic or tryptic enzymes, but there is no formation of hæmatin; on prolonged digestion, the iron is gradually liberated. It is suggested that chlorates and bromates may be useful in distinguishing hæmoglobin from other pigments, and as fixing agents for hæmoglobin in microscopical work. W. D. H.

Hæmatin. WILLIAM KÜSTER [with K. FUCHS] (*Zeitsch. physiol. Chem.*, 1908, 55, 505—556. Compare this vol., i, 303).—Further experiments were carried out on the reduction of the synthesised anhydrides of the methylethylmaleic and methylpropylmaleic acids to the corresponding succinic acids. The operations were carried out in acid solutions by zinc dust. In both cases the fumaroid form was obtained in the largest quantity (that is, 4 grams of the fumaroid form and 0.25 gram of the maleoid form). The two forms were separated from one another by means of their calcium salts.

As hæmopyrrole, on oxidation, yields an imide of a dibasic acid, in order to determine its constitution, synthetical imides were prepared. In addition to the imides of methylethylmaleic and methylpropylmaleic acids, there were also prepared diethylmaleimide and the imide of Δ^1 -cyclohexene-1:2-dicarboxylic acid, which could be derived from a hæmopyrrole with the constitution of a tetrahydroisindoline, thus:



The diethylmaleic acid was prepared from citraconic acid, which reacts with its anhydride presumably according to the following

equation: $C_5H_6O_4 + C_5H_4O_8 = C_8H_{10}O_3 + 2CO_2$. The imide prepared from this acid was an oil, boiling at 138—140°. Neither this nor the imide of Δ^1 -cyclohexene-1:2-dicarboxylic acid was identical with the oxidation product of hæmopyrrole. The latter was obtained from Δ^1 -cyclohexene-1:2-dicarboxylic acid by first heating it above its melting point (240°), and then heating the anhydride so formed with alcoholic ammonia, also by the distillation of the substance obtained by treating the anhydride with ammonia in alcoholic and ethereal solutions; the latter substance thus prepared was amorphous, and had a composition corresponding with the formula $C_8H_{14}O_3N_2$. The anhydrides of Δ^2 -cyclohexene-1:2-dicarboxylic acid, *trans*- Δ^4 -cyclohexene-1:2-dicarboxylic acid, and *cis*- Δ^4 -cyclohexene-1:2-dicarboxylic acid were also prepared by the Baeyer methods; from these, the corresponding imides were obtained, which do not agree in properties with the oxidation product of hæmopyrrole. These properties are indicated in the following table:

	Anhydride.	Imide.
Phthalic acid	m. p. 128°	233°
Δ^1 -cyclohexene-1:2-dicarboxylic acid	„ 73—74	169—170
Δ^2 -cyclohexene-1:2-dicarboxylic acid	„ 78—79	172—173
<i>cis</i> - Δ^4 -cyclohexene-1:2-dicarboxylic acid...	„ 59—60	?
<i>trans</i> - Δ^4 -cyclohexene-1:2-dicarboxylic acid	„ 140	232—233

Evidence is given as to the existence of two hæmopyrroles, obtainable by the reduction of hæmatin with hydriodic acid, one, an acid substance, which can be extracted from acid solutions with ether, and the other, a basic substance. An account is given of the attempts to prepare pure derivatives, and also of some oxidation experiments. A preliminary account of some oxidation experiments carried out with the non-volatile by-products in the hæmopyrrole preparation is also given, by means of which hæmatinic acid was obtained. S. B. S.

A New Method of Tanning. LOUIS MEUNIER and ALPHONSE SEYEWETZ (*Compt. rend.*, 1908, 146, 987—989).—Hides are not greatly changed by quinol in the absence of oxygen, but, when oxygen and alkali are present, the fibre gradually becomes pink, then violet, and finally brown, and acquires perfect resistance to boiling water. The tanning depends on the formation of benzoquinone, and is also brought about by a solution of the latter substance; during the tanning process, the benzoquinone is again partly reduced to quinol. The explanation is sought in a reaction between benzoquinone and the amino-groups of the protein, similar to that between aniline and benzoquinone, which results in a condensation of aniline with part of the benzoquinone, and in the reduction of the rest of the benzoquinone to quinol. G. B.

Nucleic Acids. XIII. PHÆBUS A. LEVENE and JOHN A. MANDEL (*Biochem. Zeitsch.*, 1908, 10, 215—220. Compare Abstr., 1907, i, 266).—A method is described of obtaining pure guanine from the cleavage products of nucleic acid. The cleavage is brought about

by acetic acid in the presence of lead acetate at 150°. The lead is removed by sulphuric acid, the acetic acid by distillation under reduced pressure, and the purine bases are precipitated by silver sulphate and then treated in the usual way. Some experiments are also given on the determination of the proportion between purine and pyrimidine bases, but this matter is still being investigated.

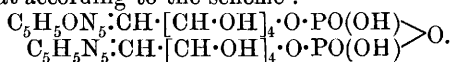
W. D. H.

The Nucleo-protein of the Liver. I. Guanylic Acid.

PHOEBUS A. LEVENE and JOHN A. MANDEL (*Biochem. Zeitsch.*, 1908, 10, 221—228).—A substance corresponding with Bang's β -guanylic acid was prepared from the liver. Its reactions were not, however, absolutely identical with Bang's acid, which was made from the pancreas. In elementary composition, the figures were fairly close. From it, guanine was prepared, but no adenine; the pyrimidine bases were absent. Hexoses were absent from the molecule; a pentose was obtained, but its identification was not very certain; glycerol was not obtained.

W. D. H.

Constitution of Thymonucleic Acid. PHOEBUS A. LEVENE and JOHN A. MANDEL (*Ber.*, 1908, 41, 1905—1909).—In continuation of an investigation of the intermediate products formed by the hydrolysis of nucleic acids (Abstr., 1904, ii, 955), it has been observed that, on hydrolysis with dilute mineral acids, thymonucleic acid yields, on the one hand, products containing carbohydrate groupings and traces of phosphoric acid, but without reducing action on Fehling's solution, and, on the other, substances which do not contain purine bases, but on further hydrolysis yield phosphoric acid, lævulic acid, and thymine. By hydrolysis of thymonucleic acid by 2% sulphuric acid at 150°, there has now been obtained an amorphous *barium thyminglucophosphate*, $C_{11}H_{15}O_{10}N_2PBa$, which, when heated with 25% sulphuric acid at 175°, yields thymine and lævulic and phosphoric acids. The composition of the thyminglucophosphoric acid is almost identical with that of hemi-nucleic acid (Schmiedeberg, Abstr., 1900, i, 267; Alsberg, Abstr., 1904, i, 791), and may be considered to be a mononucleotide. It is suggested that the nucleic acids are composed of simpler complexes, the nucleotides, each formed of phosphoric acid, a carbohydrate, and a base, these complexes uniting to form polyphosphoric acids. The bases are combined with the carbohydrates, probably in the form of glucosides, somewhat according to the scheme:



According to this view, the complex nucleic acids are constituted in the same manner as the simpler guanylic and inosic acids, but, whilst these readily yield free carbohydrates or reducing glucophosphoric acids when hydrolysed, the presence of the carbohydrate groups in the immediate products of the hydrolysis of thymonucleic acid can be detected only by the colour reactions with orcinol, or by hydrolysis to lævulic acid.

G. Y.

Adsorption of Ferments. LEONOR MICHAELIS and M. EHRENREICH (*Biochem. Zeitsch.*, 1908, 10, 283—299).—The electrochemical nature

of ferments is considered to be proved. Invertin and pepsin are adsorbed in all reactions by clay, and in none by kaolin; they therefore have the character of acids. In neutral and alkaline fluids, malt-diastrase is not adsorbed by kaolin, but in acid fluids it is; it is therefore amphoteric, but with stronger acid than basic properties. Corresponding with this, it is completely adsorbed by clay when neutral or alkaline, and only incompletely when acid. Ptyalin and trypsin are also amphoteric, being adsorbed by both clay and kaolin under all conditions of reaction.

W. D. H.

The Identity of Pepsin and Rennin. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1908, 56, 18—80).—A long critical and experimental examination of the much-debated point as to whether or not pepsin and rennin are identical. The conclusion reached is that they are not, and the most striking proof of this is that solutions of each ferment were prepared from which the other was absent. If lead acetate or, better, magnesium carbonate is added to the mixture, both ferments are precipitated, but the precipitate of pepsin is more insoluble and the ferment is destroyed; extracts of the precipitate then contain practically only rennin. If, on the other hand, the original mixture is heated to a little over 40°, the rennin is destroyed rapidly, but the pepsin is destroyed less rapidly, and so can be obtained free from rennin.

W. D. H.

Systematic Investigation of Oxydases. OCTAVE DONY-HÉNAULT (*Bull. Acad. roy. Belg.*, 1908, 105—163. Compare Abstr., 1907, i, 1100).—The experimental methods used by Bertrand (Abstr., 1895, i, 385, 386; 1896, i, 534; ii, 61; 1897, i, 53; ii, 117, 338; 1898, i, 53; ii, 128; 1899, i, 313; 1904, i, 157) in his investigation of the ferment laccase of Japanese lac, and the conclusions this author draws from his results, are criticised, and evidence is brought forward in favour of the view that the oxidising action of laccase is really due, not to a specific enzyme, but to the presence of a manganous salt, the activity of which is stimulated by the action of hydroxyl ions.

When a solution containing a colloid and a manganous salt is precipitated by the addition of alcohol, the precipitate obtained contains some of all the constituents originally present in the solution, and this is the case even if the precipitation is repeated. Such precipitates exhibit feebly all the oxidising properties attributed to laccase and other oxidising ferments, and their activity can be greatly enhanced by the addition of minute traces of alkalis, so small as to be unrecognisable by the usual indicators. Bertrand's laccase is feebly alkaline, and always contains manganese, and its activity is practically paralysed in presence of acids. In view of these and other observations, it is contended that it is unnecessary to assume that Bertrand's laccase preparations, obtained by precipitating the latex of the lac tree by means of alcohol, contain any specific ferment, and that their oxidising action on quinol, pyrogallol, &c., is fully accounted for by the presence of an organic salt of manganese and the accidental presence of alkali. It is suggested, however, that these do not account for the oxidation of guaiacol by "laccase" and that some other

constituent, possibly an iron salt, intervenes in this instance. The results of a number of quantitative experiments on the oxidation of quinol by manganous salts, showing the influence of concentration, time, temperature, and other factors on this action, are tabulated in the original. It is also shown that animal charcoal rapidly oxidises quinol to benzoquinone in presence of air. It is also pointed out that too much stress is often laid on the mere inhibition of catalytic activity by the application of heat, as an indication of the presence of enzymes. For example, "laccase" becomes inactive at 100°, but there is good reason to believe that, in presence of colloids, organic manganous salts would decompose at this temperature and lose their oxidising activity. The oxidation of quinol to benzoquinone by salts of mercury, nickel, and other metals is possibly also due to their action in presence of alkalis or like impurities. T. A. H.

The Occurrence of Anticatalase in the Animal Organism. FR. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1908, 10, 275—276).—Polemical against Vanderveelde and de Waele (this vol., i, 491). The present authors use the prefix anti- in the same sense as it is employed in the words antipepsin, antitrypsin, &c. W. D. H.

Rôle of the Reductase in Alcoholic Fermentation. WLADIMIR N. PALLADIN (*Bull. Acad. Sci. St. Petersburg*, 1908, [iv], 8, 667—672 *).—It is shown that both vegetable and animal reductase are directly concerned in alcoholic fermentation. The reduction of sodium selenite and of methylene-blue by zymin is retarded greatly by the addition of dextrose, and to a less extent by sucrose and galactose, but glycerol, lactose, and mannitol hasten the process of reduction.

An analogy is drawn between these processes and the selective assimilation by fungi of the more nutritive of two substances in a mixture, and also of *d*- rather than *l*-tartaric acid by certain bacteria. Z. K.

The Properties of Yeast Juice; the Zymase Formation in Yeast. EDWARD BUCHNER and FRITZ KLATTE (*Biochem. Zeitsch.*, 1908, 9, 415—435).—Fresh yeast juice has but small optical rotation, varying in Munich yeast between + 0.12° and - 0.28° and in Berlin yeast between + 1.68° and 2.48°. This activity appears to depend on the glycogen (of which $[\alpha]_D = +196$ —213°), for the rotation almost disappears on allowing the juice to ferment without addition of sugar. When sugar is added, the decrease in the dextro-rotation does not correspond with its diminution as measured by collecting the carbon dioxide. In two cases, in spite of the disappearance of sugar, the rotation remained approximately constant. This phenomenon is possibly due to the concurrent formation of dextrorotatory polysaccharides. In the presence of disodium hydrogen phosphate, however, there was a decrease in the dextrorotation, which corresponded more nearly with the disappearance of the sugar.

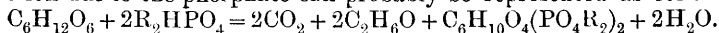
Lange has shown that by keeping yeast for two hours in a solution

* and *Zeitsch. physiol. Chem.*, 1908, 56, 81—88.

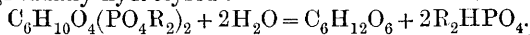
containing 0.1% asparagine and 4% potassium phosphate, with or without the addition of 10% sucrose, the fermentative power can be increased. Further experiments have shown that this treatment causes a regeneration of the zymase, and that the increased power is not due to the formation of fresh enzyme. The asparagine, furthermore, plays a very subordinate part, and the regeneration is due mainly to the presence of potassium dihydrogen phosphate; the corresponding dipotassium salt does not possess the like power.

S. B. S.

The Alcoholic Ferment of Yeast-Juice. III. The Function of the Phosphates in the Fermentation of Dextrose by Yeast-Juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1908, 80, B, 299—311).—The addition of a phosphate to a fermenting mixture of dextrose and yeast-juice, not only produces a temporary acceleration in the rate of fermentation, but also an increased total fermentation. The last effect is due to the fact that the hexose phosphate formed during the period of temporary acceleration is continually hydrolysed by an enzyme with the production of free phosphate, which again enters into reaction and thus brings about fermentation. The reaction due to the phosphate can probably be represented as follows:



This reaction is only realised in the presence of ferment and co-ferment, phosphate alone being unable to bring about fermentation in presence of ferment and dextrose (Abstr., 1907, i, 104). The hexose phosphate formed is gradually hydrolysed:

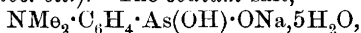


The conditions affecting this hydrolysis have been investigated; the rate at which it occurs, determines the rate of action when dextrose is fermented with yeast-juice. An optimum concentration of phosphate exists which produces a maximum initial rate of fermentation; an increase beyond this optimum diminishes the rate.

S. B. S.

p-Dimethylaminophenylarsonic Acid (Dimethylatoxyl).

AUGUST MICHAELIS (*Ber.*, 1908, 41, 1514—1516).—*p*-Dimethylaminophenylarsonic acid, previously prepared by the action of mercuric oxide and water on *p*-dimethylaminophenylarsenious oxide (Abstr., 1902, i, 412), is now obtained by heating dimethylaniline with arsenic trichloride and treating the crude *p*-dimethylaminophenylarsenious oxide so formed with water, sodium hydroxide, and hydrogen peroxide, or by the action of methyl sulphate on aminophenylarsonic acid in sodium hydroxide solution. *p*-Dimethylaminophenylarsonic acid blackens when heated, and does not sublime as previously stated (*loc. cit.*). The sodium salt,



crystallises in leaflets.

G. Y.

An Isomeric Aminophenylarsonic Acid. ALFRED BERTHEIM (*Ber.*, 1908, 41, 1655—1657).—The nitrophenylarsonic acid described by Michaelis and Loesner (Abstr., 1894, i, 187) may be reduced to the corresponding *aminophenylarsonic acid*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$, by

means of hydrogen sulphide (compare Michaelis, preceding abstract), provided that, after treating the solution of the nitro-compound in ammonium hydroxide with hydrogen sulphide, the product obtained on evaporating to dryness is extracted with hydrochloric acid, the extract rendered alkaline with sodium hydroxide, and then treated with a solution of copper sulphate. The reduction may also be performed with sodium amalgam. Whether this substance, which is isomeric with *p*-aminophenylarsonic acid (compare Ehrlich and Bertheim, Abstr., 1907, i, 812), is an ortho- or meta-compound has not been determined, although the latter is more probable. It crystallises in colourless prisms, m. p. 214° . It does not couple with diazobenzene or diazosulphanilic acid, but does so with *p*-nitrodiazobenzene, yielding a yellow *dye*, dissolving in alkalis with a red colour. It may itself be diazotised, and then forms *azo-dyes* with amines and phenols, which are soluble in sodium carbonate. W. H. G.

Diazophenylarsonic Acid and its Products of Decomposition. ALFRED BERTHEIM (*Ber.*, 1908, 41, 1853—1857).—*p*-Diazophenylarsonic acid (Ehrlich and Bertheim, Abstr., 1907, i, 812) undergoes the usual diazo-decomposition. On boiling in acid solution, it yields *p*-hydroxyphenylarsonic acid, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, crystallising from dilute alcohol in white needles containing $2\frac{1}{2}\text{H}_2\text{O}$. *p*-Ethoxyphenylarsonic (phenetylarsonic acid) is obtained by diazotising the base, dissolved in absolute alcohol by means of hydrogen chloride, with ethyl nitrite. It has m. p. 185° (Michaelis, Abstr., 1902, i, 413, gives $209\text{--}210^{\circ}$). By acting on the diazo-compound with sodium hypophosphite, phenylarsonic acid is obtained, m. p. $158\text{--}162^{\circ}$ (Michaelis gives 158°), and, by treating with copper powder, *p*-chlorophenylarsonic acid is formed, of which the barium salt was analysed. Treatment of the diazo-solution with cuprous cyanide, and hydrolysis of the resulting *nitrile*, furnishes *p*-carboxyphenylarsonic acid. Arsenious carboxyphenyl iodide has m. p. 172° (La Coste, Abstr., 1881, 903, gives m. p. 153°). J. C. C.

Preparation of Acyl Derivatives of *p*-Aminophenylarsonic Acid. [KURATORIUM DER GEORG UND FRANZISKA SPEYERSCHEN STUDIENSTIFTUNG] (D.R.-P. 191548).—Sodium *p*-aminophenylarsonate is readily acylated by the ordinary processes, and in this way the following derivatives have been obtained: *p*-formylaminophenylarsonic acid, slender needles, soluble in methyl alcohol or hot water, and *p*-acetylaminophenylarsonic acid, leaflets; the *phthalyl*-, *butyryl*-, *chloroacetyl*-, *benzoyl*-, and *malonyl*-*p*-aminophenylarsonic acids are similar compounds. The *carbonyl* derivative, $\text{CO}[\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2]_2$, was also prepared. G. T. M.

Some Homologues and Derivatives of Arsanilic Acid. I. LUDWIG BENDA and ROBERT KUHN (*Ber.*, 1908, 41, 1672—1678. Compare Ehrlich and Bertheim, Abstr., 1907, i, 812; O. and R. Adler, this vol., i, 492).—Homologues of aniline not substituted in the para-position readily condense with arsenic acid when heated at $170\text{--}200^{\circ}$, yielding substituted arsanilic acids; at the same time,

aromatic cacodylic acids of the type $\text{AsO}(\cdot\text{Ar}\cdot\text{NH}_2)_2\cdot\text{OH}$ are obtained as by-products. All the substituted arsanilic acids obtained give white silver salts. The amino-group may be acetylated and diazotised; the diazo-compounds couple with amines and phenols, yielding azo-dyes soluble in alkalis. The diazo-group is also readily replaceable by hydroxyl and halogens. The acetyl derivatives of the methyl homologues of arsanilic acid yield the corresponding carboxylic acids on oxidation.

6-Aminotolyl-3-arsonic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, obtained from arsenic acid and *o*-toluidine, crystallises in hexagonal prisms, m. p. 195° ; the *acetate*, $\text{C}_9\text{H}_{12}\text{O}_4\text{NAs}$, crystallises in brittle needles and prisms, decomposing at 306° .

5-Aminotolyl-2-arsonic acid, $\text{C}_7\text{H}_{10}\text{O}_3\text{NAs}$, from arsenic acid and *m*-toluidine, crystallises in long, rectangular prisms, m. p. 180° ; the *acetate* forms prismatic crystals, decomposing above 240° .

5-Amino-p-xylyl-2-arsonic acid, $\text{C}_8\text{H}_{12}\text{O}_3\text{NAs}$, from *p*-xylylene and arsenic acid, crystallises with $1\text{H}_2\text{O}$ in compact, hexagonal plates; the anhydrous substance has m. p. 215° ; the *acetate*, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{NAs}$, forms compact, prismatic crystals, decomposing at 278° .

1-Naphthylamine-4-arsonic acid, $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{AsO}(\text{OH})_2$, from arsenic acid and α -naphthylamine, forms small prisms, m. p. 175° . *3-Chloro-4-aminophenylarsonic acid*, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{AsO}(\text{OH})_2$, from *o*-chloroaniline and arsenic acid, forms white crystals, m. p. 305° . *o-Cresol-5-arsonic acid*, $\text{C}_6\text{H}_3\text{Me}(\text{OH})\cdot\text{AsO}(\text{OH})_2$, is prepared by diazotising 1-methyl-2:5-arsanilic acid and boiling the aqueous solution of the diazo-compound; it crystallises with $1\text{H}_2\text{O}$ in white prisms and needles, m. p. 180° ; the anhydrous substance has m. p. 222° .

W. H. G.

The Magnesium Derivatives of the Aromatic Chloro-compounds. A. HESSE (D.R.-P. 189476).—In the Grignard reaction, chloro-derivatives behave quite differently from the bromo- and iodo-compounds, the latter readily react, giving rise both to alkyl and aryl magnesium halides, but aryl magnesium chlorides have not hitherto been produced by the ordinary methods. By the intervention of a more reactive alkyl halide, the reaction with magnesium may be started, and then this metal combines with the aromatic chloro-derivative.

Magnesium tolyl, benzyl or cymyl chloride can be produced by adding magnesium to an ethereal solution of ethyl bromide and then introducing chlorotoluene, benzyl chloride, or chlorocymene, or, conversely, the magnesium alkyl halide (from methyl bromide, ethyl iodide, &c) may be added to an ethereal solution of the aromatic chloro-derivative in the presence of the requisite amount of magnesium.

G. T. M.

Organic Chemistry.

Estimation of Active Hydrogen in Organic Compounds. TH. ZEREWITNOFF (*Ber.*, 1908, 41, 2233—2243. Compare *Abstr.*, 1907, ii, 509).—An extension of the method previously described to the determination of the number of replaceable hydrogen atoms in hydroxy-, thiol-, amino-, and imino-compounds. Frequently the results obtained are high, owing to the development of heat from the formation of the compound of pyridine and magnesium methiodide, and the further interaction of the pyridine and iodide with evolution of gas. The mixture is therefore cooled after the first evolution of gas has occurred. Care should also be taken that no barium oxide is introduced with the dry pyridine.

Ten hydroxy-compounds of the flavone type have been examined, and good results obtained even where the hydroxyl group is in the ortho-position; thus euxanthone is shown to contain two and hæmatoxylin five hydroxyl groups. The method also succeeds with mercaptans, such as the propyl, *isobutyl*, or phenyl derivatives, and with imido-compounds, such as succinimide, oxanilide, or phthalimide (compare Hibbert and Sudborough, *Trans.*, 1904, 85, 933). The acid amides, like acetamide, react in the cold with one mol. of magnesium methiodide, and on heating at 85° with another mol.; the error due to the action of the pyridine is estimated by carrying out a blank experiment. Aldehyde-ammonia is shown in this way to have three active hydrogen atoms, two of which react in the cold. Carbamide and thiocarbamide have only three instead of four active hydrogen atoms, and phenylcarbamide, phenylthiocarbamide, and menthonesemicarbazone have two such hydrogen atoms; in all these cases the compound contains two amino- or one amino- and one imino-groups attached to the same carbon atom.

The reaction has been applied to tautomeric compounds, such as acetylacetone and ethyl acetoacetate, and at 100° these possess one active hydrogen atom; malonic acid contains three replaceable hydrogen atoms.

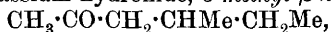
W. R.

Methylethylisobutylmethane [$\beta\delta$ -Dimethylhexane]. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1908, 30, 1144—1151).—In continuation of the work on the octanes (*Abstr.*, 1907, i, 169), $\beta\delta$ -dimethylhexane has been synthesised by two different methods.

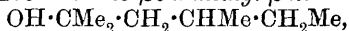
When methyl *isobutyl* ketone, prepared by the hydrolysis of ethyl *isopropyl*acetoacetate, is treated with magnesium ethyl bromide, $\beta\delta$ -dimethyl- δ -hexanol, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2\text{Me}$, b. p. 151°/768 mm., is produced. On converting this compound into the corresponding iodide and reducing the latter with zinc and hydrochloric acid, $\beta\delta$ -dimethylhexane, $\text{CH}_2\text{Me} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHMe}_2$, b. p. 109·8—110°/762 mm., is obtained as an odourless, mobile liquid with D_{15}^{25} 0·7083, and n_D^{25} 1·3986.

When *ethyl sec.-butyl*acetoacetate, b. p. 210—211°/762 mm., is

hydrolysed with potassium hydroxide, δ -methyl- β -hexanone,



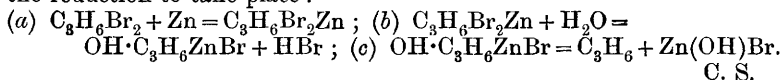
b. p. $139^\circ/762$ mm., is produced, and on treatment with magnesium methyl iodide is converted into $\beta\delta$ -dimethyl- β -hexanol,



b. p. 150 — $150.5^\circ/766$ mm. If this carbinol is converted into the iodide and the latter reduced with zinc and hydrochloric acid, $\beta\delta$ -dimethylhexane is obtained, identical with the compound prepared by the first method.

β -Chloro- δ -methyl- $\Delta^{\alpha\beta}$ -amylene, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CCl} \cdot \text{CH}_2$, b. p. $102.5^\circ/760$ mm., obtained by the action of phosphorus pentachloride on methyl isobutyl ketone, is a colourless, mobile liquid, and on oxidation with potassium permanganate yields isovaleric acid. E. G.

Behaviour of Trimethylene Dibromide towards Zinc Dust and Acetic Acid. NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1908, 41, 2429—2431).—After pointing out that no reaction occurs between glacial acetic acid and zinc dust, the authors state that carefully-dried trimethylene dibromide, glacial acetic acid, and zinc dust evolve with extreme slowness a gas which is found to be hydrogen, showing that a trace of water must still have been present. When 50% acetic acid is used, the gas which is evolved more rapidly, but still only slowly, proves to be cyclopropane, and not propane, which would be expected to be obtained. If the dibromide is gradually heated with glacial acetic acid, zinc dust, and concentrated hydrochloric or hydrobromic acid, the issuing gas consists of hydrogen free from hydrocarbon. As a result of these experiments, the authors consider that the first step in the reduction of trimethylene dibromide is the formation of a zinc additive compound, which is then decomposed by water; the latter must be present in not inconsiderable amount for the reduction to take place:



C. S.

Action of Metallic Oxides on Primary Alcohols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 146, 1376—1378).—The oxides examined fall into four classes: (1) those which undergo no reduction and which exert no appreciable effect on primary alcohols below 400° . This group includes titanium dioxide and the oxides of calcium, barium, strontium, magnesium, and silicon; (2) those rapidly reduced either to the metal or to a lower oxide; (3) oxides which are not reduced, but which decompose the alcohols catalytically, giving rise to hydrogen and an aldehyde, or to water and an ethylenic hydrocarbon, or to a mixture of aldehyde and hydrocarbon; (4) those oxides which are slowly reduced and at the same time exert a catalytic action. W. O. W.

Action of Metallic Oxides on the Primary Alcohols (Case of the Reducible Oxides). PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 147, 16—18).—As already stated (preceding abstract), primary alcohols are oxidised when passed over many

oxides heated below 400° . These oxides may be divided into four classes.

The simplest case is that in which the oxidation is limited to the formation of aldehyde and water, the oxide having no action on the aldehyde and the reduced oxide or metal having no catalytic power. The oxides of antimony and bismuth act in this way.

In the case of the more readily reducible oxides, the aldehyde formed is partly oxidised either to the corresponding acid or to carbon dioxide and water. Mercuric oxide is reduced by ethyl alcohol vapour at 150° , giving acetaldehyde and a large proportion of carbon dioxide, but not acetic acid. Manganese dioxide at 200° is reduced by ethyl alcohol to the sesquioxide, acetaldehyde being formed; at 250° , however, the sesquioxide formed is reduced, carbon dioxide and acetic acid being formed in addition to the aldehyde.

The third and largest class of oxides contains those of which the reduced metal or lower oxide has a catalytic action on the alcohol, the catalytic reaction being superposed on the initial oxidation. The oxides of nickel, cobalt, lead (PbO_2 , Pb_3O_4 , PbO), and copper (Cu_2O and CuO) at 350° belong to this class; the reduced metals have a dehydrogenating action on ethyl alcohol, giving acetaldehyde and hydrogen. In the case of nickel and lead oxides, but not with the copper oxides, acetic acid is produced. Manganese sesquioxide at 350° is slowly reduced by ethyl alcohol to the pale green manganous oxide, which decomposes ethyl alcohol into aldehyde and hydrogen. On the other hand, the yellow tungsten trioxide, WO_3 , at 350° is readily reduced by ethyl alcohol vapour, giving a blue intermediate oxide, which has a powerful dehydrating catalytic action, thus causing the formation of increasing amounts of ethylene besides the acetaldehyde, carbon dioxide, and acetic acid initially produced. Other oxides are reduced by alcohol vapour to lower non-reducible oxides, which are both dehydrating and dehydrogenating catalysts. Thus uranium trioxide, UO_3 , is reduced to UO_2 , and V_2O_5 to V_2O_3 , by alcohol vapour, giving aldehyde and carbon dioxide, whilst the reduced oxides act on further quantities of alcohol, giving aldehyde, hydrogen, ethylene, and water. In this class, the completion of the reduction is indicated by the disappearance of carbon dioxide in the gases produced.

The fourth class of oxides contains those which have themselves a catalytic action on alcohols. The latter is readily observed if the reduction is slow, but if this is rapid it is perceived only with difficulty. Thus ferric oxide, like alumina, is a dehydrating catalyst towards ethyl alcohol vapour, giving at 340° a mixture of ethylene and water, and being reduced to ferrous oxide and metallic iron. The latter, being a dehydrogenating catalyst, decomposes the alcohol into aldehyde and hydrogen. From this it follows that the proportion of ethylene gradually diminishes. Cadmium and stannous oxides, which are reduced very slowly by alcohol vapour at 340° , similarly act as dehydrogenating catalysts.

E. H.

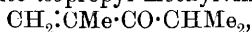
Decomposition of Alcohols under the Catalytic Influence of Charcoal (Braise). GEORGES LEMOINE (*Compt. rend.*, 1908, 146, 1360—1366. Compare Senderens, *Abstr.*, 1907, ii, 248).—The author

has examined the gaseous and liquid products formed when alcohols in the state of vapour are passed over "quenched charcoal" (Braise de boulanger) heated to a temperature not exceeding 400° and usually below 385° . Methyl, ethyl, *n*-propyl, isopropyl, isobutyl, and amyl alcohols were treated in this way, and it was found in each case that the liquid product consisted of unaltered alcohol and substances having the reducing properties of aldehydes. Complete analyses of the gaseous products have been made, and it is found that hydrogen is always an important constituent of the mixture, except in the case of isopropyl alcohol, which becomes dehydrated with formation of trimethylene.

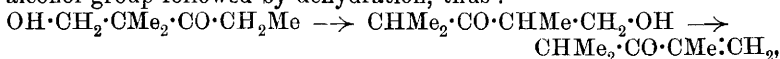
W. O. W.

$\alpha\alpha$ -Dialkyl- β -keto-alcohols. Transformation by Dehydration.

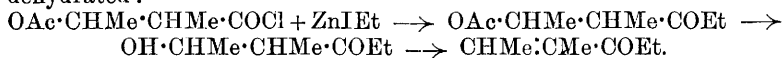
EDMOND E. BLAISE and I. HERMAN (*Compt. rend.*, 1908, 146, 1326—1328).—The transformation of ethyl hydroxypivalyl ketone, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{COEt}$, into isopropyl methylvinyl ketone,



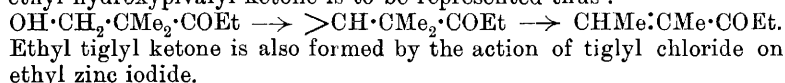
by the action of alkalis can be explained by a migration of the primary alcohol group followed by dehydration, thus :



or the dehydration may occur first and then a migration of the methyl group : $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me} \rightarrow >\text{CH}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me} \rightarrow \text{CH}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{CHMe}_2$. From the second hypothesis, it would be expected that the action of dehydrating agents would be similar to that of alkalis. When ethyl hydroxypivalyl ketone is treated with phosphoric oxide, however, the product is not isopropyl methylvinyl ketone, but another unsaturated ketone. The latter is identical with the ketone formed when β -acetoxy- α -methylbutyryl chloride is treated with ethyl zinc iodide and the product saponified and dehydrated :



It is therefore *ethyl tiglyl ketone*, $\text{CHMe}:\text{CMe}\cdot\text{COEt}$, has b. p. $52^{\circ}/15$ mm., and gives a *p*-nitrophenylhydrazone, m. p. 134° , and a *semicarbazone*, m. p. 161 — 162° . Its formation by dehydration of ethyl hydroxypivalyl ketone is to be represented thus :



The conclusion is drawn that the action of alkalis on ethyl hydroxypivalyl ketone is represented by the first of the above schemes, the dehydration being preceded by the transposition. E. H.

Basic Properties of Oxygen. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1908, 30, 1097—1104).—Baeyer and Villiger (*Abstr.*, 1901, i, 658 ; 1902, i, 112, 355), in studying the basic properties of oxygen, have prepared a large number of compounds of organic substances with ferrocyanic acid. In order that the acid should be attached to the oxygen base in the simplest possible way, 4 mols. of the latter should unite with 1 mol. of the former, but in many of the

compounds described this ratio does not exist. For this reason, and also since water may have been present in the salts, an investigation has been made of the compounds of ferrocyanic acid with methyl and ethyl alcohols, acetone, and ether. A study of the vapour pressure of the products obtained by the absorption of ether and acetone by the acid has shown that they are not quadrivalent oxygen compounds, but solid solutions. With ethyl alcohol, a crystalline *compound*, m. p. -45° , containing 35.7% of the acid was obtained, and with methyl alcohol a *compound*, m. p. -33° , containing 37% of the acid. These compounds contain about 10 mols. of the alcohol to one of the acid, and are much more complex than those obtained by Baeyer and Villiger; their properties indicate that they are molecular compounds in which the alcohols are present as alcohol of crystallisation.

Acetic acid dissolves in liquid hydrogen bromide and hydrogen iodide with development of heat and formation of crystalline substances. The hydrogen bromide *compound*, m. p. 5° , contains 46—49% HBr. Tschitschibabin (Abstr., 1907, i, 276) has described a compound, $2C_2H_4O_2 \cdot HBr$, m. p. $7-8^{\circ}$. The hydrogen iodide *compound*, m. p. -50° , contains 59—70% HI.

Methyl ethyl ether unites with liquid hydrogen bromide and hydrogen iodide to form white, crystalline *compounds*, $MeEtO \cdot HBr$ and $MeEtO \cdot HI$, m. p. -30° and -22° . If these compounds have the constitution $\begin{array}{c} Me \\ \diagup \\ Et-O \\ \diagdown \\ H \\ X \end{array}$, the oxygen atom is asymmetric. Attempts to separate them into optically active isomerides were not successful.

E. G.

Preparation of Methyl Sulphate. SOCIÉTÉ ANONYME DES PRODUITS CHIMIQUES DE FONTAINES IN LYON-MONPLAISIR (D.R.-P. 193830).—Methyl sulphate is conveniently prepared by adding chlorosulphonic acid (24 kilos.) to a mixture of 6.5 kilos. of methyl alcohol (90%) and 20 kilos. of carbon tetrachloride. After boiling off the diluent, the methyl sulphate is distilled under reduced pressure. A similar result is obtained on adding sulphur trioxide to the mixture of methyl alcohol and carbon tetrachloride. G. T. M.

Reduction of Alkyl Nitrates to Nitrites in Alkaline Solution. AUGUST GUTMANN (Ber., 1908, 41, 2052—2056).—Nitrite and arsenate are formed when an alcoholic solution of amyl or ethyl nitrate is heated in a pressure flask at 100° with a solution of arsenious oxide in sodium hydroxide.

The author draws the conclusion that the presence of these products points to the intermediate formation of ethyl hydroperoxide: $NO_2 \cdot OEt + NaOH \rightarrow NO_2Na + EtO \cdot OH$ and $EtO \cdot OH + As(ONa)_3 \rightarrow EtOH + AsO(ONa)_3$.

Potassium cyanide and sulphide also reduce ethyl and amyl nitrates yielding potassium nitrite, potassium thiocyanate, and the alcohol. In this reaction, the author assumes the intermediate formation of ethyl hydropersulphide: $NO_2 \cdot OEt + KSH \rightarrow KNO_2 + EtO \cdot SH$ and

$\text{EtO} \cdot \text{SH} + \text{KCN} \longrightarrow \text{EtOH} + \text{KCNS}$. The sulphide solution used should be free from polysulphides and thiosulphate.

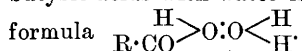
The reaction may be used in testing for alkyl nitrates in presence of the corresponding nitrites, as the latter do not give the yellow coloration and do not produce thiocyanates. J. J. S.

Character of the Compound formed by the Addition of Ammonia to Ethyl Phosphite-platochloride. CHARLES H. HERTY and R. O. E. DAVIS (*J. Amer. Chem. Soc.*, 1908, 30, 1084—1089).—Rosenheim and Levy (*Abstr.*, 1905, i, 183) have found that when dry ammonia is passed into a solution of triethyl phosphite-platochloride in benzene, the compound $\left[\text{Pt} \begin{smallmatrix} (\text{NH}_3)_2 \\ \text{P}(\text{OEt})_{3.12} \end{smallmatrix} \right] \text{Cl}_4$ separates in white crystals, and that this salt is hydrolysed by water, forming an acid solution which exhibits abnormal molecular conductivity. The present authors, although following Rosenheim's method as closely as possible, have been unable to prepare this substance, but have obtained only the normal salt, $\left[\text{Pt} \begin{smallmatrix} \text{Cl} \\ (\text{NH}_3)_2 \\ \text{P}(\text{OEt})_3 \end{smallmatrix} \right] \text{Cl}$, which forms white crystals, and dissolves in water to give a neutral solution. Determinations of the molecular conductivity at 25° are recorded, and agree closely with the values obtained by Werner for all di-ionic complex ammonia compounds. E. G.

Molybdenum Compounds of Lecithin. RICHARD EHRENFELD (*Zeitsch. physiol. Chem.*, 1908, 56, 89—94).—Alcoholic lecithin solutions, when precipitated in the cold with an alcoholic nitric acid solution of ammonium molybdate, yield a substance, 10MoO_3 , 3 mols. of lecithin, when the lecithin is in excess, and 2MoO_3 , 1 mol. of lecithin, when the precipitant is in excess. A substance, $5[(\text{NH}_7)_6\text{Mo}_7\text{O}_{24}]$, 1 mol. of lecithin, is precipitated by an aqueous ammonium molybdate solution when there is a large excess of lecithin. G. B.

Preparation of Concentrated Formic Acid. CHEMISCHE FABRIK GRÜNAU, LANDSHOFF & MEYER (D.R.-P. 193509).—Although highly concentrated sulphuric or phosphoric acid acts destructively on formic acid, yet their acid salts decompose formates without exhibiting this action, and sodium hydrogen sulphate, when intimately mixed with dry sodium formate and heated in a retort, gives rise to 97—98% formic acid. G. T. M.

Hydrates of the Fatty Acids. D. E. TSAKALOTOS (*Compt. rend.*, 1908, 146, 1272—1274. Compare this vol., i, 498).—The constitution of the molecular combinations of acetic, propionic, and butyric acids with water is considered to be best represented by the



The coefficients of viscosity of mixtures of formic acid with *m*-cresol are only slightly lower than the coefficients calculated from the rule of mixtures. Formic acid therefore shows less tendency than its homologues to form additive products with phenols. W. O. W.

Preparation of Phosphoric Esters from Phosphoric Oxide and the Diglycerides of Fatty Acids and their Bromo- and Iodo-derivatives. FERDINAND ULZER and J. BATIK (D.R.-P. 193189).—*Glyceryl distearophosphate*, $\text{PO}(\text{HO})_2 \cdot \text{O} \cdot \text{C}_3\text{H}_5(\text{OCOC}_{17}\text{H}_{35})_2$, m. p. 58° , is obtained in almost quantitative yield by mixing together phosphoric oxide and melted distearin and slowly adding water. The corresponding oleyl derivative is oily. Glyceryl dibromodistearophosphate is a brown, viscid mass, having an acid number 109.3 and a saponification number 218.3. Other similar glycerides are referred to in the patent, all of which are obtained by the same general method of adding the requisite amount of water to an intimate mixture of phosphoric oxide and to the diglyceride of a fatty acid. G. T. M.

Catalytic Actions of Colloidal Metals of the Platinum Group. III. Reduction Catalysis with Colloidal Palladium and Platinum. CARL PAAL and JOSEF GERUM (*Ber.*, 1908, 41, 2273—2282. Compare *Abstr.*, 1905, ii, 397, 533; 1907, ii, 559; Willstätter, this vol., i, 383).—When the investigation was extended to unsaturated acids, it was found that the method applicable for the reduction of nitrobenzene did not lead to the conversion of sodium fumarate into succinate, but that when the salt and the hydrosol of palladium hydride are left together in a closed vessel filled with hydrogen, the gas is quickly absorbed.

In this way, fumaric, maleic, and cinnamic acids, as well as methyl cinnamate, have been reduced to the corresponding saturated acid and the rate of absorption measured. As a general rule, there is a little more hydrogen absorbed than that required by theory; this may be due to the metal, but in one case an aldehyde-like odour was observed, so that the reduction may proceed further than the acid. Palladium-black may be used, as also colloidal platinum, but the action is slower.

W. R.

Catalytic Actions of Colloidal Metals of the Platinum Group. IV. Reduction Catalysis with Colloidal Palladium. CARL PAAL and KARL ROTH (*Ber.*, 1908, 41, 2282—2291. Compare preceding abstract).—The reduction of oleic acid to stearic acid has been carried out at the ordinary temperature by Fokin (*Abstr.*, 1907, i, 819), and it may be accomplished by using sodium oleate and palladium hydrosol, the yield of pure stearic acid obtained being 60%. The method has been extended to the reduction of fats, the Hübl iodine value being used to determine percentage of unsaturated acids before and after. The fats used were castor oil, olive oil, and cod-liver oil. A quantitative yield of saturated fats was obtained from the castor oil in the form of a white, hard, crystalline mass, sintering at 77° , m. p. 81° . Although three times the quantity of hydrogen required was absorbed by the olive oil, the reduction was not quite complete (iodine value before, 81—82; after, 9); the tallow has m. p. 47° . Cod-liver oil was very nearly completely reduced; the product obtained was crystalline, m. p. 43 — 45° . The method therefore appears to be the only one yet discovered for reducing the unsaturated glycerides in a fat at the ordinary temperature.

W. R.

Preparation of Glycollic Acid by the Electrolytic Reduction of Oxalic Acid. DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT (D.R.-P. 194038).—When oxalic acid is electrolysed in moderately concentrated sulphuric acid contained in an electrolytic cell fitted with a diaphragm and electrodes having a high supertension, a good yield of glycollic acid is produced. The following are details of this reduction. Cathode compartment, 700 parts of crystallised oxalic acid, 1100 parts of concentrated sulphuric acid, and 3300 parts of water; lead cathodes, current density 25 to 250 amperes per square metre; anode compartment, 30% sulphuric acid with an intermediate cell containing acid of the same strength. The temperature of the cathode solution was maintained above 25° throughout the electrolysis.

G. T. M.

Ethyl Chlorocynoacetoacetate and its Derivatives. ERICH BENARY (*Ber.*, 1908, 41, 2399—2411).—Whilst chloroacetyl chloride reacts with ethyl sodiomalonate to form mainly ethyl tetrone-4-carboxylate (*Abstr.*, 1907, i, 381), its behaviour with ethyl sodiocynoacetate in dry ether leads smoothly to the formation of *ethyl γ-chloro-α-cynoacetoacetate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 42—43°, which crystallises in colourless needles, has an acid reaction, develops a red coloration with ferric chloride, and is best purified by means of the green, crystalline *copper salt*, m. p. 171—172° (decomp.). The corresponding *methyl ester*, $\text{C}_6\text{H}_6\text{O}_3\text{NCl}$, m. p. 72—73°, forms a *copper salt*, which decomposes at 188—189°. Bromoacetyl bromide reacts with ethyl sodiocynoacetate in a similar manner, yielding *ethyl γ-bromo-α-cynoacetoacetate*, $\text{C}_7\text{H}_8\text{O}_3\text{NBr}$, m. p. 59—61°, which has properties similar to those of the chlorinated compound; the *copper salt* has m. p. 163—164° (decomp.).

The dry silver salt of ethyl chlorocynoacetoacetate reacts with ethereal ethyl iodide to form *ethyl γ-chloro-α-cyano-β-ethoxycrotonate*, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{OEt})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 93—94°, which forms colourless needles, does not give a coloration with ferric chloride, and yields with alcoholic ammonia, *ethyl γ-chloro-β-amino-α-cyanocrotonate*, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$,

m. p. 128—129°, in which the position of the amino-group is determined by the fact that the same compound is obtained by the action of ammonia on ethyl γ-chloro-α-cyano-β-methoxycrotonate.

Ethyl chlorocynoacetoacetate reacts with potassium cyanide in aqueous solution at 50—60° to form *ethyl α-dicyanoacetoacetate*, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 87—89°, in which the presence of the reactive methylene group enables the compound to condense with benzaldehyde and cinnamaldehyde, yielding the *benzylidene* and the *cinnamylidene* derivatives, the m. p. of which are 145—146° and 159—160° respectively; the latter is orange-coloured and the former yellow, having acid properties, and developing a blood-red coloration with ferric chloride.

The course of the reaction between ethyl chlorocynoacetoacetate and ammonia or organic bases in aqueous solution at the ordinary temperature depends on the base. Whilst with tertiary amines betaines are formed, and with ammonia a pyrrolidone derivative,

secondary amines cause a simple replacement of the halogen, and primary amines, in addition, the formation of pyrrolidone derivatives; the production of the heterocyclic compound, however, does not occur in the case of primary aromatic amines. The addition of sodium hydroxide facilitates the preceding reactions. 4-Cyano-3:5-diketo-

pyrrolidine, $\text{NH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CH} \cdot \text{CN} \end{smallmatrix}$, begins to decompose at 210° and melts

completely at $220-221^\circ$; the silver salt, $\text{C}_5\text{H}_3\text{O}_2\text{N}_2\text{Ag}$, crystallises in small needles. The compound is not attacked by boiling baryta, but is hydrolysed by boiling 30% potassium hydroxide, yielding the amide,

$\text{NH} \text{---} \text{CO} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{NH}_2$, which decomposes at 215° . Ethyl α -cyano-

γ -ethylaminoacetoacetate, $\text{NH} \text{Et} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, m. p. 225° , decomposition commencing at 215° , separates from hot water in long needles, reduces Fehling's solution, and forms a sodium salt and a hydrochloride, which decomposes at $173-174^\circ$. 4-Cyano-3:5-diketo-

1-ethylpyrrolidine, obtained from the filtrate in the preceding preparation, darkens at 200° , and decomposes and melts completely at 228° ; the ammonium salt has m. p. $194-195^\circ$. Ethyl α -cyano- γ -anilino-

acetoacetate, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, decomposes at $212-213^\circ$; the hydrochloride has m. p. $182-183^\circ$ (decomp.). Ethyl α -cyano- γ -o-methoxyphenylaminoacetoacetate,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, m. p. $207-208^\circ$, crystallises in white needles. Ethyl α -cyano- γ -piperidinoacetoacetate, $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, decomposes at $215-216^\circ$, and forms a hydrochloride, m. p. $159-160^\circ$ (decomp.), a sodium salt, which darkens at 300° and has m. p. 310° (decomp.), and a copper salt, which decomposes at $226-227^\circ$. Ethyl α -cyano- γ -dimethylaminoacetoacetate, m. p. $208-209^\circ$ (decomp.), forms a hydro-

chloride, m. p. $143-144^\circ$, and a violet copper salt, which decomposes at $226-227^\circ$. The betaine of ethyl α -cyano- γ -trimethylaminoaceto-

acetate, $\text{NMe}_3 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, m. p. $205-206^\circ$ (decomp.), separates from hot water in hexagonal plates, and has a neutral reaction, bitter taste, and very feebly basic properties. The analogous

pyridine derivative, $\text{C}_5\text{H}_5\text{N} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, decomposes at $250-251^\circ$. All the preceding substances, obtained by the action of bases on ethyl chlorocyanoacetoacetate, reduce warm ammoniacal silver solutions and develop a red coloration with ferric chloride; the pyrrolidine derivatives are strongly acidic, whilst the others have a neutral reaction and very feeble acid properties.

Ethyl chlorocyanoacetoacetate and phenylhydrazine in aqueous solution yield Rupe's α -phenylhydrazino- β -acetylphenylhydrazine (Abstr., 1898, i, 572).

C. S.

Potassium Ammonium Oxalate. PHILLIPPE BARBIER (*Bull. Soc. chim.*, 1908, [iv], 3, 725-726).—Anhydrous potassium ammonium oxalate separates in colourless, slender needles when a concentrated solution of potassium oxalate is added to a saturated solution of

ammonium carbonate to which a small quantity of ammonia solution has been added. When potassium oxalate is replaced by sodium oxalate, no separation of the corresponding sodium ammonium oxalate occurs.

T. A. H.

Tautomerism of Succinyl Chloride. RICHARD MEYER and KARL MARX (*Ber.*, 1908, 41, 2459—2471. Compare Meyer and Jugilewitsch, *Abstr.*, 1897, i, 350).—From the investigation of Auger (*Abstr.*, 1888, 952), succinyl chloride is apparently a mixture of the symmetrical with the asymmetrical compound; nevertheless, on treating succinyl chloride with an alcohol, the same ester is obtained as by acting on silver succinate with the corresponding alkyl iodide. In no case was an isomeride isolated from the product formed from the succinyl chloride; this fact speaks for the tautomeric character of succinyl chloride (compare Emery, *Abstr.*, 1890, 236).

The following new esters of succinic and dibromosuccinic acid have been prepared:

Cetyl succinate, $C_2H_4(CO_2 \cdot C_{16}H_{33})_2$, crystallises in small, glistening leaflets, m. p. 58°. *p-Nitrobenzyl succinate*, $C_2H_4(CO_2 \cdot CH_2 \cdot C_6H_4 \cdot NO_2)_2$, crystallises in slender needles, m. p. 90°; the corresponding *o-nitrobenzyl* ester has m. p. 104—105°. *Cetyl dibromosuccinate*,

$C_2H_2Br_2(CO_2 \cdot C_{16}H_{33})_2$, has m. p. 36—37°. *Benzyl dibromosuccinate*, $C_2H_2Br_2(CO_2 \cdot CH_2Ph)_2$, forms short, stout crystals, m. p. 92—93°.

When succinyl chloride is heated with bromine at 140—150° in a flask fitted with a reflux condenser, the principal product formed is succinyl bromide; this reacts with benzene and aluminium chloride, yielding an *additive* product which is decomposed by water with the formation of dibromosuccinophenone (compare Paal and Schulze, *Abstr.*, 1902, i, 228).

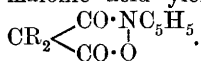
The fraction, b. p. 115—127°, obtained during the fractionation of the impure succinyl bromide, prepared as just described, yields on treatment with benzene and aluminium chloride a mixture of dibromosuccinophenone and a *substance* crystallising in colourless leaflets, m. p. 97—100°.

Dibromosuccinophenone yields on treatment with phenylhydrazine a *substance* which probably has the formula $C_2H_2(CPh:N \cdot NPh)_2$; it softens at about 60°, and decomposes at 100°. Similarly, a *substance*, $C_2H_2(CPh:N \cdot NPh \cdot CH_2Ph)_2$, is obtained by acting on the ketone with *as*-phenylbenzylhydrazine; it crystallises in colourless needles, m. p. 109°.

W. H. G.

Ketens. X. Malonic Semichloride, Malonic Anhydride, and its Transformation into Keten. HERMANN STAUDINGER and E. OTT (*Ber.*, 1908, 41, 2208—2217. Compare this vol., i, 411).—In attempting to prepare malonyl chloride by acting on an ethereal solution of malonic acid with thionyl chloride, a product was obtained which proved to be malonic semichloride. It was thought possible that by acting on this compound with tertiary bases, the hitherto unknown unimolecular anhydride of malonic acid would be obtained.

Instead, however, *additive* products were formed of the type $C_5NH_5Cl \cdot CO \cdot CR_2 \cdot CO_2H, NC_5H_5$. The product obtained from malonic semichloride decomposes when warmed, yielding a tarry substance; the products from the semichlorides of dimethyl- and diethylmalonic acid yield amorphous *substances* having the constitution



When heated under reduced pressure, malonic semichloride yields acetyl chloride and carbon dioxide; the corresponding diethyl derivative yields α -ethylbutyryl chloride and carbon dioxide, whilst dimethylmalonic semichloride yields isobutyryl chloride, carbon dioxide, and dimethylmalonic anhydride. The latter compound was found to be identical with that described by Einhorn (this vol., i, 312) as a duodecimolecular anhydride of dimethylmalonic acid. It is insoluble in most solvents; in others it dissolves with decomposition, consequently the mol. wt. cannot be determined. The slight depression of the freezing point observed by Einhorn, which led to the belief in the existence of a duodecimolecular form, was undoubtedly due to the presence of impurity. The same also applies to diethylmalonic anhydride (Abstr., 1906, i, 398).

Both anhydrides, although undoubtedly highly polymerised, react as if unimolecular; thus, both compounds decompose when heated, yielding ketens: $CR_2(CO)_2O \rightarrow CO_2 + CR_2 \cdot CO$.

Malonic semichloride, $COCl \cdot CH_2 \cdot CO_2H$, crystallises in small needles, m. p. about 65° (decomp.). It readily decomposes both at the ordinary temperature and when heated. *Dimethylmalonic semichloride*, $C_5H_7O_3Cl$, forms compact crystals, m. p. about $64-65^\circ$ (decomp.), having a characteristic odour. The corresponding *diethyl* compound was obtained as an oil, which could not be solidified.

Dimethylmalonic anhydride (compare Einhorn, *loc. cit.*) is a slightly grey powder, which when rapidly heated decomposes at $170-175^\circ$. It decomposes when heated under a pressure of 12 mm. at $160-180^\circ$, yielding dimethylketen (compare Staudinger and Klever, Abstr., 1906, i, 234). The latter compound distils with slight decomposition at $34^\circ/750$ mm.; it has m. p. -97.5° , b. p. $48.5^\circ/12$ mm.

Diethylketen, $CEt_2 \cdot CO$, prepared from diethylmalonic anhydride, is a liquid, b. p. $91-92^\circ/749$ mm., which solidifies to a yellow, crystalline mass at the temperature of liquid air. It is slightly more yellow than the dimethyl compound.

W. H. G.

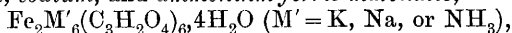
Ferrous and Ferric Double Salts of Polybasic Acids.

A. SCHOLZ (*Monatsh.*, 1908, 29, 439-450).—Whilst ferrous salts are usually green and ferric salts yellow, Eder and Valenta (Abstr., 1881, 713) found that oxalic acid forms a yellow potassium ferrous, but a green potassium ferric, salt. These results have now been confirmed, and double ferrous and ferric salts of malonic acid prepared and found also to have the usual colours reversed.

Potassium and ammonium ferrous malonates, $FeM'_2(C_3H_2O_4)_2 \cdot 2H_2O$ ($M' = K$ or NH_3), are prepared from ferrous iodide and potassium and ammonium malonates, and form yellow crystals which oxidise rapidly

on exposure to air. A sodium ferrous malonate could not be prepared.

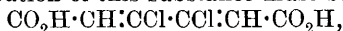
Potassium, sodium, and ammonium ferric malonates,



are prepared from ferric hydroxide, malonic acid, and potassium, sodium, or ammonium malonate, and form emerald-green crystals which are readily soluble in water.

Attempts to prepare double salts of succinic, glutaric, and fumaric acids led to the formation of the known basic ferric salts; maleic acid yields a *basic ferric* salt, $\text{C}_4\text{H}_2\text{O}_4\text{Fe} \cdot \text{OH}$. G. Y.

Muconic Acid Derivatives. Constitution of Dichloromuconic Acid. DAN RADULESCU (*Chem. Zentr.*, 1908, i, 1832—1833; from *Bul. Soc. Stiinte Bucuresti*, 1907, 16, 191—206).—In view of the fact that when ethyl dichloromuconate is treated with sodium ethoxide a disodium compound is produced, and that Canizzaro's reaction yields diacetyl, the constitution of this substance must be



and the stability of the free acid, acid chloride, and amide points to

the configuration $\begin{array}{c} \text{Cl} \cdot \text{C} \text{---} \text{C} \cdot \text{Cl} \\ | \quad \quad | \\ \text{CO}_2\text{H} \cdot \text{C} \cdot \text{H} \quad \text{H} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{array}$ Details are given for the

preparation of dichloromuconic acid chloride from a mixture of dry muconic acid and phosphorus pentachloride. It is a colourless, tasteless, and odourless substance, giving an *amide* which does not melt below 210° . An apparatus is described enabling the preparation and filtration of this ester to be performed in an atmosphere of an inert gas. J. V. E.

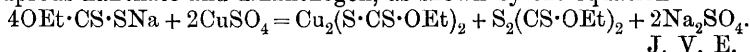
Preparation of Methyleneclitric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193767. Compare Abstr., 1904, i, 649).—The reactions formerly employed in preparing methyleneclitric acid are more or less reversible, owing to the presence of water among the products. The condensation becomes complete when methylene derivatives, such as methylene sulphate, methyl methylenediacetate, or chloromethyl acetate, are employed which can condense without the elimination of water.

Anhydrous citric acid, when heated at 140 — 150° with the calculated amount of methyl methylenediacetate and a few drops of concentrated sulphuric acid, yields pure methyleneclitric acid, which is crystallised from boiling water. When methylene sulphate is employed, the condensation is effected in the presence of sodium acetate or glacial acetic acid. A good yield of methyleneclitric acid is obtained when trioxymethylene condenses either with acetylclitric acid or with citric acid in the presence of acid chlorides or anhydrides.

G. T. M.

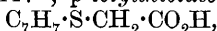
Xanthic Acid. MANFRED RAGG (*Chem. Zeit.*, 1908, 32, 630—631, 654—656, 677—679).—In the reaction of a copper salt with an ethylxanthate, a brownish-black precipitate is obtained, the colour of which soon changes to yellow. It has frequently been suggested that cupric xanthate is first formed, which then is decomposed with

formation of the cuprous salt. The author has re-investigated this question, and comes to the following conclusions: (1) The yellow precipitate just referred to is cuprous xanthate. (2) Cupric xanthate is not formed in the reaction. The evanescent, brownish-black precipitate also formed initially consists mainly of cupric thiocarbonate. (3) This is due to the fact that in the preparation of the xanthate a certain proportion of thiocarbonate is also formed, owing to a reaction between alkali hydroxides and xanthates. (4) The author shows that the reaction between an alkali xanthate and a cupric salt yields cuprous xanthate and dioxanthogen, as shown by the equation

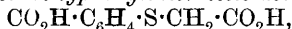


Preparation of Dithioglycollic Acid and Arylthioglycollic Acids. KALLE & Co. (D.R.-P. 194039, 194040).—When aqueous solutions of sodium disulphide and sodium chloroacetate are mixed in the cold, there is little or no deposition of sulphur. The mixture becomes warm, and, after heating to boiling, the solution contains sodium dithioglycollate.

When thioglycollic acid is treated with a soluble diazo-salt, a diazo-derivative, $\text{R}\cdot\text{N}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, of this acid is produced as an insoluble, crystalline precipitate, which, on heating, loses nitrogen and gives rise to an arylthioglycollic [arylthiolacetic] acid, $\text{R}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The following have been prepared: *phenylthiolacetic acid*, $\text{SPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, colourless needles, m. p. 117° ; *p-tolylthiolacetic acid*,



needles, m. p. 93° ; *o-carboxyphenylthiolacetic acid*,



obtained from diazotised anthranilic acid; *α -naphthylthiolacetic acid*, white needles.

G. T. M.

Preparation of Formaldehydesulphoxylate. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 194052).—Normal zinc sulphite, in aqueous solution, when treated successively with zinc dust and formaldehyde at 100° furnishes a sparingly soluble basic zinc formaldehydesulphoxylate, $\text{ZnSO}_3 + \text{Zn} + \text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2\text{O}\cdot\text{ZnSO}_2 + \text{Zn}(\text{OH})_2$. Ammonium sulphite, when treated similarly, furnishes ammonium formaldehydesulphoxylate.

G. T. M.

Inversion of Sucrose by Invertase. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, 30, 1160—1166).—O'Sullivan and Tompson (*Trans.*, 1890, 51, 834) have found that the inversion of sucrose by invertase is a unimolecular reaction, and have shown that the results of other observers who held the opposite view were vitiated by a systematic error in their polarimetric measurements. This error is due to the fact that the dextrose formed is initially in a birotatory state, and therefore the optical activity of a solution undergoing inversion does not indicate the amount of inversion which has taken place. If, however, alkali hydroxide is added to the solution and the optical activity is allowed to become constant, the true amount of inversion

which has taken place at the moment of adding the alkali is accurately indicated.

In the present paper, an account is given of a study of this question, and data are quoted which show that the inversion of sucrose by acids is a unimolecular reaction, even in its first stages, and that the polarimetric measurement of the inversion of sucrose by invertase involves a large source of error which can be obviated by adding alkali hydroxide to the solution before each reading. When this source of error is eliminated, as was done by O'Sullivan and Tompson, the inversion follows the unimolecular order.

E. G.

Formation of Molasses. SERGIUS LEBEDEFF (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 599—621).—In order to trace the causes of molasses formation, the effect of some non-sugar constituents of molasses on the solubility of sucrose has been determined. Betaine has a slight salting-out effect at 30°, but at higher temperatures (50—70°) it increases the solubility of sucrose, and potassium glutamate (the other chief non-sugar constituent of molasses) increases the solubility of sucrose both at low and at higher temperatures.

G. B.

Action of Formaldehyde on Starch. ALBERT REICHARD (*Chem. Zentr.*, 1908, i, 1834—1835; from *Zeitsch. ges. Brauwesen*, 1908, 31, 161—163).—Solutions of formaldehyde lower the temperature at which starch gelatinises. In the same space of time, a 2% formaldehyde solution of starch was completely gelatinised at 59°, and a 37% solution at 49°. If left a sufficiently long time, gelatinisation is completed at the ordinary temperature.

J. V. E.

Gum of the Almond Tree. R. HUERRE (*J. Pharm. Chim.*, 1908, [vi], 27, 561—569).—This gum differs from that of the closely-related apricot and plum trees in containing a small proportion of matter soluble in water (10—20% instead of 80—90%). Nevertheless, there is a close chemical relationship, all three consisting largely of pentosans, yielding arabinose on hydrolysis. From the almond tree gum, galactose has now, in addition, been isolated.

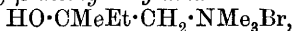
G. B.

Decomposition Curves of some Nitrocelluloses of American Manufacture. OSWIN W. WILLCOX (*Zeitsch. angew. Chem.*, 1908, 21, 1407—1411).—During an investigation of the stability of ordinary collodion wool by Obermüller's method (Abstr., 1905, ii, 291), the author has found that the amount of decomposition in a definite interval of time is greater when the gaseous decomposition products are left in contact with the sample during the preceding interval than when they are removed. From an examination of the curves, it appears that a given sample of nitrocellulose, when heated at 140°, has a characteristic decomposition pressure; as the heating is continued, a new component or phase is produced, which reinforces the previous one by its decomposition pressure; the pressure increase then remains more or less constant until a new phase is again produced, and so the process repeats itself.

P. H.

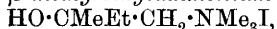
Preparation of the Alkyl Halides of Dialkylaminodimethylethylcarbinol and their Benzoyl Derivatives. J. D. RIEDEL (D.R.-P. 195813).—The dialkylaminodimethylethylcarbinols and their benzoyl derivatives, when treated with alkyl halides, furnish quaternary salts which have valuable therapeutic properties.

Trimethyl-β-hydroxy-β-methylbutylammonium bromide,



colourless spicules, m. p. 168—169°, is produced by adding methyl bromide to dimethylaminodimethylethylcarbinol; its *benzoyl* derivative (stovaine methobromide) forms colourless needles.

Trimethyl-β-hydroxy-β-methylbutylammonium iodide,

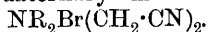


colourless prisms, m. p. 123—125°, and its *benzoyl* derivative, needles, m. p. 169—170°. *Dimethylethyl-β-hydroxy-β-methylbutylammonium bromide*, $\text{HO} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NMe}_2\text{EtBr}$, its *benzoyl* derivative, the corresponding quaternary *ethiodide*, and its *benzoyl* derivative, needles, m. p. 155—157°, are prepared similarly. G. T. M.

Synthesis of Alanine and α-Aminobutyric Acid. NICOLAI D. ZELINSKY and GEORG STADNIKOFF (*Ber.*, 1908, 41, 2061—2063).—α-Aminopropionitrile hydrochloride is obtained in a 23%, together with alanine in a 40%, yield from acetaldehyde by the authors' method for the synthesis of aminonitriles. In the same manner, α-aminobutyronitrile hydrochloride is obtained in a 25%, together with α-aminobutyric acid in a 29.4%, yield from propaldehyde. In support of the authors' view of the mechanism of the reaction, experiments are quoted showing that α-aminophenylacetoneitrile and α-aminocyclohexylacetoneitrile are formed from benzaldehyde and cyclohexanone respectively only in the presence of water. G. Y.

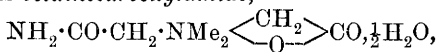
A New Synthesis of isoLeucine. WALTHER BRASCH and ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 376—380).—*sec*.-Butylmalonic acid, $\text{CHMeEt} \cdot \text{CH}(\text{CO}_2\text{H})_2$, yields on bromination the α-derivative, $\text{CHMeEt} \cdot \text{CBr}(\text{CO}_2\text{H})_2$, which, when heated, is converted into α-bromo-β-methylvaleric acid, $\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$; this, when left in contact with concentrated ammonia solution, yields α-amino-β-methylvaleric acid, $\text{CHMeEt} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, or *isoleucine*. S. B. S.

Betainecarboxylic Acids and Betainecarboxyamides. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2123—2129).—Bromoacetonitrile unites with tertiary aminoacetonitriles which do not contain an aromatic group to form quaternary ammonium salts,

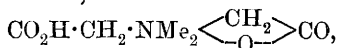


When these are shaken with silver hydroxide, not only is the bromine replaced by hydroxyl, but at least one of the cyanomethyl groups undergoes change, and on removing silver from the solution with hydrogen sulphide and evaporating, quantitative yields of betainecarboxyamides, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NR}_2 \cdot \text{CH}_2 \cdot \text{CO}$, are obtained. On hydrolysis, these are converted into the corresponding betainecarboxylic acids.

s-Di-ω-cyanotetramethylammonium bromide, $\text{NMe}_2\text{Br}(\text{CH}_2\cdot\text{CN})_2$, prepared from dimethylaminoacetonitrile and bromoacetonitrile in the cold, forms glistening crystals, m. p. 135° (decomp.), this with silver hydroxide yields *betainecarboxylamide*,



white powder, m. p. 122° , and this on hydrolysis with hydrochloric acid furnishes the *chloride*, $\text{NMe}_2\text{Cl}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, white, crystalline powder, m. p. 207° , which, on treatment with silver hydroxide, gives *betainecarboxylic acid*,

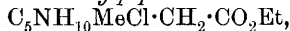


white, crystalline powder, m. p. 245° . Similarly, *biscyanomethylpiperidinium bromide* (Abstr., 1907, i, 899) gives the *compound*, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}\left\langle\begin{array}{c}\text{CH}_2\\ \text{O}\end{array}\right\rangle\text{CO}$, white powder, m. p. 230° , which, on hydrolysis, yields the corresponding *acid*,



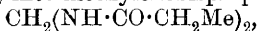
white powder, m. p. 249° ; the *chloride*, $\text{C}_9\text{H}_{16}\text{O}_4\text{NCl}\cdot 2\text{H}_2\text{O}$, crystallises in rosettes of needles, m. p. 137° (decomp.); the anhydrous salt has m. p. 200° ; the *bromide*, $\text{C}_9\text{H}_{16}\text{O}_4\text{NBr}\cdot 2\text{H}_2\text{O}$, crystallises in shining needles, m. p. $147\text{--}148^\circ$.

The compound $\text{C}_5\text{NH}_{10}\text{Me}\left\langle\begin{array}{c}\text{CH}_2\\ \text{O}\end{array}\right\rangle\text{O}$ (Klages and Margolinsky, Abstr., 1904, i, 145) was prepared as follows: ethyl iodomethylpiperidiniumacetate (Wedekind and Oechslen, Abstr., 1902, i, 392) is converted into *ethyl chloromethylpiperidiniumacetate*,



m. p. 189° , which gives a *platinichloride*, small, yellowish-red crystals, m. p. 225° , and, on treatment with hydrochloric acid, furnishes the required compound. The *chloride*, $\text{C}_5\text{NH}_{10}\text{MeCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has m. p. 213° (decomp.), and the *platinichloride* forms small, reddish-yellow crystals, m. p. 219° .
J. C. C.

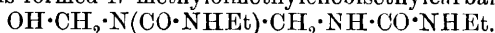
N-Methylol Compounds of Acid Amides. II. ALFRED EINHORN [and, in part, RICHARD FEIBELMANN, MAX GOTTLER, ALEXANDER HAMBURGER, and EDUARD SPRÖNGERTS] (*Annalen*, 1908, 361, 113—165. Compare Abstr., 1906, i, 245).—The *N*-methylol compounds of propionamide, isobutyramide, and dipropylacetamide have been prepared in amplification of the earlier paper. *N*-Methylolpropionamide, $\text{CH}_2\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, is readily converted by alkalis at the ordinary temperature into *N*-methylolmethylenebispropionamide, $\text{OH}\cdot\text{CH}_2\cdot\text{N}(\text{CO}\cdot\text{CH}_2\text{Me})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, or, when heated gently with acids, into methylenebispropionamide,



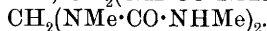
whilst on oxidation with chromic acid and sulphuric acid, it yields formylpropionamide, $\text{CHO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$. As with benzoyl ethylamide, attempts to prepare an *N*-methylol derivative of isovaleryl ethylamide have been unsuccessful. Urethane forms an *N*-methylol compound, $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which behaves in the same manner as

N-methylolpropionamide, being converted by alkalis into *N*-methylol-methylenebisurethane, $\text{OH}\cdot\text{CH}_2\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, and by acids into methylenebisurethane (Conrad and Hock, Abstr., 1903, i, 605).

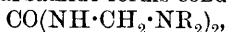
Whilst carbamide forms mono- and di-methylol derivatives (this vol., i, 141), a methylolethylcarbamide could not be obtained, but in its place is formed *N*-methylolmethylenebisethylecarbamide,



Both dimethylcarbamides, on the other hand, yield monomethylol compounds, $\text{NMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{NHMe}\cdot\text{CO}\cdot\text{NHMe}\cdot\text{CH}_2\cdot\text{OH}$ respectively. This is remarkable, as monoalkylamides do not form methylol compounds. In acid solution, the dimethylcarbamides yield methylene derivatives, $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{NMe}_2)_2$ and

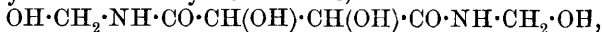


Triethylcarbamide does not form a methylol derivative; this and the fact that *s*-dimethylcarbamide forms a mono-, but not a di-, methylol derivative may be looked upon as evidence in favour of the ψ constitution for carbamides, $\text{OH}\cdot\text{C}(\text{NEt})\cdot\text{NEt}_2$ and $\text{OH}\cdot\text{C}(\text{NMe})\cdot\text{NHMe}$. Like other acid amides, carbamide forms condensation products,

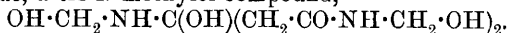


with formaldehyde and secondary bases.

Also the amides of hydroxy-carboxylic acids form *N*-methylol compounds; these contain one methylol for each amide group; lactic acid yields *N*-methylol-lactamide, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$; tartramide yields di-*N*-methyloltartramide,



and citramide, a tri-*N*-methylol compound,



N-Methylol-lactamide and *N*-methylolmandelamide yield dibenzoyl derivatives in which the methylol hydroxyl, as well as that of the hydroxy-acid, is benzoylated. Methylol compounds of the amides of quinoline-6-carboxylic acid and camphocarboxylic acid are described.

N-Methylolpropionamide, $\text{C}_4\text{H}_9\text{O}_2\text{N}$, prepared in a 90% yield from propionamide and formaldehyde in presence of barium hydroxide, crystallises in colourless prisms, m. p. 64° , is hygroscopic, and when heated evolves formaldehyde. *N*-Methylolmethylenebispropionamide, $\text{C}_8\text{H}_{16}\text{O}_3\text{N}_2$, crystallises in rhomboids, m. p. 76 – 77° , does not evolve formaldehyde when boiled with water, and reduces Tollens's silver solution more slowly than the preceding substance. *Methylenebispropionamide*, $\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2$, crystallises in needles, m. p. 201° , and remains unchanged when boiled with potassium chromate and sulphuric acid or when heated with bromine. *N*-Formylpropionamide, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHO}$, formed by oxidation of *N*-methylolpropionamide with chromic acid in sulphuric acid solution, crystallises in prismatic needles, m. p. 65° , decomposes when heated, and yields formylphenylhydrazide, m. p. 142° , when boiled with alcoholic phenylhydrazine.

N-Methylolisobutyramide, $\text{CHMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, crystallises in needles, m. p. 77° .

α -Ethylbutyramide is best prepared by treating diethylmalonic acid with phosphorus trichloride, and the resulting ethylbutyryl chloride

with ammonia in ethereal solution. *Methylenebis- α -ethylbutyramide*, $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{CHEt}_2)_2$, prepared by the action of hydrochloric acid on equal amounts of α -ethylbutyramide and its *N*-methylol derivative (*loc. cit.*), forms needles, m. p. 235° . *α -Ethylbutyryldiethylglycyl-methylenediamine*, $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NEt}_2$, formed by the action of *N*-methylol- α -ethylbutyramide on diethylglycylamide in concentrated sulphuric acid solution, crystallises in prismatic leaflets, m. p. $78-79^\circ$, and has very weak basic properties.

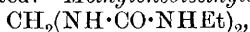
N-Methylol- α -propylvaleramide, $\text{CHPr}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, formed from α -propylvaleramide and formaldehyde, crystallises in needles, m. p. 117° , evolves formaldehyde when heated, reduces Tollens's silver solution in a few minutes, and differs from the methylol derivatives of other amides of the fatty series by its insolubility in water.

isoValerylethylamide, $\text{CH}_2\text{Pr}^2\cdot\text{CO}\cdot\text{NHEt}$, prepared by the action of *isovaleryl* chloride on ethylamine and sodium hydroxide, has m. p. $20-30^\circ$, b. p. $121^\circ/20$ mm.

The action of formaldehyde and barium hydroxide on urethane leads to the formation of *N-methylolurethane*, $\text{C}_4\text{H}_9\text{O}_3\text{N}$, which is obtained in colourless prisms, m. p. 53° ; it evolves formaldehyde when heated alone or in aqueous solution, and yields methylenebisurethane when treated with dilute hydrochloric acid. *N-Methylolmethylenebisurethane*, $\text{C}_8\text{H}_{16}\text{O}_5\text{N}_2$, crystallises from benzene in prisms, m. p. $68-69^\circ$, evolves formaldehyde when heated, and reduces silver solutions slowly.

Methylolcarbamide has m. p. 111° (116° : this vol., i, 142), and when treated with dilute hydrochloric acid forms di-*N*-methylolcarbamide or, on prolonged treatment, an amorphous substance, decomp. 260° . The action of concentrated hydrochloric acid on di-*N*-methylolcarbamide leads to the formation of a substance, $\text{C}_{18}\text{H}_{33}\text{O}_{12}\text{N}_{13}$, which crystallises in needles, not melted at 250° , and forms two *hydrochlorides*, crystallising from dilute hydrochloric acid in leaflets and from concentrated hydrochloric acid in strongly refracting, rhombic prisms respectively.

N-Methylolmethylenebisethylcarbamide, $\text{C}_8\text{H}_{18}\text{O}_3\text{N}_4$, prepared by gently heating ethylcarbamide with formaldehyde and barium hydroxide, crystallises in needles, m. p. $168-170^\circ$ (decomp.), and evolves formaldehyde when heated. *Methylenebisethylcarbamide*,



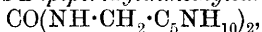
formed by the action of concentrated hydrochloric acid on formaldehyde and ethylcarbamide, crystallises in small needles, m. p. 204° , and yields a *picrate*, crystallising in reddish-yellow needles, m. p. $115-116^\circ$.

N-Methylol-as-dimethylcarbamide, $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2$, prepared from *as*-dimethylcarbamide, crystallises in plates from alcohol or from ethyl acetate in needles, m. p. 110° , and evolves formaldehyde when heated. *Methylenebis-as-dimethylcarbamide*, $\text{C}_7\text{H}_{16}\text{O}_2\text{N}_4$, formed from *as*-dimethylcarbamide and formaldehyde in concentrated hydrochloric acid solution, crystallises in rhombic prisms, m. p. $183.5-184^\circ$.

N-Methylol-s-dimethylcarbamide crystallises in prisms, m. p. 92° , is hygroscopic, reduces silver solutions fairly rapidly, and evolves

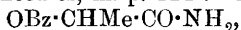
formaldehyde when heated. *Methylenebis-s-dimethylcarbamide* crystallises from chloroform-ethyl acetate in prisms, m. p. 149—151°.

Condensation Products of Carbamide, Formaldehyde, and Secondary Bases.—*s-Tetraethylldiaminodimethylcarbamide*, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2)_2$, prepared by heating carbamide with formaldehyde and diethylamine in aqueous solution, is obtained in a 35% yield as an oil, which decomposes on distillation in a vacuum. The *picrate*, $\text{C}_{23}\text{H}_{32}\text{O}_{15}\text{N}_{10}$, has m. p. 145—147°. *s-Dipiperidylldimethylcarbamide*,



prepared from carbamide, piperidine, and formaldehyde in a 60% yield, crystallises from ethyl acetate in needles, m. p. 136°.

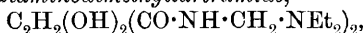
N-Methylol Compounds of Hydroxy-acid Amides.—*N-Methylol-lactamide*, $\text{C}_4\text{H}_9\text{O}_3\text{N}$, prepared by the action of formaldehyde and barium hydroxide on lactamide, crystallises from alcohol in colourless pyramids, m. p. 82—84°, and evolves formaldehyde when heated. The *dibenzoyl* derivative, $\text{OBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OBz}$, formed by the action of benzoyl chloride on methylol-lactamide in pyridine solution, crystallises in needles, m. p. 124°. *Benzoyl-lactamide*,



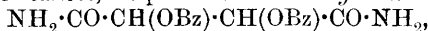
formed from lactamide by Schotten-Baumann's method, crystallises in needles, m. p. 115°.

isoValeryl-lactamide, $\text{C}_4\text{H}_9\cdot\text{CO}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$, formed by the action of *isovaleryl* chloride on lactamide in pyridine solution, is obtained as a deliquescent mass or as a colourless oil, b. p. 157—158° in a vacuum.

Di-N-methyloltartramide, $\text{C}_6\text{H}_{12}\text{O}_6\text{N}_2$, from tartramide in a 70% yield, forms colourless crystals, m. p. 166°, and evolves formaldehyde when heated. When boiled with diethylamine in alcoholic solution, it forms *tetraethylldiaminodimethyltartramide*,



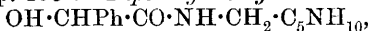
which is obtained as an oil. The *dipicrate*, $\text{C}_{26}\text{H}_{36}\text{O}_{18}\text{N}_{10}$, forms yellow needles or leaflets, m. p. 155°. *Dibenzoyltartramide*,



formed by the Schotten-Baumann method from tartramide, crystallises in needles, m. p. 240°.

Tri-N-methylolcitramide, $\text{C}_9\text{H}_{17}\text{O}_7\text{N}_3$, forms colourless prisms, m. p. 149—161° (decomp.), and evolves formaldehyde when heated.

N-Methylolmandelamide, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, forms colourless crystals, m. p. 73—81° (decomp.), and evolves formaldehyde when heated. The *dibenzoyl* derivative, $\text{OBz}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OBz}$, formed from the methylol compound in pyridine solution, crystallises in slightly red needles, m. p. 110—115°. *Diethylaminomethylmandelamide*, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NEt}_2$, prepared by boiling mandelamide, diethylamine, and formaldehyde in molecular proportions in alcoholic solution, is a basic oil; the *hydrochloride*, $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}$, forms needles, m. p. 155°. *Piperidylmethylmandelamide*,



crystallises in colourless needles, m. p. 133—134°; the *hydrochloride*, $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2\cdot\text{HCl}$, forms needles, m. p. 188°.

Catecholdiacetamide (Carter and Lawrence, Trans., 1900, '77, 1225)

was prepared by boiling catechol with chloroacetamide, sodium ethoxide, and sodium iodide in alcoholic solution; when treated with formaldehyde and potassium carbonate, it forms *di-N-methylol-catecholdiacetamide*, $C_6H_4(O\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot OH)_2$, which separates in spherical crystals, m. p. 136—137°.

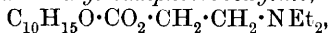
Resorcinoldiacetamide, prepared in the same manner as catecholdiacetamide, reacts with formaldehyde and potassium carbonate, forming *di-N-methylolresorcinoldiacetamide*, $C_{12}H_{16}O_6N_2$, which crystallises in microscopic needles, m. p. 192° (decomp.).

Additive Products of Halogenoacetamides and their Methylol Compounds with Hexamethylenetetramine.—The following additive compounds are described, $N_4(CH_2)_6\cdot R$.

R = Chloroacetamide: needles, m. p. 160° (decomp.); R = bromoacetamide: white needles, m. p. 170—171° (decomp.); R = iodoacetamide: leaflets, m. p. 166—167° (decomp.); R = methylolchloroacetamide: needles, m. p. 152° (decomp.); R = methylolbromoacetamide: needles, m. p. 155—158° (decomp.); R = methyloliiodoacetamide: stellate needles, m. p. 150° (decomp.).

N-Methylol Compounds of Amides of Quinoline-6-carboxylic and Camphocarboxylic Acids.—*Quinoline-6-carboxylamide*, $C_{10}H_8ON_2$, prepared by the action of concentrated sulphuric acid on the corresponding nitrile, crystallises in yellow leaflets, m. p. 174°. The *ethiodide*, $C_{12}H_{13}ON_2I$, forms red or greenish-yellow crystals, m. p. 220° (partial decomp.). *Quinoline-6-carboxylmethylolamide*, $C_9H_6N\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared by the action of formaldehyde and potassium carbonate on the amide, forms colourless crystals, m. p. 179°, and evolves formaldehyde when heated. *Quinoline-6-carboxylpiperidylmethylamide*, formed from the amide, piperidine, and formaldehyde, crystallises in needles, m. p. 98°. The *hydrochloride*, $C_{16}H_{19}ON_3\cdot HCl$, forms colourless crystals, m. p. 192°, and is neutral in aqueous solution.

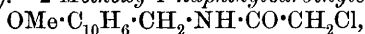
Camphocarboxylamide, $C_{10}H_{15}O\cdot CO\cdot NH_2$, prepared by the action of alcoholic ammonia on the ethyl ester at 140—150°, crystallises in colourless leaflets, m. p. 116—117°, and forms a *di-N-methylol* derivative, $C_{10}H_{15}O\cdot CO\cdot N(CH_2\cdot OH)_2$, which crystallises in colourless needles, m. p. 152—153°, and evolves formaldehyde when heated. It yields a *dibenzoyl* derivative, $C_{10}H_{15}O\cdot CO\cdot N(CH_2OBz)_2$, microscopic crystals, m. p. 95°. *Diethylaminoethyl camphocarboxylate*,



is formed by prolonged action of hydrogen chloride on diethylaminoethyl alcohol and camphocarboxylic acid in chloroform solution at the ordinary temperature; it crystallises from acetone in needles, m. p. 153° (decomp.). *Chloroethyl camphocarboxylate*, $C_{13}H_{19}O_3Cl$, formed in the same manner from the acid and chlorohydrin, is obtained as a colourless liquid, b. p. 190—191°/15 mm., having an odour of camphor. The *diethylamide*, $C_{10}H_{15}O\cdot CO\cdot NEt_2$, prepared by heating the ethyl ester with diethylamine at 110—120°, crystallises in colourless leaflets, m. p. 60—61°. The *piperide*, $C_{10}H_{15}O\cdot CO\cdot C_5NH_{10}$, crystallises in colourless leaflets, m. p. 101°.

Action of Methylolchloroacetamide on β -Naphthol.—The action of methylolchloroacetamide on β -naphthol in alcoholic hydrogen chloride solution leads to the formation of *2-hydroxy-1-naphthylcarbinylchloro-*

acetamide, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, which crystallises in colourless needles, m. p. 132° , and on hydrolysis with aqueous alcoholic hydrochloric acid yields 2-hydroxy-1-naphthabenzylamine (Betti, Abstr., 1906, i, 653). 2-Methoxy-1-naphthylcarbinylchloroacetamide,



formed from the hydroxy-compound by the action of methyl sulphate and potassium hydroxide, crystallises in needles, m. p. 170° , and on hydrolysis with boiling alcoholic hydrogen chloride yields 2-methoxy-1-naphthylcarbinylamine, $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{NH}_2$, crystallising in needles, m. p. about 100° ; the *hydrochloride*, m. p. 233° (decomp.); the *hydrobromide*, $\text{C}_{12}\text{H}_{13}\text{ON}\cdot\text{HBr}$, m. p. 242° (decomp.). The action of sodium nitrite on the hydrochloride leads to the formation of a *nitroso-derivative* of the corresponding alcohol, $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$, which separates from alcohol in crystals, m. p. 112° .

G. Y.

Carbethoxycarbimide. II. OTTO DIELS and ERNST JACOBY (*Ber.*, 1908, 41, 2393—2398. Compare Abstr., 1906, i, 237).—Attempts to prepare carbethoxycarbimide from potassium cyanate and ethyl chloro-carbonate led to the formation of only small amounts of the desired product, which is difficult to separate from the ethyl carbonate formed simultaneously (compare Wilm, Abstr., 1878, 851; Wurtz and Henninger, Abstr., 1885, 968). Carbethoxycarbimide is extremely stable at high temperatures, and could not be converted into Wurtz and Henninger's polymeride by heating. When treated with concentrated sulphuric acid, it is hydrolysed, yielding carbon dioxide and urethane, whereas with water, carbon dioxide and carbonyldiurethane, $\text{CO}(\text{NH}\cdot\text{CO}_2\text{Et})_2$, are formed. Carbethoxycarbimide reacts energetically with amines, forming ethyl allophanates, $\text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, but with anthranilic acid, it yields carbon dioxide and the *derivative*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which decomposes at 225° , and has acid properties, forming a crystalline *potassium salt*.

With alcohols, phenols, and oximes, carbethoxycarbimide reacts normally, forming iminodicarboxylic esters, $\text{CO}_2\text{R}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, whilst with acetic anhydride, acetylurethane, $\text{NHAc}\cdot\text{CO}_2\text{Et}$, is formed, diacetylurethane, $\text{NAc}_2\cdot\text{CO}_2\text{Et}$, being probably the intermediate product. With phenol, carbethoxycarbimide forms a *product*, $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}$, which is obtained as a hygroscopic oil, b. p. $136-139^\circ$. *iso*-Nitrosomethyl propyl ketone and carbethoxycarbimide form a *substance*, $\text{C}_9\text{H}_{14}\text{O}_5\text{N}_2$, crystallising in small needles, m. p. $44-46^\circ$.

The action of hydrogen cyanide on carbethoxycarbimide leads to the formation of a *product*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CO}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CN}$ or $\text{CO}_2\text{Et}\cdot\text{N} \begin{smallmatrix} \text{CO} \\ \diagup \end{smallmatrix} \text{C}(\text{NH}) \begin{smallmatrix} \text{CO} \\ \diagdown \end{smallmatrix} \text{N}\cdot\text{CO}_2\text{Et}$, which is obtained as a white, crystalline powder, m. p. 125° (decomp.), has slight acid properties, and when dissolved in alkali and treated with carbon dioxide evolves hydrogen cyanide.

G. Y.

Preparation of Soluble and Stable Additive Compounds of Thiocarbamide and Silver Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193661).—The double compounds of thio-

carbamide and silver salts hitherto known, which contain one atom of silver combined with one to three molecules of thiocarbamide, are sparingly soluble and readily decomposed. It has now been found that soluble and stable additive compounds may be produced by combining the components in the proportion of 1 atom of silver to 5 molecules of the base. The substance, $5\text{CH}_4\text{N}_3\text{S}, \text{AgCl}$, is obtained by evaporating to dryness an aqueous solution of its components and crystallising the residue from alcohol. A similar product may be obtained from silver nitrate. G. T. M.

Action of Iodine on Certain Thiocyanates. PAUL PFEIFFER and M. TILGNER (*Zeitsch. anorg. Chem.*, 1908, 58, 433—442).—The compound, $[\text{CoPy}_4(\text{SCN})_2]2\text{I}_2$, prepared by boiling an alcoholic solution of tetrapyridinecobalt thiocyanate, $\text{CoPy}_4(\text{SCN})_2$, and iodine for one to two hours, separates from the solution on cooling in black, lustrous crystals, which lose about 2 mols. of pyridine and almost all the iodine on heating to 100° . The corresponding *nickel* compound, $[\text{NiPy}_4(\text{SCN})_2]2\text{I}_2$, prepared by an analogous method, also occurs in lustrous, black crystals, which decompose slowly in the air, and behave like the cobalt compound when heated at 100° . Both compounds are additive products of iodine and the corresponding salts. An isomeric form of tetrapyridinecobalt thiocyanate, described by Sand (Abstr., 1903, i, 467) as being formed by the action of iodine on the ordinary form of the salt, does not appear to exist.

When triethylenediaminecobalt thiocyanate, $[\text{CoEn}_3](\text{SCN})_3$, is heated with iodine in alcoholic solution, the thiocyanate group is displaced by iodine, and from the solution the additive compound, $[\text{CoEn}_3]\text{I}_3 \cdot 2\text{I}_2$, separates in lustrous, deep black needles. The same compound is obtained by the action of iodine on triethylene diaminecobalt iodide, $[\text{CoEn}_3]\text{I}_3$; it is decomposed on boiling with dilute acids.

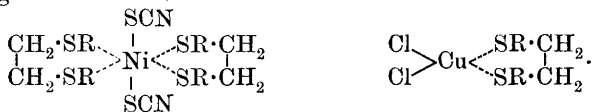
The compound, $[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\text{NH}_4\text{I}$, first obtained by Nordenskiöld (Abstr., 1893, i, 290), has been prepared, and the above formula confirmed. As the halogens appear invariably to unite as molecules, it is probable that the compound in question has the doubled formula $\{[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\text{NH}_4\}_2\text{I}_2$. G. S.

Halogen Compounds of Molybdenum and Tungsten. IV. Thiocyanates of Tervalent Molybdenum. ARTHUR ROSENHEIM and ABRAHAM GARFUNKEL (*Ber.*, 1908, 41, 2386—2392. Compare Abstr., 1905, ii, 717; 1906, i, 603; 1907, i, 688).—A discussion of the constitution of the molybdenum salts described by Sand and his co-workers (Abstr., 1906, i, 487; this vol., i, 11, 397, 513). Maas and Sand's potassium salt, $[\text{Mo}(\text{SCN})_6(\text{OH}_2)]\text{K}_3 \cdot 4\text{H}_2\text{O}$, is considered not to contain water or hydroxyl of constitution, and to be identical with Chilesotti's salt, $\text{K}_3\text{Mo}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$ (Abstr., 1906, ii, 263, 365). When treated with thallium nitrate in aqueous solution, it forms an amorphous, light yellow *precipitate*, $\text{Tl}_3\text{Mo}(\text{SCN})_6$. It is found that the molybdenum of these salts can be oxidised by ammoniacal silver nitrate and the equivalent of the molybdenum calculated from the amount of silver liberated. The results obtained are sufficiently in agreement with those required by a trivalent molybdenum atom.

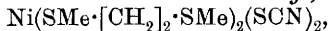
The metal-ammonium salts described by Sand and his co-workers must therefore be considered to be salts of the complex anion, $\text{Mo}(\text{SCN})_6'''$. The zinc-ammonium salt on analysis gives figures agreeing with the formula $[\text{Zn}(\text{NH}_3)_4]_3[\text{Mo}(\text{SCN})_6]_2$. Sand and Burger's pyridine salt, $6\text{C}_5\text{H}_5\text{N}, \text{H}_3\text{Mo}(\text{SCN})_6$ (Abstr., 1905, i, 923; 1906, i, 487), loses $3\text{C}_5\text{H}_5\text{N}$ over sulphuric acid in a vacuum, yielding a dark red salt, $3\text{C}_5\text{H}_5\text{N}, \text{H}_3\text{Mo}(\text{SCN})_6$; 3 mols of pyridine must therefore be pyridine of crystallisation. Sand and Burger's tetra-pyridine salt is the dark red tripyridine salt crystallised with $3\text{H}_2\text{O}$.

G. Y.

Complex Compounds of Organic Disulphides. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2222—2226. Compare Abstr., 1906, i, 814, 984; 1907, i, 17, 392, 595, 830, 896; Werner, this vol., i, 440).—A survey of the previous work shows that the most stable complex metal compounds are those where penta-atomic rings are formed; the hexa-atomic rings are less stable, and there appears to be little or no tendency for other rings to be formed. Phillips (Abstr., 1901, i, 444) has shown that organic sulphides form double compounds with the salts of heavy metals, and the author has prepared and investigated the behaviour of disulphides of the general formula $\text{R}\cdot\text{S}\cdot[\text{CH}_2]_n\cdot\text{S}\cdot\text{R}'$. The monosulphides do not give or give very unstable complexes with nickel or cupric salts; on the other hand, the disulphides, where $n=2$, give stable compounds with nickel thiocyanate and cupric chloride, where $\text{R}=\text{Me}$, *Et*, *isobutyl*, or *isoamyl*. In compounds where $n=0, 1, 3$, or 5 , no such complexes are formed. The only exception so far found is $\text{Ph}\cdot\text{S}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{Ph}$, which does not give a complex compound with copper chloride or nickel thiocyanate. On the basis of Werner's co-ordination theory, these compounds are assigned the following constitutions:

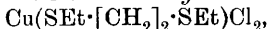


The *ethyl* compound, $\text{Ni}(\text{SEt}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{Et})_2(\text{SCN})_2$, prepared by shaking the disulphide with an aqueous solution of the nickel salt for a few minutes, forms blue needles from 80—90% alcohol, and is quickly decomposed by water into its components. It loses half of its disulphide at 100° , and does not melt at 210° . The *methyl*,



and *isoamyl*, $\text{Ni}(\text{SC}_5\text{H}_{11}\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{C}_5\text{H}_{11})_2(\text{SCN})_2$, derivatives are similar.

The copper derivatives are prepared in a similar way in the presence of hydrochloric acid. The *ethyl* derivative,



forms dark green, almost black, prismatic needles, m. p. 113° ; the *isobutyl* compound is similar, m. p. 115° . They are more easily decomposed by water than the nickel compounds.

The diselenides appear to behave in a similar manner. W. R.

Cobalt Dioximines. III. New Complex Acid. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2226—2232).—One series of monobasic

salts has been described, which contain the cation $(\text{Co}2\text{aD}_2\text{H}_2)$ (Abstr., 1906, i, 814), and another series (Abstr., 1907, i, 904) of the general type $(\text{CoaXD}_2\text{H}_2)$, which are non-ionisable. $[\text{D} = \text{R} \cdot \text{C}(\cdot\text{NO} \cdot) \cdot \text{C}(\cdot\text{NO} \cdot) \cdot \text{R}$, a = ammonia or amine, X = an acidic radicle.] In accordance with the co-ordination theory, a third series should be capable of existence in which the cobalt group would be the anion, and this type has now been obtained.

Sodium cobaltidinitrodimethylglyoximate, $\text{Na}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2]$, is obtained by digesting a 10% solution of sodium cobaltihexanitrite with excess of dimethylglyoxime until nitrous fumes cease to be evolved. After filtration, the salt crystallises out on evaporation:

$\text{Na}_3[\text{Co}(\text{NO}_2)_6] + 2\text{DH}_2 = \text{Na}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] + 2\text{NaNO}_2 + 2\text{HNO}_2$,
a reaction similar to the formation of the diamminochloride,
 $[\text{Co}2\text{NH}_3\text{D}_2\text{H}_2]\text{Cl}$,

from the luteo-salt, $[\text{Co}6\text{NH}_3]\text{Cl}_3$. The other salts described are obtained from this by double decomposition; the *ammonium* salt, $\text{NH}_4[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] \cdot \text{H}_2\text{O}$, forms brownish-yellow needles; the *ethylammonium*, $\text{NH}_3\text{Et}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] \cdot \text{H}_2\text{O}$, *diisobutylammonium*, $\text{NH}_2(\text{C}_4\text{H}_9)_2[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2]$, *potassium*, *rubidium*, and *caesium* salts have been prepared. The *acid*, $\text{H}[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] \cdot \text{H}_2\text{O}$, separates from a 5–10% solution of the sodium salt on the addition of hydrochloric acid as microscopic, hexagonal plates. It reddens litmus and decomposes carbonates, and from determinations of the molecular conductivity of the acid and its alkali salts, it is calculated that the mobility of the anion $[\text{Co}(\text{NO}_2)_2\text{D}_2\text{H}_2] = 18 \cdot 0$ at 25° , and that the free acid is ionised to the extent of 88% at $\nu = 250$. The molecular conductivity of its aqueous solutions gradually decreases (thus $\nu = 250$, $\mu = 338 \cdot 3$, after forty hours $320 \cdot 0$), due to the liberation of nitrous acid. It is fairly stable in the solid state in the air, but in a closed vessel it quickly decomposes, due perhaps to catalytic action of the nitrous acid. It rapidly loses water and nitrous acid at $100\text{--}110^\circ$. When an aqueous solution is gently warmed, a dark brown, crystalline precipitate of *cobaltinitroaquodimethylglyoximine*, $[\text{CoNO}_2, \text{H}_2\text{O}, \text{D}_2\text{H}_2]$, is produced. It is a non-electrolyte ($\mu = 3 \cdot 0$, $\nu = 1000$), and the nitro group is firmly attached to the molecule.

Stable compounds containing the thiocyanate radicle instead of the nitro-group and less stable derivatives containing chlorine and iodine are under examination. W. R.

Crystalline Compound of Magnesium Methiodide and Amyl Ether. TH. ZEREWITNOFF (*Ber.*, 1908, 41, 2244–2245).—The compounds of ether and magnesium alkyl iodides hitherto obtained are not crystallisable (Grignard, Abstr., 1901, i, 679; Blaise, 1901, i, 317; Baeyer and Villiger, 1902, i, 355; Tschelinzeff, 1906, i, 241), but when paraffin is added to the product obtained after interaction of 78–80 c.c. of amyl ether, 6 grams of magnesium, and 35.5 grams of methyl iodide, and the mixture left for some days, large, transparent crystals of the compound, $(\text{C}_5\text{H}_{11})_2\text{O} < \overset{\text{I}}{\text{MgMe}}$, separate. They are unstable in the air.

W. R.

Synthesis of α -Hydroxymercuri-fatty Acids. I. Methyl Mercuridimalonate and its Product of Hydrolysis, Hydroxymercuriacetic Anhydride. WALTER SCHRAUTH and WALTER SCHOELLER (*Ber.*, 1908, 41, 2087—2094. Compare Fischer, this vol., i, 200).—The physiological importance of the α -amino-acids led to the idea of substituting different basic radicles for the amino-group and so forming other α -basic acids, which might be expected to have interesting physiological actions. The present paper is a study of the introduction of the hydroxymercuri-group, $\cdot\text{Hg}\cdot\text{OH}$, into the α -position in fatty acids.

Methyl mercuridimalonate, $\text{Hg}[\text{CH}(\text{CO}_2\text{Me})_2]_2$, is formed when methyl malonate suspended in water is gently heated and shaken with mercuric oxide; it crystallises from chloroform-ether in colourless plates, m. p. 127° (corr.), is readily soluble in organic solvents, is decomposed by halogens, forming the mercuric haloids, and yields mercuric sulphide when treated with ammonium sulphide. When shaken with *N*-sodium hydroxide, the mercuri-ester yields *hydroxymercuriacetic anhydride*, $\text{Hg}\langle\text{CH}_2\text{O}\rangle\text{CO}$, which is formed also by the action of mercuric oxide on sodium malonate; it is obtained as a hard mass, which becomes brown at 200° , decomp. 250° (detonates). The *sodium* salt forms needles, is alkaline in aqueous solution, does not coagulate albumin, and does not yield mercury in contact with copper, but forms mercuric sulphide, as does also the anhydride, when treated with ammonium sulphide, and on electrolysis in alkaline solution deposits sodium amalgam at the cathode; this reaction is not reversible, as a mercury anode is not dissolved, and hence the mercury in sodium mercuriacetate is not ionised. The *copper* salt, $\text{Hg}_2\text{C}_4\text{H}_6\text{O}_6\text{Cu}$, was analysed; the *calcium*, *silver*, *lead*, and *mercuric* salts are white powders. The sodium and calcium salts act as antiseptics towards yeast; at the same time, the poisonous action of the mercury is much diminished. With hydrochloric acid, the anhydride forms mercuric chloride, but it is not attacked by cold dilute sulphuric acid, and when dissolved in nitric acid (D 1.2) and further diluted with water or alcohol, yields a white *precipitate*, which is probably the nitrate of mercuriacetic acid. Treatment of the anhydride with 10% ammonia leads to the formation of a yellowish-white, granular precipitate of varying and complicated composition.

When treated with anhydrous formic acid, the anhydride is converted into the *formate* of dihydroxymercuriacetylhydroxymercuriacetic acid, $\text{CHO}\cdot\text{O}\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is obtained as a colourless, crystalline substance, decomposing on exposure to light.

Attempts to isolate mercuridimalonic acid or mercuridiacetic acid as intermediate products in the hydrolysis of methyl mercuridimalonate were unsuccessful. G. Y.

Ethylcyclobutane. NICOLAI ZELINSKY and J. GUTT (*Ber.*, 1908, 41, 2431—2434).—The scanty knowledge of *cyclobutane* hydrocarbons has induced the authors to commence an investigation of such compounds. The reaction between magnesium methyl iodide and

cyclobutanecarboxylamide leads to the formation of methyl *cyclobutyl ketone*, b. p. 136—136·5°/750 mm., $n_D^{19.3}$ 1·4322, D_4^{10} 0·9112, D_4^{20} 0·9020 (compare Perkin, *Trans.*, 1892, **61**, 48), the *semicarbazone* of which has m. p. 148—149°. By reduction with sodium in moist ether at 0°, the ketone yields methyl*cyclobutylcarbinol*, b. p. 144°/752 mm., $n_D^{18.8}$ 1·14451, D_4^{10} 0·9075, of which the *phenylurethane* has m. p. 87·5—88°. When treated with hydriodic acid, D 1·96, the carbinol yielded an oily iodide which, without being isolated, was reduced by glacial acetic acid and zinc dust, forming a saturated *hydrocarbon*, C_6H_{12} , b.p. 72·2—72·5° (corr.), $n_D^{19.5}$ 1·4080, D_4^{20} 0·7450; this is oxidised by nitric acid to succinic acid. The hydrocarbon is therefore ethyl*cyclobutane*.

The authors are investigating methyl*cyclopentane*, which closely resembles the preceding isomeric hydrocarbon, and is oxidised by nitric acid to succinic acid and not to glutaric acid, as would be expected.

C. S.

Occurrence of Nononaphthene in Coal Tar. FELIX B. AHRENS and LEO VON MOŹDŹEŃSKI (*Zeitsch. angew. Chem.*, 1908, **21**, 1411—1414).—Xylene obtained from coal tar was found on nitration to yield an oil (b. p. 137—139°, D^{15} 0·7662) which had escaped nitration and proved on analysis to be *nononaphthene*, C_9H_{18} . Ten c.c. of this oil heated for eight hours at 125—130° with 50 c.c. of nitric acid, D 1·075, yielded on fractionation an oil, b. p. 125—135°/40 mm., which by means of alcoholic sodium hydroxide was shown to consist of a mixture of tertiary and secondary nitro-derivatives. The *secondary* nitro-derivative, $C_9H_{17} \cdot NO_2$, is a colourless oil which turns yellow; it has a characteristic pungent odour, and has b. p. 115—120°/15 mm., 220—224°/760 (decomp.), D^{20} 0·9778, and n_D^{20} 1·451; on treatment with bromine it yields an oil containing 31·74% of bromine. The *tertiary* nitro-derivative, $C_9H_{17} \cdot NO_2$, b. p. 102—105°/12 mm., 217—225°/760 (decomp.), D^{20} 0·9771, n_D^{20} 1·449, is a colourless oil which also turns yellow. The *tertiary* nitro-derivative when reduced by means of hydrochloric acid and tin foil yielded a mixture of amines which were separated by conversion into their *picrates*, one of which, *A*, was soluble in benzene, the other, *B*, being insoluble in benzene, but soluble in water. The *picrate A* crystallises in rhombic leaflets, m. p. 176—177°; when decomposed with potassium hydroxide and distilled with steam it yields an *amine*, $C_9H_{17} \cdot NH_2$, b. p. 175—176°/760 mm., D^{15} 0·8205, n_D^{21} 1·447; the *hydrochloride*, $C_9H_{17} \cdot NH_2 \cdot HCl$, m. p. 155° (approx.); the *oxalate*, $C_{20}H_{40}O_4N_2$, white scales, darkens at 270° and decomposes without melting; the *platini-chloride* and *aurichloride* are oils which gradually solidify, but were not analysed. The *picrate B*, which separates from water in long crystals, m. p. 187—188°, yields an *amine*, $C_9H_{17} \cdot NH_2$, b. p. 172—173°/773 mm., D^{20} 0·8500, n_D 1·448, which yields a *hydrochloride*, glistening crystals from alcohol, m. p. 184—185°, an *oxalate*, $C_{20}H_{40}O_4N_2$, white, amorphous mass, which decomposes without melting at 265°, a *platini chloride*, $(C_9H_{19}N)_2 \cdot H_2PtCl_6$, orange-yellow, envelope-shaped crystals, decomp. 290°, and an *aurichloride*, which crystallises like the platini-chloride, m. p. 193—194° (decomp.).

The *secondary* amine, obtained by the reduction of the secondary nitro-derivative, has b. p. 175—177°/748 mm., D^{20}_D 0.8314, and n^{20}_D 1.445. Its *picrate* crystallises in four-sided plates, m. p. 173—174°, its *hydrochloride* is a liquid; its *platinichloride* forms glistening, yellow plates from water, decomp. 290°; the *aurichloride* is an amorphous, sticky substance; the *oxalate* forms white, glistening scales, decomp. 265°.

On oxidation with nitric acid, D 1.075, nononaphthene is converted into succinic acid; oxidation with nitric acid, D 1.5, converts it into butyric acid.

When treated with moist chlorine at 30° in diffused daylight, nononaphthene yields a monochloro-derivative, which is a colourless liquid with a pungent odour, b. p. 103—104°/40 mm., D^{20} 0.9229.

Bromine in the presence of aluminium bromide or finely-divided iron converts nononaphthene into tribromo- ψ -cumene, m. p. 234°. P. H.

Isomeric Dihydrobenzenes and Optically Active Dihydro-toluene. NICOLAI D. ZELINSKY and A. GORSKY (*Ber.*, 1908, 41, 2479—2487).—An investigation on $\Delta^{1:3}$ - and $\Delta^{1:4}$ -cyclohexadienes and on 1-methyl- $\Delta^{2:4}$ -cyclohexadiene, carried out chiefly with the object of ascertaining the effect of ethylene linkings on the optical properties of compounds.

The conclusions of Markownikoff (*Abstr.*, 1899, i, 22) and Harries and Antoni (*Abstr.*, 1903, i, 613) are shown to be incorrect. The tetrabromide, m. p. 188°, is derived from $\Delta^{1:4}$ -cyclohexadiene, whilst the tetrabromide obtained from $\Delta^{1:3}$ -cyclohexadiene has m. p. 140—141° (compare Crossley, *Trans.*, 1903, 83, 505).

Although $\Delta^{1:3}$ -cyclohexadiene and 1-methyl- $\Delta^{2:4}$ -cyclohexadiene contain contiguous double linkings, they do not follow Brühl's rule (*Trans.*, 1907, 91, 115). It is, however, not impossible that these compounds may have a dicyclic structure, since they do not readily form tetrabromo-derivatives, and are not readily oxidised.

$\Delta^{1:4}$ -cycloHexadiene has b. p. 85.5° (corr.), D^{20}_D 0.8471, D^{20}_D 0.8519, n^{20}_D 1.4729, mol. ref. 26.50 (compare von Baeyer, *Abstr.*, 1892, 1074; Brühl, *Abstr.*, 1894, i, 366). It readily forms a tetrabromide, m. p. 188° (corr.); the *dibromide*, $C_6H_8Br_2$, has m. p. 95°, b. p. about 105°/15 mm.

$\Delta^{1:3}$ -cycloHexadiene has b. p. 80.5° (corr.), D^{20}_D 0.8423, D^{20}_D 0.8376, n^{20}_D 1.4700, mol. ref. 26.66. It only combines readily with 1 mol. of bromine, forming a dibromide, m. p. 102—104, b. p. about 105°/14 mm. (compare Crossley, *loc. cit.*). A small quantity of the *tetrabromide*, $C_6H_8Br_4$, is obtained by acting on the hydrocarbon with bromine in light petroleum; it crystallises in prisms, m. p. 140—141° (corr.). The tetrabromide is not formed by acting on a solution of the dibromide with bromine in chloroform. $\Delta^{1:3}$ -cycloHexadiene when shaken with nitric acid (1.4) becomes violet, whilst $\Delta^{1:4}$ -cyclohexadiene when similarly treated undergoes violent oxidation.

1-Methyl- $\Delta^{2:4}$ -cyclohexadiene, C_7H_{10} , is obtained by the action of quinoline on the dibromide of 1-methyl- Δ^3 -cyclohexene; it is a colourless liquid, b. p. 105.5—106° (corr.), D^{20}_D 0.8324, D^{20}_D 0.8274, n^{20}_D 1.4680, $[\alpha]_D$ 36.42. It is also obtained in small quantities by the action of

an alcoholic solution of potassium hydroxide on the dibromide, when it has α_D 57.48° (100 mm. tube). The principal product is, however, *ethoxymethylcyclohexene*, $C_9H_{16}O$; it is a colourless liquid, b. p. 169°/750 mm., D_4^{20} 0.8762, D_4^{22} 0.8746, n_D^{22} 1.4480, mol. ref. 42.72, α_D 18.56° (100 mm. tube).

1-Methyl- $\Delta^{2:4}$ -cyclohexadiene becomes violet-blue when shaken with nitric acid (1.4); it combines with 1 mol. of bromine, yielding a *dibromide*, $C_7H_{12}Br_2$, b. p. 107—108°/15 mm., α_D 33.2° (100 mm. tube); a tetrabromide could not be obtained. W. H. G.

Lecture Experiments on the Preparation of Hydrocarbons. JAMES F. SPENCER (*Ber.*, 1908, 41, 2302—2303).—The author gives instructions for the preparation of benzene and naphthalene by the action of magnesium on the corresponding halogen derivative as already described (Spencer and Stokes, *Trans.*, 1908, 93, 68). Pentane or isopentane is prepared by heating amyl or isoamyl iodide respectively with magnesium and adding water to the product. J. C. C.

Derivatives of 2-Iodo-4-nitrotoluene with Polyvalent Iodine. CONRAD WILLGERODT and B. R. KOK (*Ber.*, 1908, 41, 2077—2083).—4-Nitro-*o*-toluidine hydrochloride, $C_7H_8O_2N_2 \cdot HCl$, forms white needles, blackens at 200°, m. p. 230° (decomp.).

2-Iodo-4-nitrotoluene crystallises in rhombic plates, m. p. 58° (51°: Reverdin, *Abstr.*, 1898, i, 180), and when treated with chlorine in chloroform solution is converted into the *iodochloride*, $NO_2 \cdot C_6H_3Me \cdot ICl_2$, which crystallises in sulphur-yellow prisms, decomp. 83°. The action of sodium carbonate and sodium hydroxide on this leads to the formation of 2-iodoso-4-nitrotoluene, $NO_2 \cdot C_6H_3Me \cdot IO$, which is obtained as an insoluble, yellowish-white powder, and explodes at 180—181°, having first changed into a mixture of the iodoxy- and iodo-compounds. 2-Iodoxy-4-nitrotoluene, $NO_2 \cdot C_6H_3Me \cdot IO_2$, formed by the action of hypochlorous acid on the iodoso-compound, is obtained as a white, flocculent precipitate, which explodes at 204°.

The following iodonium salts, $R = (NO_2 \cdot C_6H_3Me)_2I$, were prepared from a mixture of the iodoso- and iodoxy-compounds.

RCl : white needles, m. p. about 140°; RBr : decomp. 145°; RI : yellow needles, decomp. 113°; RNO_3 : white needles, m. p. 147°; $RHSO_4$: white needles, m. p. 165°; $R_2Cr_2O_7$: orange-yellow, amorphous precipitate, explodes 128°; R_2PtCl_6 : yellow leaflets, decomp. 180°.

Phenyl-4-nitro-2-tolylodonium hydroxide, $NO_2 \cdot C_6H_3Me \cdot IPh \cdot OH$, prepared by the action of silver oxide and water on a mixture of 2-iodoxy-4-nitrotoluene and iodosobenzene, is a strongly alkaline base. The following salts, $R' = NO_2 \cdot C_6H_3Me \cdot IPh$, are described.

$R'Cl$: white needles, m. p. 183°; $R'Br$: yellow, flocculent precipitate, m. p. 165°; $R'I$: yellow needles, decomp. 131°; $R'I_3$: dark brown prisms, m. p. 50°; $R'NO_3$: white prisms, m. p. 167° (decomp.); $R'HHSO_4$: white prisms, m. p. 142°; $R'_2Cr_2O_7$: yellow powder, m. p. 137—138° (explodes); $(R'Cl)_2HgCl_2$: white needles, m. p. 157° (decomp.); R'_2PtCl_6 : yellowish-red prisms, m. p. 175° (decomp.).

4-Nitro-2-tolyl-*o*-tolylodonium hydroxide is prepared in the usual

manner from a mixture of 2-iodoxy-4-nitrotoluene and 2-iodosotoluene. The following salts, $R = \text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{I}(\text{C}_7\text{H}_7)$, are described.

RCl : white needles, m. p. 170° ; RBr : needles, m. p. 151° ; RI : decomp. 116° ; $\text{R}_2\text{Cr}_2\text{O}_7$: explodes 136° ; R_2PtCl_6 : golden leaflets, m. p. 158° ; $(\text{RCl})_2\text{HgCl}_2$: needles, m. p. 168° . G. Y.

New Catalytic Effect of Aluminium Chloride. EYVIND BÆDTKER (*Bull. Soc. chim.*, 1908, [iv], 3, 726—729.—It is shown that when nitro-compounds are employed in the Friedel-Crafts reaction, the nitro-group is eliminated and that through its agency the condensation product formed is in part oxidised. In certain cases it is possible to nitrate compounds by using nitrates in the Friedel-Crafts reaction.

Trichloronitromethane reacts with benzene in presence of aluminium chloride to form triphenylmethane and some triphenylcarbinol, the latter being formed by oxidation of the hydrocarbon by the eliminated NO_2 group.

Ethyl nitrate reacts with benzene in presence of aluminium chloride to form nitrobenzene, the other possible products of the reaction, namely, ethyl chloride, ethylbenzene and nitroethylbenzene, being formed, if at all, only in minute quantity. With toluene the principal product is the *o*-nitro-compound, with small quantities of the para-isomeride. With benzaldehyde a vigorous reaction, apparently involving the $-\text{CHO}$ group, ensues, and *o*-nitrobenzaldehyde is not obtained. In these nitration reactions the hydrocarbon should be used in excess, and as water is always formed, considerable quantities of aluminium chloride are required. With benzene and amyl nitrite under similar conditions, some nitrosobenzene is formed, but the quantity is too small to be isolated. T. A. H.

Naphthalenesulphonates of Cerium. HUGO ERDMANN and THEODOR NIESZYTKA (*Annalen*, 1908, 361, 166—189. Compare Abstr., 1893, i, 651).—The cerium salts described were prepared by the action of the naphthalenesulphonic acids on cerium carbonate in aqueous solution and evaporation to crystallisation. The solubilities of the salts in water and methyl and ethyl alcohol are tabulated; the solubility increases with the number of sulphonic groups, but is small if a β -substituting group is present. The solubilities of cerium hydrogen naphthalene- β -sulphonate and the basic 1:5-disulphonate could not be determined, as the salts are unstable. The small solubility of cerium anthraquinonesulphonate is remarkable; the complete insolubility of cerium 8-hydroxynaphthalene-1-sulphonate and its characteristic colour allow of its utilisation in analysis.

Cerium naphthalene- α -sulphonate, $(\text{C}_{10}\text{H}_7\text{O}_3\text{S})_3\text{Ce}$, crystallises in nacreous leaflets, has an acid reaction, and forms precipitates with ammonia, potassium hydroxide, potassium hydroxide and hydrogen peroxide, ammonium oxalate, and barium hydroxide or chloride in aqueous solution, or with benzidine in acetic acid solution, and a bluish-red precipitate with ammonium 1:8-hydroxynaphthalene-sulphonate; these precipitations in aqueous solution are retarded by the presence of hydroxy-acids of the fatty series.

Cerium naphthalene-β-sulphonate, $(C_{10}H_7O_3S)_3Ce \cdot H_2O$, forms large, white leaflets, and gives similar precipitates to those of the α-salt.

Cerium naphthalene-1 : 5-disulphonate, $[C_{10}H_6(SO_3)_2]_3Ce_2 \cdot \frac{1}{2}H_2O$, loses $\frac{1}{2}H_2O$ at 180° , and can be recrystallised without decomposing.

Cerium naphthalene-2 : 7-disulphonate, $[C_{10}H_6(SO_3)_2]_3Ce_2 \cdot 3H_2O$, loses $3H_2O$ on prolonged exposure to air, more quickly in a desiccator, has a strong acid reaction, and with benzidine in hot acetic acid solution forms the benzidine salt.

Cerium naphthalene-2 : 6-disulphonate, $[C_{10}H_6(SO_3)_2]_3Ce_2 \cdot H_2O$, loses $\frac{1}{2}H_2O$ at 135° , but H_2O at the ordinary temperature.

Cerium naphthalene-1 : 6-disulphonate, $[C_{10}H_6(SO_3)_2]_3Ce_2 \cdot 4H_2O$, loses $4H_2O$ in a desiccator.

Cerium naphthalene-1 : 3 : 5-trisulphonate, $C_{10}H_5(SO_3)_3Ce \cdot \frac{3}{4}H_2O$, crystallises in white scales, loses its water of crystallisation in a desiccator, has an acid reaction, is decomposed slowly by hydrogen peroxide, and forms a precipitate with benzidine in aqueous hydrochloric acid solution.

Cerium naphthalene-1 : 3 : 6-trisulphonate ($\frac{3}{4}H_2O$) forms yellow scales and loses water slowly in a desiccator.

Cerium naphthalene-1 : 3 : 7-trisulphonate ($1\frac{1}{4}H_2O$) loses its water of crystallisation slowly on exposure to air.

Cerium 1-naphthol-8-sulphonate, $(C_{10}H_7SO_4)_3Ce \cdot 3H_2O$, formed from the ammonium sulphonate, forms a bluish-brown, amorphous precipitate, loses $3H_2O$ at 110° , has an acid reaction, is unstable, and dissolves in acids, forming bluish-red solutions. The action of the free naphtholsulphonic acid on cerium carbonate leads to the formation of a blue basic salt, $(C_{10}H_6SO_4)_3Ce_2$, which also dissolves in acids, forming bluish-red solutions.

Cerium chromotropate, $[C_{10}H_4(OH)_2(SO_3)_2]_3Ce_2 \cdot 4H_2O$, formed from 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, is salted out of its solution; it forms a greyish-brown, microcrystalline mass, loses $4H_2O$ at 195° , has an acid reaction, and in concentrated solution commences only after some weeks to change into a basic salt, the edges of the solution becoming blue.

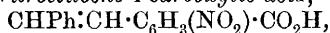
Cerium anthraquinonesulphonate, $(C_{14}H_7O_2 \cdot SO_3)_3Ce \cdot 3H_2O$, forms green leaflets, loses $3H_2O$ at $187-195^\circ$, is very stable, has a strong acid reaction, and gives insoluble precipitates with benzidine, aniline, and toluidine. G. Y.

[Naphthalenesulphonates and Malonates of the] Rare Earths. HUGO ERDMANN and FRITZ WIRTH (*Annalen*, 1908, 361, 190—217).—See this vol., ii, 694.

The Stilbene Series. FRITZ ULLMANN and MEINRAD GSCHWIND (*Ber.*, 1908, 41, 2291—2297).—It is well known that a halogen atom in the benzene nucleus can readily be replaced by other substituents provided it is accompanied by a nitro-group in the ortho- or para-position; moreover, when the number of nitro-groups in the molecule is increased, the reactivity increases, and this is not diminished when, in the dinitro-derivatives, one nitro-group is replaced by a sulphonic, carboxylic, or aldehydic group. The authors have accordingly examined

the behaviour of negatively-substituted toluene derivatives and find that, when one of the nitro-groups in 2:4-dinitrotoluene is replaced by a carboxylic, sulphonic, or cyanogen group, the resulting compound condenses with benzaldehyde in presence of piperidine with the production of the corresponding stilbene derivatives just as 2:4-dinitrotoluene itself, under similar conditions, yields dinitrostilbene (Thiele and Escales, Abstr., 1901, i, 689). Further, 2:4:6-trinitrotoluene condenses with benzaldehyde more readily and at a lower temperature than do the disubstituted derivatives.

2-Nitrostilbene-4-sulphonamide, $\text{CHPh}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{SO}_2\cdot\text{NH}_2$, prepared by condensing *o*-nitrotoluene-*p*-sulphonamide (Reverdin and Crépieux, Abstr., 1901, i, 685), forms yellow needles, m. p. 184° . It is readily reduced by stannous chloride and hydrochloric acid to *2-amino-stilbene-4-sulphonamide*, which crystallises from alcohol in colourless leaflets, m. p. $206\text{--}207^\circ$. Its solutions in glacial acetic acid or alcohol exhibit a blue fluorescence. The *acetyl* derivative forms stellate aggregates of white needles, m. p. 205° . 4-Nitrotoluene-2-sulphonamide does not condense well with benzaldehyde, but 4-nitrotoluene-2-sulphonanilide, m. p. 148° , prepared by condensing 4-nitrotoluene-2-sulphonyl chloride with aniline, readily condenses, forming 4-nitrostilbene-2-sulphonanilide, which crystallises from glacial acetic acid in yellow needles, m. p. 206° . Similarly, *o*-nitro-*p*-toluonitrile furnishes 2-nitro-4-cyanostilbene, $\text{CHPh}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CN}$, yellow needles, m. p. 170° , the *dibromo*-derivative, $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$, of which forms colourless needles, m. p. $155\text{--}160^\circ$ (decomp.). 2-Amino-4-cyanostilbene forms pale yellow crystals, m. p. 123° ; its solutions in benzene, acetic acid, and ether show a blue fluorescence, whilst that in alcohol is bluish-green. The *acetyl* derivative, colourless needles, has m. p. 220° . 2-Nitrostilbene-4-carboxylic acid,



prepared by hydrolysis of the nitrile, crystallises from glacial acetic acid in small, yellow needles, m. p. 236° . It is also formed when ethyl 2-nitrotoluene-4-carboxylate is condensed with benzaldehyde, the ester being hydrolysed in the reaction.

2-Aminostilbene-4-carboxylic acid, prepared by reducing the nitro-compound, is a pale yellow, crystalline powder, m. p. $197\text{--}198^\circ$. Its solutions show a bluish-green fluorescence.

4-Nitro-2-cyanostilbene, prepared from *p*-nitro-*o*-toluonitrile, separates from glacial acetic acid in small, yellow needles, m. p. 142° . 2:4:6-Trinitrostilbene, obtained from 2:4:6-trinitrotoluene, crystallises from glacial acetic acid in yellow, glistening needles, m. p. 156° . 2:4:6:4-Tetranitrostilbene, prepared by condensing 2:4:6-trinitrotoluene and *p*-nitrobenzaldehyde, forms yellow, glistening needles, m. p. 196° . J. C. C.

Colourless and Coloured Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, 41, 2471—2479. Compare this vol., i, 150; Gomberg, Abstr., 1907, i, 504; Tschitschibabin, Abstr., 1907, i, 1022).—A freshly-prepared solution of pure triphenylmethyl in benzene remains colourless for a few seconds and then gradually becomes orange-yellow. The colour of the solution disappears, however, when the latter is

shaken with air, reappearing again after a time, and again disappearing when agitated with air, until finally the solution remains permanently colourless. The conclusion is therefore drawn that the yellow solutions of triphenylmethyl contain both a coloured and a colourless form of triphenylmethyl. The two forms are convertible one into the other, and are present in solutions and in the solid substance in a definite state of equilibrium, which depends both on the nature of the solvent and on the temperature.

The disappearance and reappearance of the colour of solutions of triphenylmethyl is due to the fact that the coloured variety oxidises far more rapidly than the colourless form. On shaking an ethereal solution of triphenylmethyl with air, the yellow form is oxidised, yielding the peroxide, which being insoluble in ether may be filtered off; the colourless filtrate quickly becomes yellow, and on shaking yields a further quantity of peroxide. It is found from the amount of peroxide formed that an ethereal solution of triphenylmethyl contains roughly ten times as much of the colourless form as of the coloured form. The latter substance must consequently have an exceedingly intense colour.

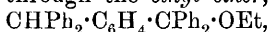
The yellow form also absorbs iodine far more rapidly than the colourless form. When a quantity of iodine, slightly more than sufficient to combine with the triphenylmethyl present in the yellow form, is added to a solution of triphenylmethyl in chloroform, a reddish-brown solution is obtained. The colour of the solution slowly changes, and when a sufficient quantity of the yellow variety has been formed, the solution has the pure yellow colour of triphenylmethyl iodide.

The state of equilibrium, triphenylmethyl (colourless) \rightleftharpoons triphenylmethyl (coloured), is displaced towards the left by lowering the temperature. A solution of triphenylmethyl in chloroform, which is orange-yellow at 15°, becomes quite colourless at -63°; the change in the colour intensity of a solution of triphenylmethyl iodide when similarly treated is barely perceptible. W. H. G.

p-Benzhydryltetraphenylmethane. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1908, 41, 2421—2428).—In connexion with the constitution of triphenylmethyl, hexaphenylethane, $\text{CPh}_3 \cdot \text{CPh}_3$, is a substance of great importance. Both Ullmann and Borsum (*Abstr.*, 1902, i, 755) and Gomberg (*Abstr.*, 1903, i, 244) thought they had obtained this hydrocarbon, the former by the action of zinc on triphenylchloromethane, and the latter by the polymerisation of triphenylmethyl. The behaviour of the hydrocarbon with bromine led the author to the view that it was *p*-benzhydryltetraphenylmethane, $\text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2$ (*Abstr.*, 1905, i, 125). He has now succeeded in definitely establishing this constitution. The stages of the proof are the following: Benzoyl chloride and triphenylmethane in the presence of aluminium chloride yield the well-known *p*-benzoyltriphenylmethane, the reaction of which with magnesium phenyl bromide leads to the formation of *p*-benzhydryltriphenylcarbinol, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OH}$; the condensation of the carbinol or its chloride and aniline hydrochloride in boiling glacial acetic acid results in the production of amino-*p*-benzhydryltetra-

phenylmethane hydrochloride, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, and from the sulphate by the replacement of the amino-group by hydrogen by the diazo-reaction, Ullmann and Borsum's "hexaphenylethane" is obtained, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_3$.

A second modification of *p*-benzoyltriphenylmethane, m. p. 150° , is obtained by crystallisation from glacial acetic acid. *p*-Benzhydryltriphenylcarbinol separates from alcohol in colourless crystals, m. p. 135 — 137° , but the crystals from other solvents obstinately retain benzene of crystallisation. The purification of the crude carbinol is therefore best effected through the *ethyl ether*,



m. p. 186° , which is obtained in nearly theoretical yield by adding a drop of acetyl chloride to the alcoholic solution of the carbinol. The *chloride* has m. p. 142° , becoming orange-coloured; the *bromide* melts at 140° to an orange liquid. *Amino-p*-benzhydryltetraphenylmethane, m. p. 195 — 198° (decomp.), is best purified through the *hydrogen sulphate*, m. p. 194 — 196° (decomp.). The *diazo-sulphate*, obtained by means of amyl nitrite in glacial acetic acid, decomposes at 120° , and by treatment with boiling alcohol yields *p*-benzhydryltetraphenylmethane and the *ethyl ether* of the phenol derived from the diazo-salt, m. p. 184° . C. S.

Preparation of Ethyl Phenylglycinate. GEORGES IMBERT UND CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 194884).—Ethyl phenylglycinate, $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, may be readily prepared by heating to boiling a mixture of ethyl chloroacetate, aniline, water, and calcium carbonate; carbon dioxide is evolved, and the fused product is separated from the calcium chloride solution. G. T. M.

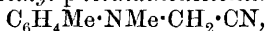
Action of Cyanogen Bromide and of Bromine on Aromatic Derivatives of Aminoacetonitrile. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2100—2113).—In order to ascertain if the action of cyanogen bromide on arylaminoacetonitriles is similar to that observed in the case of the alkylamino-derivatives (Abstr., 1907, i, 899), the author has selected the cases of methyl- and ethyl-anilinoacetonitrile, and finds that the interaction is quite different, the chief product in each case being the corresponding *p*-bromophenyl derivative. As by-products were obtained compounds of the formulæ $\text{C}_{18}\text{H}_{18}\text{N}_4$ and $\text{C}_{20}\text{H}_{22}\text{N}_4$ respectively, the constitution of which has not yet been elucidated.

p-Bromophenylmethylaminoacetonitrile, $\text{C}_6\text{H}_4\text{Br} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CN}$, prepared by heating methylanilinoacetonitrile and cyanogen bromide in a closed vessel for five hours on the water-bath, has b. p. 205 — $206^\circ/22$ mm., m. p. 40° . On warming with 25% sulphuric acid, *p*-bromodimethylaniline is formed. The compound, $\text{C}_{18}\text{H}_{18}\text{N}_4$, crystallises from alcohol in colourless, glistening leaflets, m. p. 103° . It is hydrolysed by hydrochloric or sulphuric acid (25—38%) to an amino-acid, obtained as a dark viscous oil, and, on one occasion only, a substance was isolated which was probably trimethyldiaminodiphenylmethane.

s-ω-Dicyanotetramethylbenzidine, $\text{C}_{12}\text{H}_8(\text{NMe} \cdot \text{CH}_2 \cdot \text{CN})_2$, prepared from *s*-dimethylbenzidine and iodoacetonitrile, forms glistening,

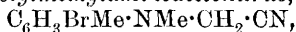
brown leaflets, m. p. 203°. *ω*-Dicyanodiphenyldimethylethylene-diamine, $C_2H_4(NPh \cdot CH_2 \cdot CN)_2$, obtained from diphenylethylene-diamine and bromo- or iodo-acetonitrile, crystallises from alcohol in white leaflets, m. p. 131°. Neither this nor the foregoing substance is identical with the compound, m. p. 103°.

p-Bromophenylethylaminoacetonitrile, $C_6H_4Br \cdot NEt \cdot CH_2 \cdot CN$, prepared from ethylanilinoacetonitrile and cyanogen bromide, has b. p. 195°/8 mm. and m. p. 56°. On hydrolysis it yields *p*-bromomethylethylaniline, of which the *platinichloride* is a red oil, and the *methiodide* a hygroscopic solid. *Methyl-p-toluidinoacetonitrile*,



prepared from methyl-*p*-toluidine by Knoevenagel's method (Abstr., 1904, i, 989), has b. p. 156—157°/9 mm. and m. p. 57°; it is not acted on by cyanogen bromide. (A convenient method of preparing methyl-*p*-toluidine consists in demethylating dimethyltoluidine with cyanogen bromide. *p*-Tolylmethylcyanamide, $C_6H_4Me \cdot NMe \cdot CN$, b. p. 147°/9 mm., m. p. 45°, is formed together with *p*-tolyltrimethylammonium bromide, which on dry distillation gives methyl bromide and dimethyltoluidine, and the cyanamide is converted into methyl-*p*-toluidine by boiling with 30% sulphuric acid for one hour. *Benzoyl-methyl-p-toluidine*, $C_6H_4Me \cdot NMeBz$, has b. p. 198—199°/9 mm. and m. p. 53°.) *α*-Methylanilinopropionitrile, prepared by Sachs and Kraft's method (Abstr., 1903, i, 335), with the difference that the components are heated with alcohol for six instead of two hours, is also unacted on by cyanogen bromide.

When methylanilinoacetonitrile is treated with bromine in chloroform solution, a white substance separates, which is probably *p*-bromophenylmethylaminoacetonitrile hydrobromide, and this, on addition of water, gives the nitrile. Similarly, methyl-*p*-toluidinoacetonitrile furnishes *m*-bromo-*p*-tolylmethylaminoacetonitrile,



strongly refracting crystals, b. p. 161—165°/10 mm., m. p. 47°, which on hydrolysis yields *m*-bromodimethyl-*p*-toluidine. The latter is most conveniently prepared by brominating dimethyltoluidine, and has b. p. 243—244°/752 mm. (Pesci, *Gazzetta*, 1898, 28, i, 101, gives b. p. 237—238°/744 mm.).

The *platinichloride* forms reddish-yellow crystals, m. p. 212° (decomp.); the *picrate* has m. p. 115°. *Dimethyl-p-toluidine picrate* has m. p. 130°. J. C. C.

Preparation of Aromatic *o*-Nitroamino-derivatives. FRITZ ULLMANN (D.R.-P. 194951).—By heating the arylsulphonyl derivatives of *o*-nitrophenol and its analogues with a primary or secondary amine, the group $O \cdot SO_2R$ is replaced by an amino-residue and a secondary or tertiary amine is produced.

o-Nitrodiphenylamine is obtained by heating a mixture of aniline, *o*-nitrophenyl *p*-toluenesulphonate, and anhydrous sodium acetate. 2:4-Dinitrodiphenylamine is produced from 3:4-dinitrophenyl benzenesulphonate and dimethylamine.

2:4-Dinitrodiphenylamine-2-carboxylic acid can be thus prepared from 2:4-dinitrophenyl *p*-toluenesulphonate and anthranilic acid.

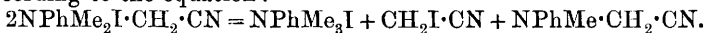
3 : 5-Dinitro-4-benzylaminotoluene, $C_6H_2Me(NO_2)_2 \cdot NH \cdot CH_2 \cdot C_6H_5$, orange needles, m. p. 80° , is produced from benzylamine and 3 : 5-dinitro-p-tolyl-p-toluenesulphonate, m. p. 152° .

4-Chloro-2 : 6-dinitro-1- β -naphthylaminobenzene, red needles, m. p. 201° , and 2 : 4-dinitro-1-naphthylphenylamine, red leaflets, m. p. 182° , can be similarly obtained from 4-chloro-2 : 6-dinitrophenol and β -naphthylamine and 2 : 4-dinitro- α -naphthol and aniline respectively by condensing the *p*-toluenesulphonates of these phenols with the appropriate amine.
G. T. M.

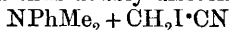
Autoracemisation of Optically Active Ammonium Salts. HANS VON HALBAN (*Ber.*, 1908, 41, 2417—2421. Compare Abstr., 1907, ii, 246).—Wedekind and Paschke have recently attributed (this vol., i, 334) the diminution with time of the rotatory power of optically active ammonium salts in chloroform to autoracemisation, despite the fact that the author has shown (*loc. cit.*) that it is due to the decomposition of the ammonium salt into a tertiary amine and benzyl haloid. He has therefore examined by his method the behaviour of phenylbenzylmethylallylammonium bromide in chloroform, bromoform, and tetrachloroethane at the temperatures used by Wedekind and Paschke, and has obtained, for unimolecular reactions, values of *K* which agree fairly well with those given by these investigators. In some experiments the constant increases with time. The author cannot give a cause for this, but shows that it is not due to a reaction between the liberated amine and the solvent.

In answer to Wedekind's contention that active ammonium salts, which contain in addition to phenyl and benzyl only saturated groups, are remarkably stable in chloroform (Abstr., 1907, ii, 246), the author shows that the decomposition of phenylbenzyl-diethylammonium bromide in chloroform increases with the time.
C. S.

Double Dissociation of Quaternary Ammonium Compounds and a Convenient Synthesis of Iodoacetonitrile. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2130—2144).—The reaction between bromoacetonitrile and dimethylaniline by which phenyltrimethylammonium bromide is formed (this vol., i, 676) is explained by a study of the interaction of dimethylaniline and iodoacetonitrile, as the latter is more reactive and a lower temperature can be employed. In this case an additive compound is first produced, which then decomposes according to the equation :

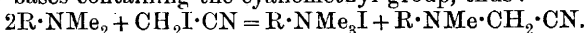


The additive compound is thus doubly dissociated into

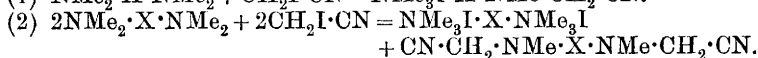
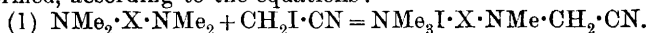


and $NPhMe \cdot CH_2 \cdot CN + CH_3I$, the first and fourth products of which at once unite. It is inferred that the analogous reaction with bromoacetonitrile proceeds in a similar manner. As the quaternary iodide is also obtained by the action of methyl iodide on methylanilinoacetonitrile, it is hence possible to convert half of the methyl iodide into iodoacetonitrile, and, by employing 2 mols. of methyl iodide in the reaction, 75% of the methylanilinoacetonitrile can be converted into iodoacetonitrile.

The author has employed iodoacetoneitrile for the preparation of tertiary bases containing the cyanomethyl group, thus :



In the case of tertiary diamines, three different compounds may be formed, according to the equations :



Phenyldimethylcyanomethylammonium iodide, $NPhMe_2I \cdot CH_2 \cdot CN$, is a white, crystalline powder, m. p. 100° (decomp.). *p-Tolyldimethylcyanomethylammonium iodide*, m. p. 100° (decomp.), on heating yields iodoacetoneitrile, *p*-tolyltrimethylammonium iodide, and methyl-*p*-toluidinoacetoneitrile. *Phenylmethylcyanomethylethylammonium iodide*, $NPhMeEtI \cdot CH_2 \cdot CN$,

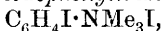
prepared from methylethylaniline and iodoacetoneitrile, is a white, crystalline powder, m. p. 100° (decomp.). On heating, it undergoes triple dissociation, giving (1) $NPhMeEt + CH_2I \cdot CN$; (2) $NPhEt \cdot CH_2 \cdot CN + MeI$, and (3) $NPhMe \cdot CH_2 \cdot CN + EtI$.

Ethylanilinoacetoneitrile and methyl iodide give phenyldimethylethylammonium iodide, m. p. 135° (Claus and Howitz, Abstr., 1884, 1005, give 126°). Methylanilinoacetoneitrile and ethyl iodide interact only slowly, with formation of a small quantity of phenylmethyldiethylammonium iodide. On warming methylcyanoethylaniline,



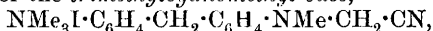
with methyl iodide, phenyltrimethylammonium iodide is produced.

By condensing iodoacetoneitrile with dimethyltoluidine and with *p*-bromodimethylaniline, methyl-*p*-toluidinoacetoneitrile and *p*-bromophenylmethylaminoacetoneitrile respectively are obtained much more conveniently than by the method previously described (this vol., i, 625). *p-Iodophenylmethylaminoacetoneitrile*, $C_6H_4I \cdot NMe \cdot CH_2 \cdot CN$, prepared from iodoacetoneitrile and *p*-iododimethylaniline, has m. p. 60° ; in the same reaction is produced *p-iodophenyltrimethylammonium iodide*,



m. p. 212° .

β -Naphthylmethylaminoacetoneitrile, $C_{10}H_7 \cdot NMe \cdot CH_2 \cdot CN$, prepared similarly from β -naphthyltrimethylamine, has m. p. 76° . *Thallylaminoacetoneitrile*, $OMe \cdot C_9NH_9 \cdot CH_2 \cdot CN$, prepared from methylthalline (Skraup, Abstr., 1886, 80), forms glistening crystals, m. p. 68° . When tetramethyldiaminodiphenylmethane is warmed with iodoacetoneitrile, a mixture of tetramethyldiaminodiphenylmethane dimethiodide, the methiodide of the trimethylcyanomethyl base,



m. p. $172-173^\circ$, and *biscyanomethyldimethyldiaminodiphenylmethane*, $CH_2(C_6H_4 \cdot NMe \cdot CH_2 \cdot CN)_2$, m. p. 107° , is produced. The latter, which is also formed by the interaction of iodoacetoneitrile and *s*-dimethyldiaminodiphenylmethane, is readily hydrolysed to the corresponding *dicarboxylic acid*, $CH_2(C_6H_4 \cdot NMe \cdot CH_2 \cdot CO_2H)_2$, sintering at 122° , m. p. 126° . *s-o*-Dicyanotetramethylbenzidine is more conveniently prepared from iodoacetoneitrile and tetramethylbenzidine than by the method previously given (this vol., i, 625). When 2 mols. of dimethylaniline are warmed with 1 mol. of iodoacetophenone, there are formed phenyl

trimethylammonium iodide and methylanilinoacetophenone. No appreciable amount of the by-product obtained by Staedel and Siepermann (Abstr., 1880, 639) was formed; the author finds this to consist of *diphenacylaniline*, $\text{NPh}(\text{CH}_2\cdot\text{COPh})_2$, m. p. 225°. Dimethylaniline with iodoacetamide (m. p. 95°: Henry, Abstr., 1885, 373, erroneously gives 157°) forms an *additive* compound, $\text{MPhMe}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 149°.

J. C. C.

Preparation of 4-Chloro-2-aminophenol-5-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 194935).—On sulphonating 4-chloro-2-acetylaminophenol and hydrolysing the product, 4-chloro-2-aminophenol-6-sulphonic acid is formed, but when 4-chloro-1-hydroxybenzoxazole, $\text{C}_6\text{H}_3\text{Cl}\langle\text{O}\rangle_{\text{NH}}\text{CO}$ or $\text{C}_6\text{H}_3\text{Cl}\langle\text{O}\rangle_{\text{N}}\text{C}\cdot\text{OH}$, is subjected to this series of operations, 4-chloro-2-aminophenol-5-sulphonic acid is obtained. The sulphonation is effected with sulphuric acid, containing 10% of sulphur trioxide, and the hydrolysis with sodium hydroxide.

The new chloroaminophenolsulphonic acid furnishes a diazo-derivative crystallising in lustrous, yellow needles. This acid is also produced by successively sulphonating and hydrolysing 4-chloro-1-methylbenzoxazole, $\text{C}_6\text{H}_3\text{Cl}\langle\text{O}\rangle_{\text{N}}\text{CMe}$.

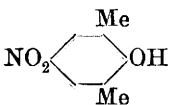
G. T. M.

Preparation of Aromatic Hydroxylated Nitro-compounds. RICHARD WOLFFENSTEIN and O. BÖTERS (D.R.-P. 194883).—The production of a nitrophenol has hitherto necessitated the preliminary introduction of a hydroxyl group into an aromatic nucleus, a process which is often somewhat difficult. It has now been found that the hydroxylation and nitration of an aromatic hydrocarbon may be effected simultaneously by the joint action of nitric acid and mercury, or a mercury compound. A mixture of benzene (400 grams), nitric acid (660 grams, D 1.48), and mercuric nitrate (150 grams) when heated on the water-bath yields 180 grams of picric acid, together with a certain amount of nitrobenzene. A similar experiment with double quantities of nitric acid furnished picric acid (380 grams), nitrobenzene (160 grams), and 2 grams of *o*-nitrophenol.

Naphthalene treated in this way gives rise to nitronaphthols and nitronaphthalene; toluene and benzoic acid furnish respectively trinitroresol and nitrohydroxybenzoic acid.

G. T. M.

***m*-2-Xylenol.** KARL AUWERS and TH. VON MARKOVITS (*Ber.*, 1908, 41, 2332—2340).—In connexion with their work on the oxidation of *m*-2-xylenol to tetramethyldiphenquinone (Abstr., 1905, i, 219), the authors have prepared a number of new derivatives.



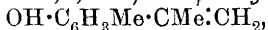
5-Nitro-*m*-2-xylenol, annexed formula, prepared by treating *m*-2-xylenol with nitric acid in glacial acetic acid solution, forms compact, colourless prisms, m. p. 169—170°. 5-Nitroso-*m*-2-xylenol is best obtained by acidifying a mixture of the phenol and sodium nitrite in dilute alkaline solution. It crystallises from benzene in yellow, glassy prisms and tablets, m. p. 170—171°. The *acetyl* derivative is a yellow, crystalline powder, m. p. 84—86°.

5-Bromo-*m*-2-*xylenol*, formed by bromination in acetic acid solution, crystallises in long, silky needles, m. p. 79·5°. 4:5-Dibromo-*m*-2-*xylenol*, obtained by brominating *xylenol* in presence of a trace of iodine or iron, forms small, colourless needles, m. p. 86—87°. By adding *xylenol* to excess of bromine, there is obtained 4:5:6-tribromo-*m*-2-*xylenol*, colourless needles, m. p. 200—201°. [The substance described under this name (Beilstein, *Handbuch*, 3rd Ed., 2, 758) is really tribromo-*p*-*xylenol*.] 4-Bromo-*m*-2-*xylenol* is prepared by brominating 2-nitro-*m*-*xylene* and replacing the nitro-group by hydroxyl. 4-Bromo-2-nitro-*m*-*xylene*, prepared by adding iron powder to a cold mixture of 2-nitro-*m*-*xylene* and bromine, forms shining needles, m. p. 70—71°. On reduction with zinc dust and acetic acid, diazotisation of the resulting base, and allowing the diazo-solution to decompose at the ordinary temperature, 4-bromo-*m*-2-*xylenol* is formed; this crystallises from light petroleum in colourless, slender needles, m. p. 60—61·5°. If steam is led into the above-mentioned diazo-solution, 4-bromo-5-nitroso-*m*-2-*xylenol* is obtained; this forms pale yellow needles, m. p. 190—192°. 4-Nitro-*m*-2-*xylenol*, prepared from 4-nitro-*m*-2-*xylidine* by the diazo-reaction, has m. p. 99—100°.

m-2-*Xylenol methyl ether*, prepared by the use of methyl sulphate, is a colourless oil, b. p. 182°. With benzoyl chloride and aluminium chloride, it yields 4-methoxy-3:5-dimethylbenzophenone, m. p. 44°, which on warming with aluminium chloride gives 4-hydroxy-3:5-dimethylbenzophenone, colourless plates, m. p. 141—142°.

5-Benzeneazo-*m*-2-*xylenol* forms chrome-yellow prisms and tablets, m. p. 95—96°. J. C. C.

Phenolic Ethers containing the ψ -Allyl Side-chain $\text{—CMe}\cdot\text{CH}_2$.
 III. Hydroxytoluic Series; Synthesis of Thymol. IV. Vanillic, Veratric, and Piperonylic Series. AUGUSTE BÉHAL and MARC TIFFENEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 729—732, 732—736). —A continuation of work on the synthesis of these esters (this vol., i, 261). Some of the data now given have been published before (Abstr., 1904, i, 742; 1905, i, 883). 3- ψ -Allyl-*o*-cresol,



D^{20} 1·040, n_D^{20} 1·543, b. p. 220—225°, obtained by the action of magnesium methyl iodide on methyl *o*-hydroxytoluate (m. p. 28—30°, b. p. 235°), has a characteristic thyme-like odour, gives a green coloration with ferric chloride, and with methyl sulphate yields the corresponding methyl ether, D^0 0·9901, D^{15} 0·9830, n_D^{15} 1·595, b. p. 217—218°, which, on reduction with sodium in alcohol, furnishes an isothymyl methyl ether, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHMe}_2$, D^0 0·9559, D^{19} 0·9430, n_D^{19} 1·50725, b. p. 210—213°. The latter on demethylation with hydriodic acid gives an isothymol, D^0 0·9962, b. p. 228—230°, which does not crystallise when cooled. Methyl *m*-hydroxytoluate, D^0 1·1629, D^{21} 1·147, m. p. 27—28°, b. p. 118—122°/12 mm., 238—240°/760 mm., cannot be methylated by Graebe and Ullmann's process (*Ber.*, 1896, 29, 824), but with methyl sulphate or iodide gives good yields of methyl *m*-methoxytoluate, D^0 1·1462, b. p. 259—261°/760 mm., and from the latter by the action of magnesium methyl iodide the tertiary alcohol, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CMe}_2\cdot\text{OH}$, D^0 1·0448, b. p. 129—130°/

11 mm., is obtained as a liquid, which, on distillation under atmospheric pressure, undergoes partial dehydration, yielding 3-methoxy-1-methyl-4- ψ -allylbenzene, D^0 0.9835, b. p. 216—219°. The latter can be prepared by heating the alcohol at 100° with acetic anhydride, a crystalline *polymeride*, D^0 1.0468, m. p. 56°, b. p. 215—223°/13 mm., being formed simultaneously. 3-Methoxy-1-methyl-4- ψ -allylbenzene on reduction with sodium in alcohol yields the methyl ether of thymol, which, on demethylation by hydriodic acid, or, better, with a mixture of hydrobromic and acetic acids, gives thymol.

Vanillyldimethylcarbinol, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CMe}_2 \cdot \text{OH}$
 $(\text{OMe} : \text{OH} : \text{CMe}_2 \cdot \text{OH} = 3 : 4 : 1),$

m. p. 55°, b. p. 165°/10 mm., obtained by the action of magnesium methyl iodide on ethyl vanillate, together with a *dimeride*, m. p. 174°, of ψ -eugenol, furnishes, on distillation at atmospheric pressure, a poor yield of ψ -eugenol, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CMe} : \text{CH}_2$ (Abstr., 1904, i, 742), m. p. 20°. The latter cannot be prepared directly by the action of magnesium methyl iodide on ethyl vanillate; it yields a crystalline benzoyl derivative, m. p. 58—59°.

Veratryldimethylcarbinol, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CMe}_2 \cdot \text{OH}$ (*loc. cit.*), m. p. 78°, b. p. 140°/7 mm., 155°/13 mm., crystallises from light petroleum, and, on distillation under atmospheric pressure, furnishes ψ -methyleugenol, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CMe} : \text{CH}_2$, D^{20} 1.045, m. p. 36 (*loc. cit.*).

ψ -Safrole (1- ψ -allyl-3:4-catechol methylene ether), D^0 1.1338, D^{15} 1.1198, n_D^{15} 1.5619, b. p. 135°/20 mm., 233—239°/760 mm. (*loc. cit.*), obtained by the action of magnesium methyl iodide on methyl piperonylate, on reduction yields 1-isopropyl-3:4-catechol methylene ether, D^0 1.0935, n_D^{15} 1.52315, b. p. 225—230° (Abstr., 1905, i, 883), and, on oxidation with iodine and excess of yellow mercuric oxide, piperonylacetone, $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Ac}$, D^0 1.2197, D^{23} 1.2035, n_D^{15} 1.54502, b. p. 163°/16 mm., 282—285°/760 mm. (compare Wallach, Abstr., 1904, i, 754); the *semicarbazone* of this has m. p. 159—160°. ψ -Safrole iodohydrin, on treatment with potassium hydroxide, yields an *ethylene oxide*, b. p. 150—155°/15 mm., which, on distillation under reduced pressure, yields 3:4-methylenedioxyhydratropaldehyde, b. p. 157—158°/16 mm., D^0 1.221 (compare Bougault, Abstr., 1901, i, 721); this yields a *semicarbazone*, of which the portion readily soluble in benzene has m. p. 156°, and that slightly soluble in the solvent, m. p. 158°.

T. A. H.

Derivatives of *p*-Nitrophenyl Mercaptan. EMIL FROMM and J. WITTMANN (*Ber.*, 1908, 41, 2264—2273. Compare Abstr., 1906, i, 656).—To obtain further insight into the nature of the solution of sulphur in alkali hydroxides, the action of *p*-chloronitrobenzene was studied, as this compound gives *p*-nitrophenyl mercaptan with potassium hydrosulphide (Willgerodt, Abstr., 1885, 519). The expected *p*-nitrophenylsulphoxide was, however, not obtained, but the interaction leads to the formation of sodium *p*-nitrophenoxide, 4:4'-dinitrodiphenyl disulphide (Willgerodt, *loc. cit.*), nitroamino-diphenyl sulphide (Kehrmann and Bauer, Abstr., 1897, i, 27), 4:4'-dinitrodiphenyl sulphide (Nietzki and Bothof, Abstr., 1895, i,

132), and the 4:4'-dinitrodiphenyl ether of *p*-azophenyl mercaptan, $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, m. p. 164° , which crystallises in golden-yellow needles from glacial acetic acid. Its constitution was determined by its conversion into thioaniline on reduction with tin and hydrochloric acid.

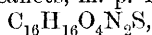
It has recently been shown that disulphides containing the grouping $-\ddot{\text{C}}-\text{S}-\text{S}-\ddot{\text{C}}-$ lose sulphur on treatment with alkalis, water, or amines (Abstr., 1906, *loc. cit.*), but little is known at present of the action of alkalis on aromatic disulphides. The dinitrodiphenyl disulphide gives with alcoholic sodium hydroxide the sodium salt of *p*-nitrophenyl mercaptan and an insoluble compound, $\text{C}_{24}\text{H}_{26}\text{O}_4\text{N}_3\text{S}_2$?, which sinters at 130° and has m. p. 158° . As this is evidently not a direct product of the hydrolysis, the experiment was repeated with excess of benzyl chloride, when the benzyl ether of the mercaptan (m. p. 123° , Kulenkampff, *Diss.*, Freiburg, 1906) and benzoic acid were obtained. When less alkali and benzyl chloride are used, in addition to the above ether, *p*-nitrobenzenesulphinate is isolated, as well as a little nitrobenzene, showing that the hydrolysis proceeds on the same lines as that of phenyl disulphide (Schiller and Otto, this Journ., 1877, i, 463). The equation

$$2\text{S}_2(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2 + 4\text{KOH} = 3\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SK} + \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{K} + 2\text{H}_2\text{O}$$

is held not to explain the change; the first products are supposed to be mercaptan and the hypothetical compound, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SOH}$, which acts as an oxidising agent.

Dinitrodiphenyl disulphide and ammonia, when heated in a closed tube, give nitroaminodiphenyl sulphide; this compound is not formed when the corresponding monosulphide is treated in a similar manner.

4:4'-Dinitrodiphenylsulphone, $\text{C}_{12}\text{H}_8\text{O}_6\text{N}_2\text{S}$, prepared by oxidising the sulphide with potassium dichromate and sulphuric acid, crystallises from glacial acetic acid; m. p. 282° . The corresponding diamino-derivative, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$, forms white leaflets, m. p. 174° ; its diacetate,

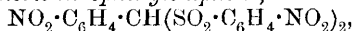


white needles, m. p. 280° .

p-Nitrophenylbenzylsulphone, $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}$, has m. p. 169° (Kulenkampff, *loc. cit.*, gives 149°). When heated with methyl iodide and alcoholic sodium hydroxide, β -phenylisopropylnitrophenylsulphone, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CPhMe}_2$, is formed, m. p. 169° .

The mercaptal, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_2$, prepared from acetone and *p*-nitrophenyl mercaptan, forms white needles, m. p. 122° . By reducing the mercaptal from benzaldehyde and *p*-nitrophenyl mercaptan (Blanksma, Abstr., 1902, i, 282), the corresponding diamino-mercaptal dihydrochloride, $\text{C}_{19}\text{H}_{20}\text{N}_2\text{Cl}_2\text{S}_2$, is obtained. The mercaptal, $\text{C}_{19}\text{H}_{13}\text{O}_6\text{N}_3\text{S}_2$, from *p*-nitrobenzaldehyde forms white needles, m. p. 166° , and on reduction gives the triamino-mercaptal trihydrochloride, $\text{C}_{19}\text{H}_{22}\text{N}_3\text{Cl}_3\text{S}_2$; the triacetate, $\text{C}_{25}\text{H}_{25}\text{O}_8\text{N}_3\text{S}_2$, has m. p. 241° .

Nitrophenylmethanebisnitrophenylsulphone,



prepared from the trinitro-mercaptal by oxidation, forms light yellow leaflets, m. p. 235° . *p*-Nitrophenylthioglycine (Friedländer and Slubek, this vol., i, 525) is formed by the interaction of monochloroacetic acid and *p*-nitrophenyl mercaptan.

W. R.

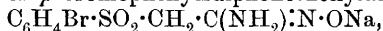
Arylsulphonated Acetonitriles. Action of Alkyl Haloids on Arylsulphon-ethenylamidoximes and -thioacetamides. JULIUS TRÖGER and BERNHARD LINDNER (*J. pr. Chem.*, 1908, [ii], 78, 1—20. Compare Abstr., 1905, i, 336).—The crystalline arylsulphon-acetonitriles, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{CN}$, described by Tröger and Hille (*loc. cit.*), are sparingly soluble in water, but dissolve readily in aqueous alkalis, forming metallic derivatives analogous to those of ethyl cyanoacetate and benzyl cyanide. Tröger and Vesterling (Abstr., 1905, i, 870) found that the action of alkyl haloids on the sodioarylsulphonacetonitriles leads to the formation of dialkyl derivatives, $\text{SO}_2\text{R}\cdot\text{CR}'_2\cdot\text{CN}$, which are even more stable towards hydrolysing agents, and form thioacetamides and amidoximes by addition of hydrogen sulphide and hydroxylamine (Tröger and Volkmer, Abstr., 1905, i, 356) with greater difficulty, than the parent nitriles. As the arylsulphonthioacetamides are readily soluble, whereas the corresponding acetamides are insoluble, in aqueous alkalis, it is considered that the thioacetamides react in the ψ -form, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{SH}$; this is in agreement with the formation of benzyl sulphide by the action of benzyl chloride on the sodium salts of the arylsulphonthioacetamides,

$$\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{SNa},$$

the benzyl ether, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, being considered to be formed intermediately. Similarly, it is probable that the alkali salts of the amidoximes have the constitution $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OM}'$. The present work was undertaken to determine in how far the arylsulphonthioacetamides and arylsulphonethenylamidoximes are capable of forming salts and ethers.

It is found that the amidoximes form stable salts only when the aryl nucleus contains a negative substituting group; if this is not the case, the alkali salt is readily hydrolysed, so that only mixtures of the salt and the free amidoxime can be obtained. The basic nature of the amidoxime group is shown by the solubility of the substances in mineral acids, and by the formation of acetyl derivatives. Whilst pure sodium salts are obtained only in certain cases, all the amidoximes studied form benzyl and methyl ethers containing the grouping $\text{N}\cdot\text{OR}$. The arylsulphonthioacetamides, on the other hand, readily form stable sodium salts, but these on treatment with benzyl chloride react, forming benzyl sulphide and not ethers of the thioacetamides.

The *sodium* salt of *p*-bromophenylsulphonethenylamidoxime,



forms a yellowish-red, voluminous precipitate.

The following *benzyl ethers* of arylsulphonethenylamidoximes,



are described. The temperatures are melting points.

$\text{R}=\text{Ph}$: white leaflets, 114° ; $\text{R}=\text{p-C}_6\text{H}_4\text{Cl}$: white needles, 114° ; $\text{R}=\text{p-C}_6\text{H}_4\text{Br}$: white needles, $132\text{—}133^\circ$; $\text{R}=\text{p-C}_6\text{H}_4\text{I}$: white needles, 165° ; $\text{R}=\text{p-C}_6\text{H}_4\text{Me}$: white prisms, 93° ; $\text{R}=\alpha\text{-C}_{10}\text{H}_7$: white leaflets, 162° ; $\text{R}=\beta\text{-C}_{10}\text{H}_7$: white leaflets, 129° ; $\text{R}=\text{o-C}_6\text{H}_4\cdot\text{OMe}$: white needles, m. p. 94° ; $\text{R}=\text{p-C}_6\text{H}_4\cdot\text{OEt}$: needles, 130° .

The *methyl ethers*, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OMe}$, $\text{R}=\alpha\text{-C}_{10}\text{H}_7$: white crystals, m. p. 137° , and $\text{R}=\beta\text{-C}_{10}\text{H}_7$: yellow, sandy powder, m. p. 159° (slight decomp.), were prepared,

The following *acetyl* derivatives, $\text{SO}_2\text{R}\cdot\text{CH}_2\cdot\text{C}(\text{NHAc})\cdot\text{N}\cdot\text{OR}'$, are described.

$\text{R} = p\text{-C}_6\text{H}_4\cdot\text{OEt}$, $\text{R}' = \text{CH}_2\text{Ph}$: white needles, m. p. 115° ; $\text{R} = p\text{-C}_6\text{H}_4\text{Br}$, $\text{R}' = \text{H}$: quadratic crystals, m. p. 193° (decomp.); $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$, $\text{R}' = \text{H}$: white needles, m. p. 186° .

The *sodium* salts of phenylsulphonthioacetamide, $\text{C}_8\text{H}_8\text{O}_2\text{NS}_2\text{Na}$, *p*-tolylsulphonthioacetamide, $\text{C}_9\text{H}_{10}\text{O}_2\text{NS}_2\text{Na}$, and β -naphthylsulphonthioacetamide, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{NS}_2\text{Na}$, were analysed. G. Y.

Acidity of the Different Phenolsulphonic Acids. JULIUS OBERMILLER (*Zeitsch. anorg. Chem.*, 1908, 59, 79—81).—According to Ley and Erler (compare this vol., i, 177), the acidity of the phenolic hydrogen atom of phenol-*o*-sulphonic acid is weaker than that of the phenolic hydrogen of the para-acid, and this is supposed to be in agreement with Ostwald's acidity rule for aromatic dicarboxylic acids. The author points out that it is doubtful whether the para-position is further removed than the meta- from the ortho-position.

The dimagnesium salt of phenol-*o*-sulphonic acid is hydrolysed to a much smaller extent than the corresponding salt of the para-acid, and this, in opposition to Ley and Erler, indicates that phenolic hydrogen in the ortho-position is the more strongly acidic. The greater tendency of the copper salt of the ortho-acid to form basic salts cannot be explained by the weaker acidity of the acid. The author's observations on the lead salts indicate that their tendency to yield basic salts increases with increasing acidity. In respect of this property, phenol-*o*-sulphonic acid is intermediate between the para-acid and the 2:4-disulphonic acid. H. M. D.

Condensation of Nitromalonaldehyde with Acetonyl-acetone. I. WILLIAM J. HALE and CHARLES A. ROBERTSON (*Amer. Chem. J.*, 1908, 39, 680—696).—Hill and Hale (*Abstr.*, 1905, i, 200) have shown that the sodium derivative of nitromalonaldehyde reacts with benzyl methyl ketone with formation of 5-nitro-2-hydroxydiphenyl. It was therefore expected that nitromalonaldehyde (2 mols.) would condense with acetonylacetone (1 mol.) to form a derivative of benzyl methyl ketone, and that the latter would react with a second mol. of the aldehyde with production of a diphenyl derivative. The present paper gives an account of a study of these reactions.

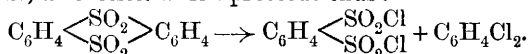
When a mixture of nitromalonaldehyde (2 mols.), acetonylacetone (1 mol.), and sodium hydroxide ($\frac{1}{8}$ mol.) was treated with carbon dioxide, a small quantity (17% of the theoretical) of 4-nitro-2-acetonylphenol separated, instead of the expected diphenyl compound. On acidifying the mother liquor with hydrochloric acid, a larger quantity (about 65%) of a light yellow, crystalline substance was obtained, the description of which is reserved for a future paper.

4-Nitro-2-acetonylphenol, $\text{COMe}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OH}$, m. p. 188.5° (corr.), forms needles or prisms; its *sodium* salt crystallises with $2\text{H}_2\text{O}$. The *methyl ether* has m. p. 60° (corr.), the *ethyl ether*, 70.5° (corr.), and the *oxime*, 146° (corr.). When the methyl ether is oxidised with potassium permanganate, methyl 5-nitrosalicylate is

produced, showing that the acetyl group is in the ortho-position to the hydroxyl group. 4:6-Dinitro-2-acetylphenol, m. p. 121° (corr.), crystallises in lustrous plates; its *ethyl ether*, m. p. 118.5° (corr.), forms small, colourless prisms.

When 4-nitro-2-acetylphenol is treated with nitromalonaldehyde in presence of a large excess of sodium hydroxide, 3:3'-dinitro-6:6'-dihydroxydiphenyl, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NO}_2$, m. p. 301° (corr.), is produced, and crystallises in small, colourless needles. Its *dimethyl ether*, m. p. 264° (corr.), and *diethyl ether*, m. p. 271° (corr.), crystallise in needles. The *mono-ethyl ether*, m. p. 224° (corr.), obtained by the condensation of 4-nitro-2-acetylphenyl ethyl ether with the sodium derivative of nitromalonaldehyde, forms silky needles. 3:3'-Diamino-6:6'-dihydroxydiphenyl is readily obtained by reducing the dinitro-compound with tin and hydrochloric acid; its *hydrochloride* forms long, colourless prisms. On oxidation with chromic acid, the diamino-compound is converted into diquinone, m. p. 192° (corr.) (compare Barth and Schreder, Abstr., 1885, 521). E. G.

Constitution of Thianthren [Diphenylene Disulphide]. J. J. B. DEUSS (*Ber.*, 1908, 41, 2329—2331).—The ortho-position of the sulphur atoms in diphenylene disulphide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$ (Graebe, Abstr., 1874, 469; 1876, i, 578), has been indicated by the work of Jacobson and Ney (Abstr., 1889, 771) and of Krafft and Lyons (Abstr., 1896, i, 297), whilst Genvresse (Abstr., 1897, i, 514) considered that the sulphur atoms were in the meta-position to each other. The author has treated diphenylene disulphide with phosphorus pentachloride, a reaction which proceeds thus:



The products were benzene-*o*-disulphonyl chloride and *o*-dichlorobenzene, thus proving the ortho-position of the sulphur atoms in diphenylene disulphide. J. C. C.

Preparation of Carbamates of 2:6-Dialkyloxyphenols. BASLER CHEMISCHE FABRIK (D.R.-P. 194034).—The carbamates of the 2:6-dialkyloxyphenols (pyrogallol 1:3-dialkyl ethers) are prepared by the following series of operations: (1) condensation of carbonyl chloride with either of these ethers in the presence of a tertiary base, such as pyridine or dimethylaniline, or with sodium salts alone; (2) treatment of these intermediate products with dry ammonia.

2:6-Dimethoxyphenyl carbamate, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NH}_2$, is a white mass melting at 148—152°. G. T. M.

Three New Primary Alcohols Resulting from the Condensation of Sodium Benzyloxide with Propyl, Butyl, and *iso* Amyl Alcohols. MARCEL GUERBET (*Compt. rend.*, 1908, 146, 1405—1407).—The author has continued his work on the action of alcohols on sodium benzyloxide (this vol., i, 162). The alcohol already obtained from *n*-propyl alcohol has been proved to be γ -phenylisobutyl alcohol, $\text{CH}_2\text{Ph} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{OH}$. It is a colourless, oily liquid, b. p. 244—246°

(corr.), D_0^{20} 0.9841, with an odour recalling that of lilac. The *phenyl-carbamate* forms colourless needles, m. p. 62—63°, and the *acetate* is a colourless liquid, b. p. 260—262° (corr.). On oxidation, the alcohol gives β -phenylisobutyric acid. When sodium benzyloxide is condensed with *n*-butyl alcohol, there is formed β -benzyl-*n*-butyl alcohol, $C_6H_5 \cdot CH_2 \cdot CHEt \cdot CH_2 \cdot OH$, a colourless, oily liquid with an odour resembling that of phenylisobutyl alcohol; it has b. p. 258—261° (corr.) and D_0^{20} 0.9780. The *acetate* has b. p. 275—276° (corr.). On oxidation, the alcohol furnishes α -benzyl-*n*-butyric acid. The constitution of the benzylamyl alcohol prepared from *iso*amyl alcohol has not yet been established, but from analogy it is probably β -benzylisobutylcarbinol, $CH_2Ph \cdot CH(C_3H_7) \cdot CH_2 \cdot OH$. It is a colourless, oily liquid, b. p. 272—274° (corr.), D_0^{20} 0.9687. The *acetate* has b. p. 279—281° (corr.). On oxidation, the alcohol yields *benzylvaleric acid*, $C_{12}H_{16}O_2$, a colourless, oily liquid with an odour of valerian, b. p. 305—308° (corr.). The *potassium*, *barium*, and *silver* salts are described. The *ethyl* ester has a strong, fruity odour; it has b. p. 274—276°. The *chloride* has b. p. 156—158°/22 mm. (corr.), and the *amide* has m. p. 94—95°. J. C. C.

Reduction with Platinum and Hydrogen. II. Dihydrocholesterol. RICHARD WILLSTÄTTER and ERWIN W. MAYER (*Ber.*, 1908, 41, 2199—2203. Compare this vol., i, 383; Windaus, *Abstr.*, 1907, i, 610).—Cholesterol is reduced when hydrogen is passed through an ethereal solution of the substance containing platinum-black in suspension, yielding dihydrocholesterol (cholestanol), $C_{27}H_{48}O$, identical with the β -cholestanol obtained by Diels and Abderhalden (*Abstr.*, 1906, i, 272) from cholestenone. This fact confirms the view of Diels and Linn (this vol., i, 164) that cholesterol and cholestenone contain the same ring complex. It follows from the values obtained for the rate of esterification of cholesterol and its dihydro-derivative that these compounds are secondary alcohols; further, as is to be expected, the absolute initial velocity of esterification of the saturated compound is greater than that of the unsaturated compound.

Dihydrocholesterol crystallises from light petroleum or acetone in prisms, m. p. 141.5—142° (corr.), and from dilute alcohol with $1H_2O$ in six-sided leaflets, which soften at 120°. The anhydrous substance in ether gives $[\alpha]_D^{25} + 28.8^\circ$. At 18°, 100 parts of alcohol dissolve 1.60 parts of cholestanol and 2.28 parts of cholesterol.

Cholestanyl acetate, $C_{29}H_{50}O_2$, obtained by acting on the alcohol with acetic anhydride, crystallises in glittering prisms, m. p. 110.5—111° (corr.). W. H. G.

Connexion of Cholesterol and Cholic Acid with Camphor and Turpentine Oil. HUGO SCHRÖTTER and RICHARD WEITZENBÖCK (*Monatsh.*, 1908, 29, 395—398).—It was shown recently (this vol., i, 532) that, when treated with concentrated sulphuric acid and mercury and thereafter with nitric acid, cholesterol and cholic acid yield rhizocholic acid, which was considered to be hydroxycyclopentadienetri-carboxylic acid. As this points to a relationship between cholesterol and cholic acid, on the one hand, and, on the other, the terpenes, which

give analogously-constituted oxidation products, it was of importance to prepare rhizocholic acid in larger quantities and to establish its constitution. It is now found that rhizocholic acid is formed in small yields when camphor and turpentine oil are treated in the same manner as cholesterol with sulphuric acid and mercury and then with nitric acid. Apart from the question as to the correctness of the constitution suggested for rhizocholic acid, these results show that cholesterol and cholic acid are genetically related to camphor and turpentine oil, and must therefore belong to the terpene group. Thus, for the first time, is demonstrated the presence of a member of the terpene group amongst the degradation products of the animal organism.

G. Y.

Ergosterol and Fongisterol. CHARLES TANRET (*Compt. rend.*, 1908, 147, 75—77).—Ergosterol is accompanied in spurred rye by a very similar crystalline substance, which also seems to exist in other fungi, and which the author designates *fongisterol*. The so-called ergosterol (Abstr., 1889, 407), having $[\alpha]_D - 114^\circ$, contains one-ninth its weight of the new compound. Separation is effected by repeated recrystallisation from ether, ergosterol being the less soluble. Pure ergosterol, $C_{27}H_{42}O, H_2O$, is not efflorescent, and is completely dehydrated only at 105° , but the anhydrous substance quickly absorbs water from moist air. It crystallises from alcohol in wide, monoclinic lamellæ, and from ether in monoclinic needles. It has m. p. 165° (on Maquenne block), $[\alpha]_D - 126^\circ$ (in chloroform), -105.5° (in ether). The acetate has $[\alpha]_D - 91.8^\circ$ and m. p. 180.5° ; the formate, $[\alpha]_D - 97.9^\circ$ and m. p. 161.5° .

Fongisterol, $C_{25}H_{40}O, H_2O$, is a lower homologue of ergosterol; it has a similar crystalline form, and is not efflorescent. It is dehydrated by chloroform, giving a milky liquid, but, when almost anhydrous, dissolves in 10 parts of this solvent at 20° . It has m. p. 144° (on Maquenne block), $[\alpha]_D - 22.4^\circ$ (in chloroform containing 2% of alcohol), -12.9° (in ether). The acetate has m. p. 158.5° , $[\alpha]_D - 15.9^\circ$ (in chloroform), -10.8° (in ether). The reactions with sulphuric acid and chloroform and with fuming nitric acid, previously indicated to distinguish ergosterol from cholesterol, serve to differentiate the latter from fongisterol.

When a particle of fongisterol is thrown on a few drops of 90% sulphuric acid, the latter acquires a ruby-red colour in a few seconds, which, after some minutes, changes into a reddish-violet. With ergosterol, a dirty red colour only appears at the end of one minute.

Ergosterol and fongisterol seem to be widely distributed. The cholesterol described by Gerard (Abstr., 1892, 1294; 1896, i, 21; 1898, i, 549) as belonging to the ergosterol group, probably consist of a mixture of these two compounds.

E. H.

Unsaponifiable Ingredients of Cocoa-Butter and their Detection in Butter. HERMANN MATTHES and EDWIN ACKERMANN (*Ber.*, 1908, 41, 2000—2001).—The ethereal extract of cocoa-butter hydrolysed by alcoholic potassium hydroxide contains, in addition to ordinary phytosterol, a second alcohol, which gives the same colour

reactions as phytosterol, but differs from it in taking up 2 mols. of bromine and in forming a sparingly soluble *tetrabromophytosteryl acetate*, $C_{31}H_{52}O_2Br_4$, m. p. 180—183° (decomp.). As butter contains only cholesterol, which does not form a tetrabromo-acetate, the authors are studying the practical application of the reaction to the detection of cocoa-fat in butter. Other fats of vegetable and of animal origin are being examined, in the hope that the reaction will differentiate between the two classes of fats.

C. S.

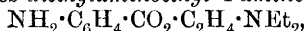
Abnormal Products of the Fission of cycloHexanecarboxylic Acid. NICOLAI D. ZELINSKY and J. GUTT (*Ber.*, 1908, 41, 2074—2076).—Whilst the corresponding hydrocarbons are readily obtained from aromatic and aliphatic acids by distillation of the calcium or barium salts with lime or soda-lime, such reactions are found in the *cyclohexane* series to be accompanied by far-reaching complications. When distilled with sodium methoxide (Mai, *Abstr.*, 1889, 1126), barium *cyclohexanecarboxylate* yields a mixture of *cyclohexadiene* with smaller amounts of *cyclohexene*, together with dihydro-toluene, whereas, when heated with zinc chloride, *cyclohexanecarboxylic acid* is converted chiefly into methyl*cyclopentane*. It is shown that Einhorn's supposed methyl*cyclohexane*, prepared by heating 1-methyl-*cyclohexane-3-carboxylic acid* with zinc chloride (*Abstr.*, 1898, i, 407), is a mixture of that substance with an isomerisation product, probably dimethyl*cyclopentane*.

G. Y.

Characteristic Reaction of Anthranilic Acid. BRONISLAW PAWLEWSKI (*Ber.*, 1908, 41, 2353—2354. Compare Suida, this vol., i, 523).—For the identification of anthranilic acid, Mohr and Köhler recommend its conversion into acetylanthranil (*Abstr.*, 1907, i, 414). A still simpler method is now based on the formation of the characteristic *additive* compound of anthranilic acid and *p*-dimethylaminobenzaldehyde, $CO_2H \cdot C_6H_4 \cdot NH_2 \cdot CHO \cdot C_6H_4 \cdot NMe_2$, which is formed when the components are ground together and moistened with water or alcohol, or boiled with aqueous alcohol or benzene. If gently heated with aqueous alcohol or benzene, the acid and aldehyde form a yellow solution, which gradually deposits the red additive compound. This crystallises in needles, m. p. 180—182°, is decomposed partially on recrystallisation, or completely by ammonia, alkalis, alkali carbonates, or acids, and when treated with acetic anhydride yields *N*-acetylanthranilic acid, m. p. 180—181°.

G. Y.

Preparation of Alkylaminoalkyl *p*-Aminobenzoates. FARRWERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.-P. 194748. Compare *Abstr.*, 1907, i, 923).—*Chloroethyl 4-aminobenzoate*, white needles, m. p. 86—87°, obtained either by reducing *chloroethyl 4-nitrobenzoate*, needles, m. p. 56°, or by treating 4-aminobenzoic acid with ethylenechlorohydrin, furnishes *diethylaminoethyl 4-aminobenzoate*,



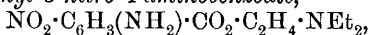
m. p. 51°, hydrochloride, m. p. 156°, on heating with diethylamine at 110°. *Chloroisopropyl 4-aminobenzoate*, needles, 69°, hydrochloride, leaflets, m. p. 186°, obtained from *chloroisopropyl 4-nitrobenzoate*, brown

oil, b. p. 195—196°/17 mm., gives rise to *piperidylisopropyl 4-aminobenzoate*, m. p. 82°, on heating with piperidine at 120°.

A similar series of esters was obtained from *p*-nitrobenzoyl chloride and α -dichlorohydrin. The final product, *dipiperidylpropyl 4-aminobenzoate*, forms prismatic plates, m. p. 158°. G. T. M.

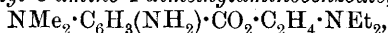
Preparation of Dialkylaminoalkyl Diaminobenzoates.

ALFRED EINHORN (D.R.-P. 194365).—*Diethylaminoethyl 3:4-diaminobenzoate*, $C_6H_3(NH_2)_2 \cdot CO_2 \cdot C_2H_4 \cdot NEt_2$, oil, *hydrochloride*, needles, m. p. 163°, may be prepared from 3:4-diaminobenzoic or 3-nitro-4-aminobenzoic acid by the following alternative series of operations. The former of these acids, or its methyl ester, is either treated with diethylaminomethylcarbinol, $CH_2(NEt_2) \cdot CH_2 \cdot OH$, or condensed successively with ethylene chlorohydrin and diethylamine. The intermediate *chloroethyl 3:4-diaminobenzoate* crystallises from benzene and petroleum in needles, m. p. 80°. The latter acid is condensed with ethylene-chlorohydrin to *chloroethyl 3-nitro-4-aminobenzoate*, brownish-yellow needles or plates, m. p. 145—146°. Diethylamine converts this ester into *diethylaminoethyl 3-nitro-4-aminobenzoate*,



yellow oil, *hydrochloride*, yellow needles, m. p. 208°, and this product, on reduction with tin and hydrochloric acid, furnishes the required ester of diaminobenzoic acid.

Diethylaminoethyl 3-amino-4-dimethylaminobenzoate,

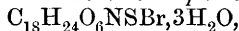


oil, *hydrochloride*, needles, m. p. 164°, is derived by a similar series of operations from 3-nitro-4-dimethylaminobenzoic acid. These products are valuable anæsthetics of the novocaine series. G. T. M.

Optical Resolution of Aminophenylacetic Acid. MARIO BETTI and MARIO MAYER (*Ber.*, 1908, 41, 2071—2073. Compare Abstr., 1907, i, 726; Ehrlich, this vol., i, 268; Fischer and Weichhold, *ibid.*, 419).— α -Aminophenylacetic acid has been resolved into its optically active constituents by means of *d*-camphorsulphonic acid and *d*-bromocamphorsulphonic acid.

l- α -Aminophenylacetic acid *d*-camphorsulphonate, $C_{18}H_{25}O_6NS$, separates from an aqueous solution of the two acids in colourless, trimetric, strongly refracting crystals, m. p. 210—212° (decomp.), $[\alpha]_D - 44.07^\circ$, and, on treatment with an alkali, yields *l*- α -aminophenylacetic acid, m. p. above 305°, $[\alpha]_D - 111.02^\circ$. *d*- α -Aminophenylacetic acid, obtained from the mother liquors, has $[\alpha]_D + 112.18^\circ$.

d- α -Aminophenylacetic acid *d*-bromocamphorsulphonate,



separates from water as a crystalline mass, and loses $3H_2O$ at 65°, m. p. 200—210° (decomp.), $[\alpha]_D + 85.94^\circ$. The *d*- α -aminophenylacetic acid obtained from this has $[\alpha]_D + 110.60^\circ$. The *l*- α -aminophenylacetic acid obtained from the mother liquors has $[\alpha]_D - 107.20^\circ$.

Attempts to resolve aminophenylacetic acid by means of bornylamine were unsuccessful, as stable salts are not formed. G. Y.

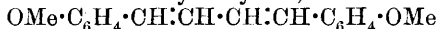
Oxidation of *allo*-Cinnamic Acid. C. N. RIIBER (*Ber.*, 1908, 41, 2411—2416).—The author confirms Fittig and Rür's statement that

careful oxidation of cinnamic acid by dilute potassium permanganate yields the phenylglyceric acid, m. p. 141° (Abstr., 1892, 986), but considers it highly improbable that the substance obtained by Michael from *allo-cinnamic* acid in a similar manner and claimed by him to be the phenylglyceric acid, m. p. 121° (Abstr., 1902, i, 32), can in reality be such, since the method of isolation and the properties of the substance indicate that Michael was dealing with benzoic acid. A repetition of Michael's experiment has resulted in the isolation only of benzoic and oxalic acids.

Phenylglyceric acid, m. p. 121° , is obtained, however, when *methyl allo-cinnamate*, b. p. $49^{\circ}/0.1$ mm., prepared from the silver salt and methyl iodide, is oxidised in alcoholic alkaline solution at -15° to -17° by 0.5% potassium permanganate. C. S.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1908, 41, 1994—1998).—The following substances are mentioned which form liquid crystals concerning which no statement is to be found in the literature of anisotropic liquids.

The anisotropic liquid phase of *p*-methoxycinnamic acid must be conditioned by the group $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot$, since the same phenomenon occurs with dianisyltetraylene,

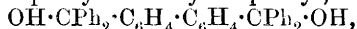


(Fittig and Politis, Abstr. 1890, 770). Several investigators have prepared *p*-methoxycinnamic acid without mentioning the anisotropic character of the liquid form. The substance prepared by Perkin's method has m. p. 170° , the turbid liquid clarifying at 185° . After being heated ten times to 200° , the acid melts at 158° to a clear liquid, but, after purification, again shows its original m. p. and clarifying point (169° and 186° respectively). The ebullioscopic method indicates that *p*-methoxycinnamic acid in nitrobenzene exists in the bimolecular form; in this connexion it is worthy of note that the acid remains unchanged under conditions such as precipitation by water from its solution in cold concentrated sulphuric acid, distillation under ordinary pressure, and deposition by prolonged evaporation in sunlight of its solution in benzene, under which the various forms of unimolecular cinnamic acid and its polymerides, α - and β -truxillic acids, undergo conversion one into another. *p*-Methoxycinnamic acid is not affected by six hours' heating with water or 20% sodium hydroxide at 175 — 180° .

p-Methylaminobenzaldehydephenylhydrazone melts at 170° to a turbid liquid, which becomes clear at 190° ; the corresponding ethyl derivative has 160° and 182° respectively (*Chem. Zentr.*, 1900, i, 1114).

s-Diethylbenzidine has m. p. 115.5° , the milky liquid clearing at 120.5° (Hofman, *Annalen*, 1860, 115, 365; Tichwinski, Abstr., 1904, i, 267).

The cases of 4 : 4'-diphenylbismethyloldiphenyl,



m. p. 160° , clarifying point 186° , and its chloride, m. p. 219° , clarifying point 223° , have not been settled, since the author could not prepare the compounds, and the discoverer, Tschitschibabin (Abstr., 1907, i, 503), could not give a definite opinion.

p-Methoxycinnamaldehyde, $N_2(\text{:CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, obtained from *p*-methoxycinnamaldehyde and hydrazine sulphate in alkaline solution, separates from benzene in yellow crystals and gives a purple-red coloration with concentrated sulphuric acid. It melts at 210° and clarifies at 218° , but, owing to decomposition, the substance resolidifies without becoming turbid.

C. S.

Clear, Transparent, Crystalline Liquids. DANIEL VORLÄNDER (*Ber.*, 1908, 41, 2033—2052).—The view that the optical properties of turbid, crystalline liquids are merely due to suspensions or emulsions is rendered untenable, as it is now shown that perfectly clear, transparent liquids can exhibit similar optical properties, for example, double refraction. Such liquids behave exactly like a thin section of quartz or calcite cut at right angles to the principal axis.

The relationship between constitution and capacity for producing liquid crystals has been further examined (compare Abstr., 1906, i, 317, 1907, ii, 337, 442) by the inclusion of a number of substituted benzylideneamino- α -alkylated cinnamic esters, obtained by condensing the esters of α -substituted cinnamic acids with anisaldehyde, *p*-ethoxybenzaldehyde, and *p*-phenylbenzaldehyde.

[With W. KASTEN.]—The following esters have been examined: *Methyl p*-methoxybenzylideneamino- α -methylcinnamate, monotropic, crystalline liquid, but indication of 2 crystalline liquid phases when sufficiently cooled, m. p. 133° ; *ethyl* ester, 1 enantiotrop. liq. cryst. phase, 2 solid phases, m. p. 89° and 93° ; *n*-propyl ester, enantiotrop. cryst liq., 2 m. p., 50° and 85° ; *n*-butyl ester, monotrop., m. p. 58° ; *isoamyl* ester, monotrop., m. p. 46 — 47° ; active *amyl* ester, 2 or 3 cryst. liq. phases, 1 enantiotrop. and 2 strongly circularly polarising, m. p. 60 — 63° .

Ethyl p-methoxybenzylideneamino- α -ethylcinnamate shows little tendency to form a crystalline liquid, and has m. p. 60 — 61° ; the active *amyl* ester has not been obtained crystalline.

Ethyl p-methoxybenzylideneamino- α -phenylcinnamate does not form a crystalline liquid, and has m. p. 108° .

Methyl p-ethoxybenzylideneamino- α -methylcinnamate, 1 enantiotrop. cryst. liq. and 1 monotrop. cryst. liq. phase, 2 solid phases, m. p. 105° and 147° ; *ethyl* ester, 1 enantiotrop. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, 2 solid phases, indications of a third cryst. liq. phase, transition temperatures 124° , 94° , and 76° ; *n*-propyl ester, 1 enantiotrop. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, m. p. 88° and 121° ; *n*-butyl ester, 2 cryst. liq. phases, enantiotrop. m. p. 55° , 65° , and 82° ; *isoamyl* ester, enantiotrop. cryst. liq., m. p. 83° and 90° ; active *amyl* ester, 3 cryst. liq. phases, 2 enantiotrop. m. p. 86° and 100° .

Ethyl p-ethoxybenzylideneamino- α -ethylcinnamate, 2 monotrop. cryst. liq. phases, both pseudoisotropic, 2 solid phases, transition temperatures 73° , 61° , and 45° ; *n*-propyl ester, monotrop. cryst. liq., m. p. 98° and 63° ; active *amyl* ester, 3 cryst. liq. phases, 2 strongly circularly polarising, m. p. 69° .

Ethyl p-ethoxybenzylideneamino- α -isopropylcinnamate, scarcely crystalline liquid, m. p. 76 — 77° .

Ethyl p-phenylbenzylideneaminocinnamate, 4 cryst. liq. phases, all

enantiotrop., and under certain conditions pseudoisotropic, 1 in needles and 1 in rods, transition temperatures 216° , 207° , 204° , 178° , and 145° ; *n-butyl* ester, 2 cryst. liq. phases, enantiotrop., m. p. 167° and 203° , liquid crystals from aqueous acetone; *isoamyl* ester, 2 cryst. liq. phases, enantiotrop., m. p. 164° , 188° , and 197° , liquid crystals from light petroleum; active *amyl* ester, 2 cryst. liq. phases, enantiotrop., m. p. 115° , 153° , and 180° .

Ethyl p-phenylbenzylideneamino- α -methylcinnamate, 3 cryst. liq. phases, all enantiotrop. and pseudoisotrop., m. p. 120° , 148° , and 175° ; *n-butyl* ester, 2 or 3 liq. cryst. phases, enantiotrop., m. p. 100° , 136° , and 148° ; active *amyl* ester, crystalline resin from aqueous acetone.

Ethyl phenylbenzylideneamino- α -ethyl cinnamate, 2 cryst. liq. phases, monotrop. and pseudoisotrop., 2 solid phases, m. p. 139° ; *n-propyl* ester, 1 enantiotrop. cryst. liq. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, m. p. 118° and 135° ; active *amyl* ester, crystalline resin, clarifies at 118° .

Ethyl p-azocinnamate, 2 enantiotrop. cryst. liq. phases, m. p. 155 — 230° , at least 3 solid phases. *Ethyl p-azo- α -methylcinnamate*, monotrop. cryst. liq., m. p. 112° , 2 solid phases. *Ethyl p-azoxy-cinnamate*, enantiotrop. cryst. liq., m. p. 141° and 250° .

Ethyl p-azoxy- α -methylcinnamate, 2 or 3 enantiomorp. cryst. liq. phases, 3 or 4 solid phases, m. p. between 110° and 140° . *Ethyl β -bromo-p-azoxy- α -methylcinnamate*, 2 pseudoisotrop. cryst. liq. phases, m. p. 110° . *Ethyl p-azoxy- α -ethylcinnamate*, m. p. 85° , scarcely crystalline liquid, and *ethyl p-azoxy- α -phenylcinnamate*, m. p. 154° , scarcely crystalline liquid.

The following general conclusions are drawn:

1. With the lengthening of the alkyl radicle of the CO_2R group, the tendency to form liquid crystals attains a maximum usually at the ethyl or *n*-propyl ester. 2. The radicles methoxyl, ethoxyl, and phenyl in the para-position strengthen the tendency to form liquid crystals; ethoxyl and phenyl have much the same effect, and this is greater than with methoxyl. 3. The tendency for liquid crystal formation is lessened by the introduction of alkyl groups in the α -position and in the order methyl, ethyl, phenyl. 4. The introduction of the optically active amyl radicle converts the crystalline liquid into a strongly circularly polarising condition.

The effect of β -substituents will be studied later. The rotation of some of the amyl esters is enormous. A mixture of amyl anisylideneaminocinnamate and amyl anisylideneamino- α -methylcinnamate in the crystalline liquid state has a rotatory power $+5300^{\circ}$ for sodium light and for a layer 1 mm. thick.

The molecules of the crystalline liquid may be regarded as arranging themselves in wavy rods, in long straight rods, or in short rods at right angles to the plates on which the drops are placed. In the last case, the pseudoisotropic form of Lehmann is obtained. Many of the new esters examined have this form, and are perfectly clear. Frequently when a turbid, crystalline liquid is rubbed with a needle or is pressed between glass plates, it becomes clear, and it is thus possible at will to obtain the clear or turbid, crystalline liquid condition.

Certain esters appear clear when examined in any position; others,

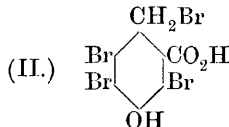
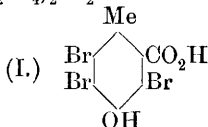
for example, ethyl and active amyl anisylideneaminocinnamate, are clear when examined in light which falls at right angles, but turbid when examined in reflected light or light at any other angle.

The crystalline liquids have been examined in many cases with the aid of the ultra-microscope, and also in converging polarised light. The result of the latter examination is to prove the uniaxial nature of the liquid crystals.

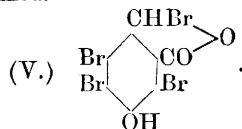
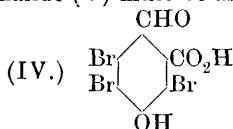
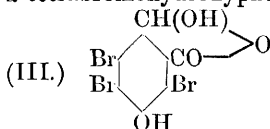
Measurements of the double refraction of many of the liquids have been made; the clear liquid esters of α -alkylated cinnamic acids are about twice as strongly refractive as calcite.

J. J. S.

Hydroxytoluic Acids. II. 4-Hydroxy-*o*-toluic Acid. THEODOR ZINCKE and M. BUFF (*Annalen*, 1908, 361, 218—250).—It was shown previously (Abstr., 1907, i, 132) that 4-hydroxy-*o*-toluic acid forms a tribromo- (I) and a tetrabromo- (II) derivative and a perbromide, $(C_8H_4O_2Br_4)_2Br_2$.

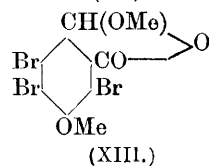
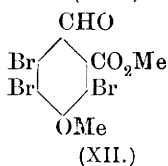
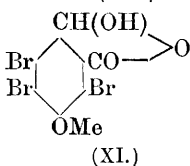
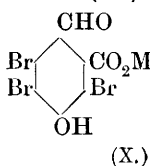
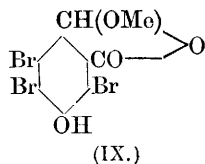
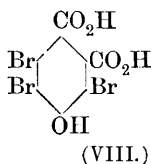
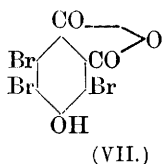
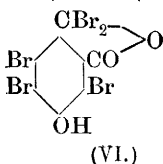


The action of an excess of bromine on the tribromo-derivative led to the formation of a mixture of compounds which could not then be separated. In some experiments, compounds were obtained which contained a smaller amount of bromine than the parent substance, and gave an intense yellow coloration with sodium carbonate. This led the authors to continue the investigation. It is now found that, in addition to the tetrabromo-acid and the perbromide, four new compounds are formed by the action of bromine on the tribromo-acid, the nature of the product depending, not on the excess of bromine, but on the presence or absence of moisture and on the temperature. In absence of moisture, the action of bromine on the tribromo-acid at 130—140° leads to the formation of the tetrabromo-acid and the perbromide, whilst at higher temperatures the product resinifies; but with a limited amount of moist bromine at 130—140°, the tribromo-acid yields a tribromohydroxyphthalide (III) or tribromoaldehydo-acid (IV). The intermediate formation of the tetrabromo-acid and of a tetrabromohydroxyphthalide (V) must be assumed.



Under certain conditions, a pentabromo-derivative (VI) is formed, which is converted by water into tribromo-4-hydroxyphthalic anhydride (VII); this is the chief product when slightly more moist bromine is employed for bromination of the tribromo-acid. The pentabromo-derivative (VI) is readily obtained by the action of bromine on tribromo-4-hydroxyphthalide (III) at 180—185°. Tribromo-4-hydroxyphthalic acid (VIII) is readily obtained from the pentabromo-compound (VI) or the tribromohydroxyphthalic anhydride (VII).

Tribromo-4-hydroxyphthalide (III) yields a diacetyl derivative and a ψ -methyl ester (IX). A normal ester (X) corresponding to this could not be obtained; the silver salt forms with methyl iodide the methyl ether (XI). The silver salt of this ether gives rise to a normal ester (XII) and a ψ -ester (XIII), which is formed also from the ψ -ester (IX).



Tetrabromo-4-hydroxyphthalide (V) could not be obtained free from the aldehyde-acid; the mixture forms crystalline aggregates, m. p. 196°, and, when heated with methyl alcohol and sulphuric acid, yields the ψ -methyl ester of the aldehyde-acid.

The *tribromo-4-hydroxyaldehyde-acid*, (III) or (IV), crystallises from tetrachloroethane in colourless needles, m. p. 238° (decomp.), and, when heated with bromine at 170—175°, yields tribromo-4-hydroxyphthalic anhydride. The *diacetyl* derivative, $\text{OAc} \cdot \text{C}_6\text{Br}_3 \langle \text{CH}(\text{OAc}) \rangle \text{CO} \rangle \text{O}$, formed

by the action of acetic anhydride and sulphuric acid on the aldehyde-acid, crystallises in white leaflets, m. p. 177—178°. The ψ -*methyl* ester (IX), prepared by heating the aldehyde-acid with methyl alcohol and sulphuric acid, forms needles, m. p. 232—233°, gives an intense yellow coloration when heated with phenylhydrazine in acetic acid, but crystallises unchanged on cooling, and forms an *acetyl* derivative $\text{C}_{11}\text{H}_7\text{O}_5\text{Br}_3$, needles, m. p. 179—180°.

The ψ -*dimethyl* ester (XIII), formed by the action of methyl iodide on the silver salt of the ψ -monomethyl ester, or by boiling the corresponding normal ester with methyl alcohol, crystallises in white needles, m. p. 184—185°, gives a yellow coloration when heated with phenylhydrazine in acetic acid, forms the acetyl derivative of the methyl ether when heated with acetic anhydride and sulphuric acid, and is hydrolysed with sodium hydroxide, forming the methyl ether.

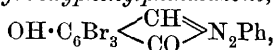
The normal *dimethyl* ester (XII) crystallises from benzene-light petroleum in prisms, m. p. 140—141°, and forms a *phenylhydrazine* derivative, $\text{OMe} \cdot \text{C}_6\text{Br}_3(\text{CO}_2\text{Me}) \cdot \text{CH} : \text{N}_2\text{HPh}$, which crystallises in yellow needles, m. p. 166—167°.

The *methyl ether* (XI), formed by the action of methyl iodide on the silver salt of the aldehyde-acid, or by hydrolysis of the two dimethyl esters, crystallises from benzene in leaflets, m. p. 202—203°, or from dilute methyl alcohol in needles, m. p. 216—218°, and forms an *acetyl* derivative, $\text{C}_{11}\text{H}_7\text{O}_5\text{Br}_3$, prisms, m. p. 188—189°. With phenyl-

hydrazine it forms a *derivative*, $\text{OMe} \cdot \text{C}_6\text{Br}_3 \begin{smallmatrix} \text{CH:N} \\ \text{CO} \cdot \text{NPh} \end{smallmatrix}$, crystallising in colourless needles, m. p. 240—242° (decomp.).

With aniline in hot glacial acetic acid solution, the aldehydo-acid forms an *anilide*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CO}_2\text{H}) \cdot \text{CH:NPh}$, which crystallises in white needles, decomp. above 200°; this forms yellow salts, which are considered to have a quinonoid constitution. The alkali salts are decomposed by water, and form colourless solutions; the *aniline salt*, $\text{O} \cdot \text{C}_6\text{Br}_3(\text{CH} \cdot \text{NHPh}) \cdot \text{CO}_2\text{H} \cdot \text{NH}_2\text{Ph}$, forms a yellow, crystalline mass, and is decomposed by alkalis with formation of aniline.

3 : 5 : 6-Tribromo-4-hydroxyphenylphthalazone,



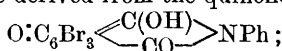
formed from the aldehydo-acid and phenylhydrazine in glacial acetic acid solution, crystallises in white needles, m. p. 224—225°. The acetyl derivative, $\text{C}_{16}\text{H}_9\text{O}_3\text{N}_2\text{Br}_3$, white needles, m. p. 171°.

The *pentabromo-4-hydroxyphthalide* (VI) crystallises from benzene-light petroleum in white leaflets, m. p. 178—179°, and on hydrolysis with alkalis yields tribromo-4-hydroxyphthalic acid. The *acetyl* derivative, $\text{C}_{10}\text{H}_3\text{O}_4\text{Br}_5$, white needles, m. p. 158°. The action of methyl alcohol, aniline, and phenylhydrazine leads to the formation of the derivatives of the tribromo-anhydride.

3 : 5 : 6-Tribromo-4-hydroxyphthalic anhydride (VII) is the final product of the action of moist bromine on tribromo-4-hydroxy-*o*-toluic acid, and is formed also by the action of moist bromine on tribromo-4-hydroxyphthalide, or of dry bromine on tribromo-4-hydroxyaldehydophthalic acid; it crystallises in stout prisms, m. p. 220°, dissolves in acetone or alcohol, forming a slightly yellow solution with fluorescence when dilute, and is slowly hydrolysed by boiling water, forming the corresponding acid. The anhydride forms yellow *alkali* and *aniline*, $\text{C}_{14}\text{H}_8\text{O}_4\text{NBr}_3$, salts, which are considered to have a quinonoid structure; the *pyridine salt*, $\text{C}_{18}\text{H}_6\text{O}_4\text{NBr}_3$, forms yellow crystals, m. p. 215—216°. The *acetyl* derivative, $\text{C}_{10}\text{H}_3\text{O}_5\text{Br}_3$, crystallises in white needles, m. p. 226°.

3 : 5 : 6-Tribromo-4-hydroxyphthalanil, $\text{OH} \cdot \text{C}_6\text{Br}_3 \begin{smallmatrix} \text{C(NPh)} \\ \text{CO} \end{smallmatrix} \text{O}$ or

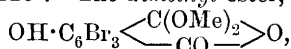
$\text{OH} \cdot \text{C}_6\text{Br}_3 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NPh}$, formed by the action of aniline on the pentabromo- or tribromo-4-hydroxyphthalic anhydride in glacial acetic acid solution, crystallises in yellow needles, m. p. 247—248°, and forms yellow salts, which are derived from the quinonoid form,



the *aniline salt*, m. p. 182—183°. The *acetyl* derivative of the anil, white needles, m. p. 224—225°. *Tribromo-4-hydroxyphthalanilic acid*, $\text{OH} \cdot \text{C}_6\text{Br}_3(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{NHPh}$, formed by boiling the phthalanil with alkalis, is obtained as a white, crystalline powder, m. p. 110—120°, and after resolidification, 240°. The *phenylhydrazone* of tribromo-4-hydroxyphthalic anhydride, $\text{OH} \cdot \text{C}_6\text{Br}_3 \begin{smallmatrix} \text{C(N}_2\text{HPh)} \\ \text{CO} \end{smallmatrix} \text{O}$, crystallises in yellow needles, m. p. 265—266° (decomp.), and with alkalis gives

a yellow coloration and then a colourless solution, which becomes violet and gives a white precipitate with acids.

3 : 5 : 6-*Tribromo-4-hydroxyphthalic acid*, $C_8H_3O_5Br_3$, crystallises in white needles, m. p. 220° , after sintering at 100° , and forms colourless salts with alkalis and aromatic bases. The *methyl hydrogen ester*, $OH \cdot C_6Br_3 \left\langle \begin{smallmatrix} C(OH)(OMe) \\ CO \end{smallmatrix} \right\rangle O$, is formed by the action of a limited amount of methyl alcohol and concentrated sulphuric acid on the anhydride; it crystallises in white needles, m. p. $130-140^\circ$, and after resolidification, 220° . The *dimethyl ester*,



is prepared by the action of methyl iodide on the silver salt of the acid or of the methyl hydrogen ester, or of methyl alcohol on the pentabromo-anhydride; it crystallises in prisms, m. p. 148° , dissolves in alkalis, forming colourless solutions, and yields an *acetyl* derivative crystallising in leaflets, m. p. 124° . G. Y.

Combination of Benzoic Acid with Amines. HANS VON LIEBIG (*J. pr. Chem.*, 1908, [ii], 78, 47—48).—When fused together, benzoic acid and phenols combine to form tritanic acids (this vol., i, 445, 540); in the same manner, benzoic acid combines with amines at $180-200^\circ$, the reaction leading at least in part to the formation of compounds of high molecular weight. Aniline and benzoic acid form a *compound*, $C_{60}H_{49}O_5N_3$, which crystallises from benzene in needles, m. p. 176° , is insoluble in aqueous sodium carbonate, and gives with concentrated sulphuric acid a brownish-red coloration rapidly becoming yellowish-brown. The composition of this product is that of 3 mols. of aminotritanic acid less 1 mol. of water.

Benzoic acid and *o*-toluidine form three *products*, which are insoluble in aqueous sodium carbonate:

(a) $C_{63}H_{55}O_5N_3$, crystallises in needles, m. p. 185° , is readily soluble in alcohol, gives a violet-brown coloration with concentrated sulphuric acid, and corresponds to the compound obtained from aniline.

(b) $C_{63}H_{48}O_3N_3$, crystallises in needles, m. p. 208° , is soluble in boiling alcohol, gives a lemon-yellow coloration with sulphuric acid, and in its composition is equivalent to 3 mols. of aminomethyltritanic acid less 3 mols. of water and 1 mol. of ammonia.

(c) The *lactam* of 2-amino-3-methyltritanic acid,



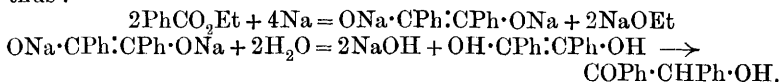
crystallises in needles, m. p. 278° , is insoluble in boiling alcohol, and gives a weak yellow coloration with sulphuric acid. G. Y.

Preparation of Anthroxanic Acid. KALLE & Co. (D.R.-P. 195812. Compare this vol., i, 421).—*o*-Nitromandelic acid or its salts are readily reduced by zinc dust and water even in the absence of ammonium chloride.

The aqueous solution when acidified after reduction yields the

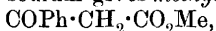
compound (nitrosomandelic acid?) melting at 130—135°; this product when treated with an alkali hydroxide passes into an alkali anthroxanate, which furnishes crystalline anthroxanic acid on treatment with acid. The reduction may be effected with other metals, providing that a temperature of 75° is not exceeded. G. T. M.

Preparation of Benzoylacetic Esters. ANDRÉ WAHL (*Compt. rend.*, 1908, 147, 72—74).—Lœwig and Werdurann (*Ann. Phys. Chem.*, 1855, 50, 95), by the action of sodium on cold ethyl benzoate, obtained a badly-defined, brown, resinous substance, which they called "hypo-benzoylous acid." From this product the author has isolated benzoin, which is probably formed by reactions similar to those observed by Bouveault and Locquin (*Abstr.*, 1905, i, 560) with aliphatic esters, thus:



Accordingly, addition of sodium to a mixture of ethyl acetate and benzoate may give rise to three reactions: (1) the action of sodium on ethyl acetate, giving ethyl acetoacetate; (2) that of sodium on ethyl benzoate, giving benzoin, and (3) that of the metal on the mixture of esters, producing ethyl benzoylacetae. In order that the last reaction shall predominate, it is necessary that the ethyl benzoate shall not come into contact with excess of sodium, whilst the latter must not meet with excess of ethyl acetate. Under these conditions, the yield is better than that obtained by Claisen and Lowman (*Abstr.*, 1887, 583).

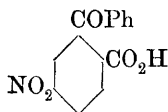
[With YOSHISAKA.]—Condensation of methyl benzoate with methyl acetate in the presence of sodium gives *methyl benzoylacetae*,



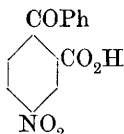
an amber-coloured liquid, b. p. 152°/15 mm., D_4^{20} 1.173, which forms a copper salt as a yellowish-green, crystalline powder, m. p. 200—201°. *Methyl nitrosobenzoylacetae* forms colourless prisms, m. p. 140°; *methyl benzeneazobenzoylacetae*, yellow prisms, m. p. 76°; *methyl p-nitrobenzeneazobenzoylacetae* crystallises in yellow spangles, m. p. 148—149°; the corresponding acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{COPh}$, forms yellow needles, m. p. 225—226° (decomp.). As in the case of the acetylacetic esters (Peters, *Abstr.*, 1890, 1096), higher esters of benzoylacetic acid can be prepared from the methyl derivative by simple displacement. Thus, when methyl benzoylacetae is boiled with excess of isobutyl alcohol, *isobutyl benzoylacetae*, a light yellow liquid, b. p. 160°/12 mm., is formed. E. H.

m-Nitro-o-benzoylbenzoic Acid. JOSEF RAINER (*Monatsh.*, 1908, 29, 431—437).—The condensation of 4-nitrophthalic anhydride with benzene in presence of aluminium chloride was found to lead to the formation of two nitrobenzoylbenzoic acids (this vol., i, 539), one of which is identical with Kliegl's acid (*Abstr.*, 1905, i, 187),

and is therefore 4-nitro-2-benzoylbenzoic acid (I). The isomeride, which is formed in the larger amount, must be 5-nitro-2-benzoylbenzoic acid (II).



(I.)



(II.)

5-Nitro-2-benzoylbenzoic acid crystallises from methyl alcohol in quadratic leaflets containing CH_4O , or from water in needles, m. p. 212° . The *silver* salt, $\text{C}_{14}\text{H}_8\text{O}_5\text{NAg}$, was analysed. The *methyl* ester, prepared by boiling the acid with methyl alcohol and sulphuric acid, crystallises in hexagonal prisms, m. p. $123.5\text{--}124^\circ$, and gives only a faint yellow coloration with concentrated sulphuric acid. The isomeric *psi*-ester (compare Goldschmidt and Lipschütz, Abstr., 1904, i, 168; 1905, i, 132; Meyer, Abstr., 1904, i, 747; 1905, i, 133), obtained by converting the acid into its *chloride* by means of thionyl chloride and treating the product with methyl alcohol in chloroform solution, has m. p. $104\text{--}105^\circ$, and gives an intense, yellow coloration with concentrated sulphuric acid. When heated with concentrated sulphuric acid, 5-nitro-2-benzoylbenzoic acid condenses to 2-nitroanthraquinone (Kliegl, *loc. cit.*).

5-Amino-2-benzoylbenzoic acid, $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}$, formed by reduction of the nitro-acid with ferrous sulphate and ammonia, crystallises in yellow, rhombic needles, m. p. $193\text{--}194^\circ$ (decomp.), or $195\text{--}196^\circ$ in a sealed capillary tube, and forms a crystalline *silver* salt. G. Y.

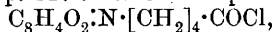
Preparation of Acylbenzoic Acids from Phthalic Anhydride, Hydrocarbons, and Aluminium Chloride. GUSTAV HELLER (D.R.-P. 193961).—The higher hydrocarbons, such as naphthalene or anthracene, do not readily condense with phthalic anhydride in the presence of aluminium chloride, but when allowed to react in the presence of benzene, toluene, or xylene, an excellent yield of naphthoylbenzoic or anthracylbenzoic acid is obtained. The reaction goes in this sense when the calculated amount of higher hydrocarbon is employed, even although the benzenoid hydrocarbon may be in excess. Apparently, naphthalene or anthracene displaces benzene in the additive compound produced from the latter hydrocarbon with phthalic anhydride and aluminium chloride. G. T. M.

Preparation of Methylthiosalicylic [*o*-Methylthiolbenzoic] Acid. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 193800).—By treating sodium dithiosalicylate with methyl sulphate in methyl-alcoholic solution, a poor yield of methyl *o*-methylthiolbenzoate is obtained, but on boiling an alkaline solution of the dithio-acid with sodium methyl sulphate, the reaction only goes as far as the production of the monomethyl derivative. The addition of dilute acid to the solution sets free *o*-methylthiolbenzoic acid, $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, b. p. $168\text{--}169^\circ$. G. T. M.

δ -Aminoketone Derivatives. SIEGMUND GABRIEL (*Ber.*, 1908, 41, 2010—2014. Compare this vol., i, 464, and following abstract).— α - and β -Aminoketones are fairly stable, whereas γ -aminoketones readily lose water, yielding phenylpyrroline derivatives. It is now

shown that δ -aminoketones are also unstable and readily yield anhydro-derivatives.

δ -Phthaliminovaleic acid, $C_8H_4O_2 \cdot N \cdot [CH_2]_4 \cdot CO_2H$, is obtained when ethyl γ -phthaliminomalonate is hydrolysed with hydriodic acid and the resulting acid heated at 168° ; it crystallises from water in rectangular plates, m. p. 117° . The corresponding chloride,



crystallises from light petroleum in snow-white plates, m. p. $78-81^\circ$, and condenses with benzene in the presence of aluminium chloride, yielding δ -phthaliminovaleerophenone, $C_8H_4O_2 \cdot N \cdot [CH_2]_4 \cdot CPh$, which crystallises from alcohol in long, colourless prisms, m. p. $94-95^\circ$.

When hydrolysed with glacial acetic and fuming hydrochloric acids at 138° , the phthaliminoketone yields the anhydride, 2-phenyl-tetrahydropyridine, $CPh \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \text{CH} - \text{CH}_2 \end{smallmatrix} > CH_2$, in the form of an oil, b. p.

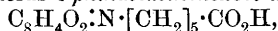
$275-277^\circ/751.5$ mm. It solidifies in a freezing mixture, and has m. p. 18° . The hydrochloride crystallises from fuming hydrochloric acid in colourless needles, m. p. $86-87^\circ$. The platinichloride forms orange-red, hexagonal plates; it sinters at 190° and melts at $191-192^\circ$, and solidifies and melts again at 202° . The aurichloride melts at 118° , after sintering at 110° . The picrate, $C_{17}H_{16}O_7N_4$, crystallises in long, yellow needles, m. p. 181° , after sintering at 160° .

When reduced with tin and hydrochloric acid, the base yields 2-phenylpiperidine. This separates from its aqueous solution in colourless crystals containing $1H_2O$. The hydrate melts at $60-61^\circ$ to a turbid liquid, and, when further heated, loses water and yields the anhydrous base, $C_{11}H_{15}N$, in the form of an oil, b. p. $255-255.5^\circ/767$ mm.

The hydrochloride crystallises in hard needles, m. p. $196-197^\circ$; the platinichloride has m. p. 197° ; the aurichloride has m. p. $159-160^\circ$ and the picrate m. p. $115-116^\circ$. J. J. S.

ϵ -Amino-ketones. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1908, 41, 2014-2017. Compare preceding abstract).— ϵ -Amino-ketones, unlike the corresponding γ - and δ -compounds, appear to be stable; they do not readily form anhydro-derivatives.

Ethyl phthaliminobutylmalonate (Gabriel and Maass, *Abstr.*, 1899, i, 595), when hydrolysed with hydriodic acid and the resulting dibasic acid heated at 160° , yields ϵ -phthaliminohexoic acid,

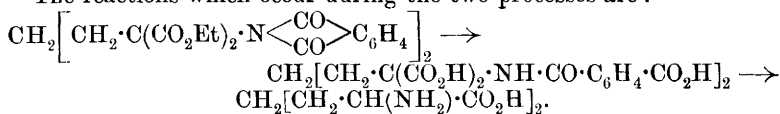


m. p. $107-107.5^\circ$. The corresponding chloride, $C_8H_4O_2 \cdot N \cdot [CH_2]_5 \cdot COCl$, melts at about 60° , and readily yields ϵ -phthaliminohexophenone, $C_8H_4O_2 \cdot N \cdot [CH_2]_5 \cdot CPh$, which crystallises from dilute alcohol in colourless plates, m. p. $90-91^\circ$. When hydrolysed at 138° with acetic and hydrochloric acids, it yields ϵ -aminohexophenone, $CPh \cdot [CH_2]_5 \cdot NH_2$, in the form of an oil. The hydrochloride has m. p. $153-154^\circ$; the platinichloride forms flat plates, and has m. p. 213° (decomp.). J. J. S.

Synthesis of Amino-acids. VIII. Diaminodicarboxylic Acids and Hydroxyamino-acids. SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1908, 56, 250-304).—Fuller details for the preparation of $\alpha\delta$ -diaminoadipic, α -amino- γ -hydroxy-

butyric, and $\alpha\epsilon$ -diaminopimelic acids are given (compare Abstr., 1905, i, 600). A 90% yield of diaminopimelic acid can be obtained by hydrolysing ethyl phthaliminotrimethylenedimalonate with sodium hydroxide and evaporating the product with hydrochloric acid.

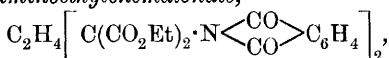
The reactions which occur during the two processes are :



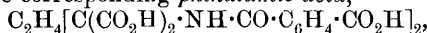
When ethyl diphthaliminoethylenemalonate is used, the first reaction proceeds in a similar manner, and a good yield of the corresponding phthalamic acid, $\text{C}_2\text{H}_4 [\text{C}(\text{CO}_2\text{H})_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}]_2$, is obtained. If this is evaporated with hydrochloric acid, the yield of diaminoadipic acid is small, as secondary reactions occur. The yield can be considerably increased by first heating the hexabasic acid at 100–105° for twenty-four hours, when carbon dioxide and a little phthalic acid are formed, and then hydrolysing with barium hydroxide and evaporating with hydrochloric acid.

In the reaction between ethyl sodiophthaliminomalonate and ethylene bromide, the yield of ethyl diphthaliminoethylenemalonate is small. Among other products formed is the lactone of ethyl phthalimino- β -hydroxyethylmalonate, obtained by the elimination of ethyl bromide from the intermediate product, ethyl phthalimino- β -bromoethylmalonate. The lactone provides a convenient material for the preparation of α -amino- γ -hydroxybutyric acid, which can be isolated in the form of its sparingly soluble benzoyl derivative. The ethyl diphthaliminoethylenemalonate is readily separated from the lactone by shaking with normal sodium hydroxide solution at the ordinary temperature and then for half-an-hour on the water-bath. Under these conditions, the lactone is dissolved, and the solution may be used for the preparation of α -amino- γ -hydroxybutyric acid.

Ethyl diphthaliminoethylenemalonate,



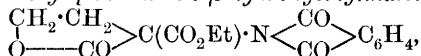
crystallises from benzene in colourless, long, thin prisms or compact crystals, m. p. 209–210°, and is insoluble in water, ether, or light petroleum. The corresponding *phthalamic acid*,



separates from solutions of its sodium salt on the addition of well-cooled hydrochloric acid in the form of compact, rectangular crystals containing $2\text{H}_2\text{O}$. When quickly heated, it has m. p. 240° (decomp.), but also decomposes at 210°.

$\alpha\delta$ -Diaminoadipic acid is practically insoluble in the ordinary neutral solvents, but dissolves in 5*N*-sulphuric or hydrochloric acid; it does not melt at 275°, but, when heated for some time at this temperature, slowly decomposes. Its *dibenzoyl* derivative has m. p. 270–275°, and is sparingly soluble in all ordinary solvents.

The lactone of *ethyl phthalimino- β -hydroxyethylmalonate*,



crystallises from alcohol in flat prisms, m. p. 132°. When the

alkaline solution is evaporated with hydrochloric acid, it yields α -amino- γ -hydroxybutyrolactone, the benzoyl derivative of which has m. p. 145° (compare Fischer and Blumenthal, Abstr., 1907, i, 191). The dibenzoyl derivative of α -amino- γ -hydroxybutyric acid can be obtained from the oily products formed in the preparation of ethyl diphthaliminoethylenemalonate, and has m. p. 210 — 211° .

Ethyl diphthaliminotrimethylenemalonate crystallises from absolute alcohol in flat, lens-shaped needles, m. p. 149° . *ac-Diaminopimelic acid*, $C_7H_{14}O_4N_2$, crystallises from aqueous alcohol in slender needles, it does not melt at 300° , and has no sweet taste. It is readily precipitated by phosphotungstic acid. Its *dibenzoyl* derivative, $C_{21}H_{22}O_6N_2$, crystallises from 25% alcohol in minute needles, m. p. 220° .

The benzoylation of certain aminohydroxy- and diamino-acids has been studied under varying conditions. When an excess of sodium hydroxide is used, so that the liquid during the process is always about $0.5N$ as regards the alkali, it is found that aminohydroxy-acids yield monobenzoyl derivatives only. When, on the other hand, the solution is kept practically neutral, a mixture of mono- and di-benzoyl derivatives is obtained. The benzoyl derivatives of hippuric acid and of diamino-acids are not affected by warming with $N/20$ -sodium hydroxide solution; under the same conditions, the dibenzoyl derivatives of aminohydroxy-acids are hydrolysed to monobenzoyl derivatives.

Monobenzoyl α -amino- δ -hydroxyvaleric acid has been obtained in a crystalline form with m. p. about 170° .

Monobenzoyl α -amino- γ -hydroxyvaleric acid has m. p. about 138° (Fischer and Blumenthal, *loc. cit.*, 121°). Its barium salt is sparingly soluble. J. J. S.

4-Amino-*o*-phthalic Acid and Some of its Derivatives.

MARSTON T. BOGERT and ROEMER REX RENSHAW (*J. Amer. Chem. Soc.*, 1908, 30, 1135—1144).—In an earlier paper (Abstr., 1906, i, 510), methyl 4-aminophthalate and some of its derivatives were described. A description is now given of the acid, its salts, and certain derivatives.

It has been found by Miller (Abstr., 1882, 404) that on reducing 4-nitrophthalic acid with tin and hydrochloric acid and treating the product with hydrogen sulphide, *m*-aminobenzoic acid is produced; this result is now confirmed. The method described by Seidel (Abstr., 1902, i, 160) for preparing 4-aminophthalic acid by reducing the nitro-compound with sodium sulphide does not readily afford a good yield. The acid can be easily prepared, however, by the hydrolysis of the dimethyl ester or of 4-nitrophthalimide.

4-Aminophthalic acid forms colourless, microscopic plates; when heated, it loses water and changes into a yellowish-grey, infusible residue. If the acid is boiled with hydrochloric acid, it is converted into *m*-aminobenzoic acid. On diazotising 4-aminophthalic acid and adding the product to a warm copper potassium cyanide solution, a yellow, granular compound, m. p. 166° (corr.), is produced, which is probably the 4-monoamide of trimellitic acid, and small quantities of another substance, possibly trimellitic acid, are formed simultaneously.

The *hydrochloride* of 4-aminophthalic acid, the *sodium*, *potassium*, *ammonium*, *calcium*, *barium*, *nickel*, *copper*, *lead*, and *silver* salts, and the *mercuric chloride* double salt are described. The *anhydride*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$, obtained by heating the acid at 180—200° for two hours, is a pale salmon-coloured, infusible solid. 4-*Acetylaminophthalic anhydride*, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$, m. p. 206—207° (corr.), obtained by the action of acetic anhydride or acetyl chloride on the amino-acid, forms microscopic needles. 4-*Aminophthalimide*, m. p. 294° (corr.), prepared by reducing 4-nitrophthalimide with stannous chloride, crystallises in golden-yellow needles; its *hydrochloride* forms grey crystals. The *methylimide*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{NMe}$, m. p. 242—243° (corr.), forms yellow crystals; its *hydrochloride* crystallises in plates. 4-*Nitrophthalmethyylimide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{NMe}$, m. p. 179—180° (corr.), forms long, white needles. 4-*Aminophthalanil* has m. p. 205·5° (corr.). The *carbamide* derivative of the methyl ester,

$\text{CO}[\text{NH} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2]_2$,
m. p. 213—214° (corr.), prepared by the action of carbonyl chloride on a pyridine solution of the methyl ester, crystallises in short needles.

Methyl 4-ethyloxalylaminophthalate (Abstr., 1906, i, 510) has m. p. 126° (corr.). Methyl 4-succiniminophthalate,

$\begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} \text{NH} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$,
m. p. 153·4° (corr.), forms large, colourless prisms or needles. Methyl 4-phthaliminophthalate, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$, m. p. 174° (corr.), crystallises in long, colourless needles. E. G.

Constitution of Phthalein Salts. RICHARD MEYER and KARL MARX (*Ber.*, 1908, 41, 2446—2453).—The results published previously (Abstr., 1907, i, 932) have been confirmed. The absorption spectra of aqueous solutions of the sodium salts of phenolphthalein, tetrabromophenolphthalein, quinolphthalein, fluorescein, and eosin have been compared. The curves obtained on plotting the concentrations against the wave-lengths are similar for all five compounds. The conclusion is drawn therefore that the salts of these substances must have a similar quinonoid structure, the difference in colour being merely one of degree.

The *potassium* salt of phenolphthalein, $\text{C}_{20}\text{H}_{12}\text{O}_4\text{K}_2$, forms a deliquescent, deep red mass; the *sodium* salt, $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Na}_2$, is almost black with a metallic glance. W. H. G.

Theory of Indicators. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, 39, 649—650). JULIUS STIEGLITZ (*ibid.*, 651—653).—With reference to this controversy (compare Abstr., 1904, ii, 17; this vol., i, 423), the authors, starting from different points of view, have now come to similar conclusions regarding the theory of indicators. These conclusions have been already put forward (this vol., i, 423). E. G.

Theory of Indicators and the Reactions of Phthaleins and their Salts. II. SALOMON F. ACREE and E. A. SLAGLE (*Amer. Chem. J.*, 1908, **39**, 789—791).—Acree (this vol., i, 423) has stated that the chief source of the colour of salts of the phthaleins is the phenol salt of a quinone compound.

It is now pointed out that Orndorff has obtained coloured salts of trimethylgallein and its tetrachloro-derivative, whilst such substances as phenolphthalein methyl ether and tetrabromophenolphthalein ethyl ether dissolve in alkalis to form colourless solutions. The sodium salt of fluorescein ethyl ether yields an aqueous solution which is much less intensely coloured than are solutions of fluorescein salts. The alcoholic solution of this salt is only faintly coloured at from -15° to 0° , but the colour increases as the temperature is raised to 80° , and decreases again as the temperature is lowered. When this sodium salt is treated with ethyl iodide, it yields a mixture of the colourless phenolic diethyl ether and the coloured quinonoid diethyl ether.

All these facts are discussed in the light of Acree's theory (*loc. cit.*), and are shown to be readily capable of explanation. E. G.

Conversion of Carboxylic Acids into their Aldehydes. GEORG MERLING (*Ber.*, 1908, **41**, 2064—2066).—In the course of his studies on the synthesis of perfumes, the author has repeatedly found it necessary to convert hydroaromatic acids into the corresponding aldehydes. As the reactions employed previously for such conversion give only poor yields and are therefore unsuitable for the purpose, a new method was required. One giving in the case of hydroaromatic acids 50% to 80% yields of the aldehyde has now been found in the following series of changes. The carboxylic acid, $R \cdot CO_2H$, is converted by way of the chloride, $R \cdot COCl$, anilide, $R \cdot CO \cdot NPh$, and phenylimide chloride, $R \cdot CCl : NPh$, into the diphenylamidine, $R \cdot C(NPh) \cdot NPh$, which is reduced by means of sodium and alcohol to the diphenylmethylenediamine, $R \cdot CH(NPh)_2$; this, when heated with dilute mineral acids, is hydrolysed, forming the aldehyde, $R \cdot CHO$, and aniline. The method is less suitable for the formation of aldehydes from aromatic or aliphatic acids; benzaldehyde is obtained from benzoic acid in only a 20% yield, whilst with many aliphatic acids the yield of aldehyde is still smaller. The amount of aldehyde formed appears to depend on the stability of the diphenylmethylenediamine; in many cases, this is decomposed by the reducing agent with formation of the Schiff's base, $R \cdot CH : NPh$, which is then further reduced, and hence does not yield the aldehyde on hydrolysis.

Δ^3 -cycloGeranic acid, $CH \begin{smallmatrix} \diagup CH_2 - CMe_2 \\ \diagdown CH \cdot CHMe \end{smallmatrix} CH \cdot CO_2H$, prepared by fission of water from ketodihydrocyclogeranic acid (*Abstr.*, 1905, i, 349), is obtained in two stereoisomeric forms, m. p. $75-76^{\circ}$ and m. p. $83-84^{\circ}$, which form two *anilides*, m. p. 178° and m. p. $143-145^{\circ}$ respectively. Δ^3 -cycloCitral, $C_{10}H_{16}O$, obtained in a 60—70% yield from the anilide, m. p. 178° , is an oil, b. p. $53-54^{\circ}/4$ mm. or $76^{\circ}/12$ mm., and has a suffocating odour of carvone.

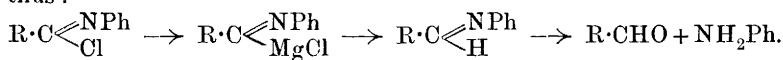
α -cycloGeranic acid yields an anilide, m. p. $157-158^{\circ}$, from which a mixture of α - and β -cyclocitral is obtained in a 60—80% yield. Whilst

the conversion of α -cyclogeranic acid into the aldehyde is thus accompanied by a transmigration of the ethylene linking, β -cyclogeranic acid is converted by way of the *anilide*, m. p. 162°, into β -cyclocitral only.

G. Y.

Transformation of Carboxylic Acids into their Aldehydes.

HERMANN STAUDINGER (*Ber.*, 1908, 41, 2217—2219. Compare Merling, preceding abstract).—Carboxylic acids may be converted into their corresponding aldehydes as follows: the imide chloride is treated with magnesium, whereby a Grignard compound is formed; water decomposes the latter, yielding a Schiff's base, from which the aldehyde is obtained by treatment with dilute hydrochloric acid, thus:



The reaction has been carried through with the imide chloride obtained from benzanilide. The imide chlorides derived from oxanilide and isobutyranilide react with magnesium, but the aldehydes have not been obtained.

The *imide chloride*, $\text{CHMe}_2\cdot\text{CCl:NPh}$, prepared by acting on isobutyranilide with phosphorus pentachloride, is a colourless liquid, b. p. 101—103°/13 mm., which decomposes slowly.

The *imide chloride*, $\text{CHPh}_2\cdot\text{CCl:NPh}$, derived from diphenylacetanilide, forms compact crystals, m. p. 94—95°. W. H. G.

Anisylidene Chloride. HANS SCHMIDT (*Ber.*, 1908, 41, 2331—2332. Compare Hoering and Baum, this vol., i, 527).—*Anisylidene chloride* is probably formed by the action of phosphorus pentachloride on anisaldehyde, but is best prepared by boiling 1 mol. of anisaldehyde with a little more than 1 mol. of thionyl chloride and about an equal volume of benzene for several hours under reflux, with exclusion of moisture. It has m. p. 20°, b. p. 130—132°/13 mm. 134°/14 mm., and is unstable. It is readily hydrolysed by cold water or alcoholic potash with formation of anisaldehyde. J. C. C.

Preparation of Aromatic Hydroxyaldehydes and Partially Alkylated Polyhydroxyaldehydes by Fission of the Corresponding Alkyl Derivatives. CAMILLE DREYFUS (*D.R.-P.* 193958).—The well-known action of aluminium chloride on mixed ethers, such as phenetole, has been examined in the case of aromatic aldehydes containing alkoxy groups, with the result that these substances have been converted into the corresponding hydroxyaldehydes.

Veratraldehyde, when dissolved in benzene or toluene and treated with re-sublimed aluminium chloride, furnishes a mixture of 3-dihydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, and isovanillin.

Anisaldehyde, when similarly treated, yields *p*-hydroxybenzaldehyde. G. T. M.

New Cyclic Ketones. GUSTAVE BLANC (*Bull. Soc. chim.*, 1908, [iv], 3, 780—786).—These ketones were prepared by the process

already given (Abstr., 1907, i, 710), namely, by heating the corresponding substituted adipic or pimelic acid with acetic anhydride and distilling the anhydride first formed. 1:1-Dimethylcyclopentan-5-one, b. p. 143°, prepared from *aa*-dimethyladipic acid (Abstr., 1906, i, 523), furnishes an *oxime*, m. p. 69°, which crystallises from light petroleum. When condensed with benzaldehyde in presence of alcohol and sodium hydroxide, the ketone gives 1:1-dimethyl-4-benzylidenecyclopentan-5-one, m. p. 36°, which separates from light petroleum in bulky crystals. 1-isoPropylcyclopentan-5-one, obtained from isopropyladipic acid (Abstr., 1905, i, 681), yields a semicarbazone, m. p. 199—200° (compare Bouveault and Locquin, this vol., i, 173). 1:1-Dimethylcyclopentan-4-one, b. p. 153—154°, obtained from $\beta\beta$ -dimethyladipic acid, is a mobile liquid, and has an odour of camphor, benzaldehyde, and menthone; its *semicarbazone*, m. p. 178—179°, crystallises from methyl alcohol in colourless needles. 1:1-Dimethylcyclohexan-5-one, obtained from $\beta\beta$ -dimethylpimelic acid (compare Leser, Abstr., 1899, i, 743), gives a semicarbazone, m. p. 203°, which crystallises in colourless needles. The 2-(or 4-)benzylidene derivative of the ketone, m. p. 56°, separates from light petroleum in bulky, nearly colourless crystals. On reduction with sodium and alcohol, the ketone yields the corresponding hexanol (Crossley and Renouf, Trans., 1905, 87, 1487). 1:1:4-Trimethylcyclohexan-5-one semicarbazone (Abstr., 1907, i, 710) crystallises in colourless needles. T. A. H.

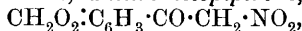
Products of Condensation of *o*- and *p*-Nitrobenzyl Chlorides with Acetylacetone. H. MECH (*Compt. rend.*, 1908, 146, 1409—1411).—The author has prepared derivatives of δ -*p*-nitrophenyl- β -butanone and of di-*o*-nitrobenzylacetylacetone which he described recently (Abstr., 1907, i, 63).

δ -*p*-Nitrophenyl- β -butanone semicarbazone is a white powder, m. p. 198.5°. When δ -*p*-nitrophenyl- β -butanone is reduced with zinc and hydrochloric acid, it yields δ -*p*-aminophenyl- β -butanone as a yellow mass, m. p. about 195° (decomp.). The *semicarbazone* forms colourless crystals, m. p. 153° (decomp.).

From the oil obtained along with di-*o*-nitrobenzylacetylacetone, it was not possible to isolate δ -*o*-nitrophenyl- β -butanone, but the *oxime*, m. p. 97°, and the *semicarbazone*, m. p. 169—170°, were prepared.

J. C. C.

Preparation of ω -Nitroacetocatechol. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 195814).—When piperonaldehyde is treated successively with nitromethane, bromine, methylalcoholic potash, and acids, ω -nitroacetopiperone,



is obtained, yellow leaflets or needles, m. p. 173°. ω -Nitroacetoveratrone, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NO}_2$, needles, m. p. 144°, is produced from veratraldehyde by a similar series of operations. These nitrated ketones, on treatment with aluminium chloride in benzene or toluene, lose their methylene and methyl groups respectively, and give rise to ω -nitroacetocatechol, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NO}_2$, yellow crystals, blackening at 170—180°, and decomposing at 188°. On

reduction, this compound furnishes aminoacetocatechol, which is of importance in connexion with the synthesis of bases of the adrenaline group.
G. T. M.

Identity of Methysticol and Piperonyleneacetone. ERICH WINZHEIMER (*Ber.*, 1908, 41, 2377—2883).—According to Pomeranz (Abstr., 1889, 278; 1890, 257), methysticol, a derivative of methysticin obtained from *Piper methysticum*, is identical with piperonyleneacetone, $\text{CH}_3\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CH:CH:COMe}$, synthesised by Scholtz (Abstr., 1895, i, 469). Pomeranz, however, states that methysticol has m. p. 94° and is readily soluble in alcohol and ether, whilst Scholtz's compound is described as having m. p. 89° and being only slightly soluble in these solvents. The present author, having obtained a quantity of methysticol in the course of other work, has prepared piperonyleneacetone, and on comparison finds the two substances to be identical, having m. p. $89.5\text{--}90^\circ$ separately and when mixed. The phenylhydrazone has m. p. $152\text{--}152.5^\circ$ (141° : Scholtz, *loc. cit.*); the semicarbazone, m. p. $199\text{--}199.5^\circ$; the benzylidene derivative, $\text{C}_{20}\text{H}_{16}\text{O}_3$, golden needles, m. p. $110\text{--}111^\circ$, forms a phenylhydrazone, crystallising in golden needles, m. p. $187.5\text{--}188^\circ$. The piperonylidene derivative, $\text{C}_{21}\text{H}_{16}\text{O}_5$, yellow needles, m. p. 195° .

Dipiperonyleneacetone (piperonylenemethysticol) has m. p. $203\text{--}204^\circ$ ($198\text{--}199^\circ$: Scholtz).

The following derivatives of piperonylacraldehyde were prepared; the m. p. in brackets are those given by Ladenburg and Scholtz (Abstr., 1895, i, 42) or by Scholtz and Kipke (Abstr., 1904, i, 508). The phenylhydrazone, m. p. $163\text{--}164^\circ$ (160°); the semicarbazone, m. p. 234° (226°); *o*-toluidide, m. p. $92\text{--}92.5^\circ$ ($94\text{--}95^\circ$); *p*-toluidide, m. p. $139.5\text{--}140.5^\circ$ (138°); acetophenone derivative, m. p. 137.5° (133°).
G. Y.

Derivatives of Phenyl β -Naphthyl Ketone. GUSTAVE PERRIER and CAILLE (*Bull. Soc. chim.*, 1908, [iv], 3, 736—739).—Phenyl β -naphthyl ketone, regenerated from its additive product with aluminium chloride (Abstr., 1896, i, 353), furnishes (1) an *oxime*, m. p. 133° , which separates from alcohol in colourless, silky crystals and is insoluble in water, soluble in alcohol or toluene, and scarcely so in light petroleum; (2) a phenylhydrazone, m. p. 123° , which forms faintly yellow crystals from alcohol, reddens slightly on exposure to air, is paramagnetic, and gives a green coloration with sulphuric acid, and (3) a semicarbazone, m. p. 175° , which forms colourless crystals from alcohol. On reduction with sodium amalgam in alcohol at 60° , the ketone furnishes phenylnaphthylcarbinol, m. p. 83° , which crystallises from alcohol in colourless, silky needles and is diamagnetic; the benzoyl derivative, m. p. 110° , forms silky needles from alcohol and is diamagnetic. With the exception of the phenylhydrazone, all these derivatives, like the ketone, give red or orange-red colorations with sulphuric acid.
T. A. H.

Preparation of 3:4-Dihydroxyphenylglyoxime and 3:4-Dihydroxyphenylalkylglyoximes. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 195655, 195656, 195657).—When treated with excess of hydroxylamine, preferably on warming, the 3:4-dihydroxyphenyl alkyl ketones of the type $C_6H_3(OH)_2 \cdot CO \cdot CHXR$ (where X is hydrogen or alkyl and R a halogen) give rise to substituted glyoximes having the general formula $C_6H_3(OH)_2 \cdot C(NO\dot{H}) \cdot CX:NO\dot{H}$. These products are of importance as the starting point in the preparation of bases having hæmostatic properties.

3:4-Dihydroxyphenylglyoxime, $C_6H_3(OH)_2 \cdot C(NO\dot{H}) \cdot CH:NO\dot{H}$, white needles, m. p. 185—186°, is produced by warming ω -chloroacetocatechol with an aqueous solution containing hydroxylamine hydrochloride and sodium carbonate. This compound is also produced by the action of hydroxylamine on ω -aminoacetocatechol or dimethyl- or diethyl- ω -aminoacetocatechol. This reaction is especially remarkable, as it does not take place with aminoacetone or the dialkylaminoacetones.

This condensation occurs most readily in dilute acetic acid, and may also be effected with methyl- ω -aminoacetocatechol and piperidylacetocatechol.

4:4-Dihydroxyphenylmethylglyoxime,
 $C_6H_3(OH)_3 \cdot C(NO\dot{H}) \cdot CMe:NO\dot{H}$,
 white needles, m. p. 201—202°.

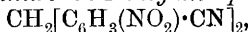
G. T. M.

Constitution of Some Derivatives of Diphenylmethane and Preparation of Some *o*-Diamino-compounds of the Same Series. HENRI DUVAL (*Compt. rend.*, 1908, 146, 1324—1326).—The constitution of acetyldiphenylmethane and dinitrodiphenylmethanedicarboxylic acid, described previously (this vol., i, 277), and of dinitrodiacetyldiphenylmethane is established.

The first compound must be 4-acetyldiphenylmethane, since, on oxidation, it gives benzophenone-4-carboxylic acid. When 2:2'-dinitro-4:4'-diaminodiphenylmethane is converted through the diazo-reaction into the corresponding dinitrile and the latter hydrolysed, the 2:2'-dinitrodiphenylmethane-4:4'-dicarboxylic acid produced is identical with the acid formed by nitrating diphenylmethane-4:4'-dicarboxylic acid.

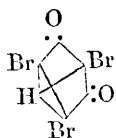
When 4:4'-diacetyldiphenylmethane is nitrated at -10° with colourless nitric acid in the presence of sulphuric acid, 2:2'-dinitro-4:4'-diacetyldiphenylmethane, $CH_2(C_6H_3Ac \cdot NO_2)_2$, is formed in yellowish-white needles, m. p. 151°, which give an *oxime*, m. p. 224°. The position of the nitro-groups in this compound is fixed by the facts that on oxidation by sodium hypobromite and esterification of the resulting acid, the ester produced is identical with that formed by the oxidation of ethyl 2:2'-dinitrodiphenylmethane-4:4'-dicarboxylate, and that 2:2'-dinitrodiphenylmethane-4:4'-dicarboxylic acid is produced by the prolonged action of a mixture of nitric and sulphuric acids on 4:4'-diacetyldiphenylmethane. 2:2'-Diamino-4:4'-diacetyldiphenylmethane is formed by reducing the corresponding dinitro-derivative, and crystallises in yellow needles, m. p. 166°. When 2:2'-dinitro-4:4'-diaminodiphenylmethane is diazotised and treated with

cuprous cyanide, 2 : 2'-dinitro-4 : 4'-dicyanodiphenylmethane,



bright yellow crystals, m. p. 195°, is formed. This on reduction gives 2 : 2'-diamino-4 : 4'-dicyanodiphenylmethane, yellow crystals, m. p. 236°. 2 : 2'-Dinitro-4 : 4'-diacetyldiaminodiphenylmethane, yellow crystals, m. p. 229°, is formed by the action of acetic anhydride on the amine, and when reduced gives 4 : 4'-diacetyl-2 : 4 : 2' : 4'-tetra-aminodiphenylmethane, $\text{CH}_2[\text{C}_6\text{H}_3(\text{NHAc})\cdot\text{NH}_2]_2$, white needles, m. p. 244°. E. H.

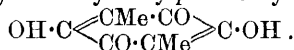
Tribromoresoquinone [*m*-Benzoquinone]. RICHARD MEYER and KURT DESAMARI (*Ber.*, 1908, 41, 2437—2445).—Experiments are being made with the object of preparing simple meta-quinones. The present communication deals with the meta-quinone first described by Liebermann and Dittler (*Journ.*, 1872, 297), namely, tribromoresoquinone. This compound has been carefully analysed and its mol.-wt. determined; the results obtained show definitely that the compound has the molecular formula $\text{C}_6\text{HO}_2\text{Br}_3$, and not the bimolecular formula proposed by Benedikt (*Abstr.*, 1879, 55, 464, 717), and that its chemical properties are best represented by the annexed formula. Tribromoresoquinone possesses the characteristic properties of quinones; thus it liberates iodine from potassium iodide.



It is reduced when treated with hydroxylamine and phenylhydrazine, yielding tetrabromodiresorcinol (compare Benedikt, *loc. cit.*). The results of mol.-wt. determinations agree with the formula $\text{C}_{12}\text{H}_6\text{O}_4\text{Br}_4$ assigned by Benedikt to this compound.

W. H. G.

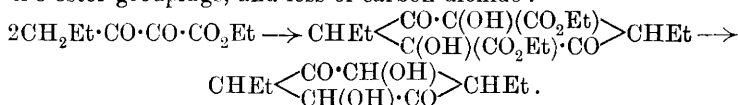
Synthetical *p*-Dialkylated Dihydroxyquinones. FRITZ FICHTER (*Annalen*, 1908, 361, 363—402).—It was shown previously (Fichter and Willmann, *Abstr.*, 1904, i, 678) that certain red, crystalline by-products, obtained when metallic sodium is used instead of sodium ethoxide as the condensing agent in the synthesis of ethyl alkylloxalacetates from ethyl oxalate and esters of monobasic fatty acids, are dihydroxyquinones derived from *p*-dialkylbenzenes. Thus ethyl oxalate and ethyl propionate yield dihydroxy-*p*-dimethylbenzoquinone,



The mechanism of the synthesis has now been studied, and a number of derivatives and hydrolysis products of dihydroxy-*p*-dialkylbenzoquinones are described.

The dihydroxy-*p*-dialkylbenzoquinones cannot be formed by way of the ethyl alkylloxalacetates, since they are obtained only when sodium is employed as condensing agent, whereas the ethyl alkylloxalacetate formation takes place most easily with sodium ethoxide; on the other hand, ethyl oxalate and ethyl acetate do not form a dihydroxybenzoquinone even with sodium. Moreover, whilst the formation of ethyl alkylloxalacetates takes place only with ethyl propionate and ethyl butyrate, and not with ethyl *isovalerate*, dihydroxybenzoquinones are formed, not only from these three esters, but also from ethyl *n*-hexoate, *n*-heptoate, phenylacetate, and hydrocinnamate. According to Claisen's view of the action of sodium on ethyl *isobutyrate* (*Abstr.*, 1897, i, 592),

the first product of the condensation of ethyl oxalate and ethyl butyrate by means of sodium must be an $\alpha\beta$ -diketonic ester, formed according to the scheme: $\text{CH}_2\text{Et}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{C}_2\text{O}_4\text{Et}_2 + \text{Na}_2 = \text{CH}_2\text{Et}\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + 2\text{NaOEt}$. In agreement with this, it is found that the yield of dihydroxyquinone is greater when 1 mol. than when 1 atom of sodium is employed for the condensation of 1 mol. of ethyl oxalate with 1 mol. of ethyl butyrate, whereas 1 atom of sodium suffices for the oxalacetate synthesis with the same amount of two esters. It is considered that the synthesis under discussion takes place by way of the $\alpha\beta$ -diketonic ester, which undergoes ring condensation, hydrolysis of the ester groupings, and loss of carbon dioxide:



1. *Synthesis of Dihydroxy-p-dialkylbenzoquinones*.—[With EUGEN WEISS.]—The following derivatives of dihydroxy-*p*-dialkylbenzoquinones, previously described, have now been prepared.

Dihydroxy-p-xylloquinone diacetate, $\text{C}_{12}\text{H}_{12}\text{O}_6$, crystallises in yellow needles, m. p. $146\cdot5^\circ$, and on reduction with zinc dust and glacial acetic acid yields *tetra-acetoxy-p-xylene*, $\text{C}_{12}\text{H}_{14}\text{O}_6$, crystallising in white needles, m. p. 242° .

Dihydroxy-p-diisopropylbenzoquinone dibenzoate, $\text{C}_{26}\text{H}_{24}\text{O}_6$, crystallises in yellow needles, m. p. 220° .

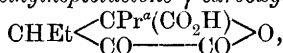
Dihydroxy-p-di-n-butylbenzoquinone, $\text{C}_{14}\text{H}_{20}\text{O}_4$, prepared from ethyl oxalate and ethyl *n*-hexoate, separates from glacial acetic acid in red crystals, m. p. 175° in a sealed capillary tube, forms in aqueous alkalis a violet, in concentrated sulphuric acid a dark blue, solution, and when boiled with aqueous sodium hydroxide undergoes the succinic acid hydrolysis. The *diacetate*, $\text{C}_{18}\text{H}_{24}\text{O}_6$, forms yellow needles, m. p. 60° .

Dihydroxy-p-diphenylbenzoquinone, $\text{C}_{18}\text{H}_{12}\text{O}_4$, prepared from ethyl phenylacetate and ethyl oxalate, forms violet-brown crystals, decomp. $280\text{--}300^\circ$, gives with aqueous alkalis a violet, with concentrated sulphuric acid a brown, coloration, and dyes mordants more feebly than the dialkyl compounds.

Dihydroxy-p-dibenzylbenzoquinone, $\text{C}_{20}\text{H}_{16}\text{O}_4$, prepared from ethyl hydrocinnamate and ethyl oxalate, crystallises in red leaflets, m. p. 225° in a sealed tube, gives colorations similar to those of the preceding substance, and is a strong dye. The *diacetate*, $\text{C}_{24}\text{H}_{20}\text{O}_6$, forms yellow needles, m. p. 182° .

2. *Synthesis of Dihydroxy-p-dialkylquinones*.—[With MAX JETZER.]—Comparative experiments on the influence of different solvents and of different alkyl groups on the formation of dihydroxy-*p*-dialkylbenzoquinones show that better yields are obtained in benzene or toluene than in ethereal solution, that methyl oxalate and methyl butyrate give better yields than the ethyl or *isoamyl* esters, and that ethyl oxalate condensed with methyl *isovalerate* gives a better yield of the dihydroxybenzoquinone than a mixture of the methyl esters, a mixture of the ethyl esters, or a mixture of methyl oxalate with ethyl *isovalerate*. The reaction takes place more easily with the *isovalerate* than with the butyrate.

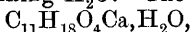
3. *Hydrolysis of Dihydroxy-p-dixyloquinone and Dihydroxy-p-diethylbenzoquinones*.—[With HANS KAPPELER.]—When boiled with sodium hydroxide in aqueous solution, dihydroxy-p-xyloquinone yields *s*-methyl-ethylsuccinic acid, m. p. 178°, and *as*-methylethylsuccinic acid, m. p. 99—100°. These two acids are obtained also by the hydrolysis of α -keto- β -methylhexolactone- γ -carboxylic acid (Fichter and Preiswerk, Abstr., 1902, i, 443) by means of boiling 5% sodium hydroxide. The hydrolysis of dihydroxy-*p*-diethylbenzoquinone in the same manner leads to the formation of *s*-ethylpropylsuccinic acid, $C_9H_{16}O_4$, m. p. 174—175°, which forms a *barium* salt, $C_9H_{14}O_4Ba \cdot H_2O$, and an *ethyl ester*, $C_{13}H_{24}O_4$, colourless oil, b. p. 134—135°/16 mm., and *as*-ethyl-propylsuccinic acid, which crystallises in stellate aggregates, m. p. 97—98°. These ethylpropylsuccinic acids are obtained also by hydrolysis of α -keto- β -ethylheptolactone- γ -carboxylic acid,



which is formed by heating butyrylformic acid with 75% sulphuric acid, crystallises in colourless needles, m. p. 110—111°, and gives an intense red coloration with ferric chloride.

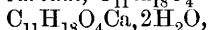
4. *Hydrolysis of Dihydroxy-p-diisopropylbenzoquinone and Dihydroxy-thymoquinone*.—[With HEINRICH GLASER.]—The hydrolysis of dihydroxy-*p*-diisopropylbenzoquinone with boiling dilute sodium hydroxide leads to the formation of two isopropylisobutylsuccinic acids, which are not identical with Beatty's acids (Abstr., 1903, i, 726).

*iso*Propylisobutylsuccinic acid, $C_{11}H_{20}O_4$, m. p. 185—186°, crystallises from hot water in colourless needles, or from cold water separates in crystals containing H_2O . The *calcium* salt,



is colourless. The *anhydride*, $C_{11}H_{18}O_3$, formed by boiling the acid with acetic anhydride, is obtained as a colourless oil, b. p. 150°/12 mm., and when boiled with water yields the acid, m. p. 185—186°.

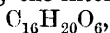
*iso*Propylisobutylsuccinic acid, m. p. 124°, crystallises from water in cubes, is volatile with steam, and can be extracted from the aqueous distillate by ether. The *barium*, $C_{11}H_{18}O_4Ba \cdot 2H_2O$, and *calcium*,



salts were analysed. The *anhydride* is formed when the anhydride of the acid of higher m. p. is distilled under the ordinary pressure; it is a slightly yellow liquid; b. p. 264—265°, and when boiled with water yields the acid, m. p. 124°. When heated with 18% hydrochloric acid at 180—220°, the acid, m. p. 124, is converted into the acid, m. p. 185—186°.

Diethyldiaminothymoquinone, $C_{14}H_{22}O_2N_2$, prepared from ethylamine, forms violet-red needles, m. p. 116°.

On hydrolysis with sodium hydroxide, dihydroxythymoquinone yields two *ethylisopropylsuccinic acids*, $C_9H_{16}O_4$. *Ethylisopropylsuccinic acid*, m. p. 210°, crystallises from water in colourless needles, and forms a *calcium* salt, $C_9H_{14}O_4Ca \cdot H_2O$. This acid can be prepared also by condensation of ethyl ethylmalonate with ethyl α -bromoiso-valerate by means of sodium; the intermediate *ethyl tricarboxylate*,



has b. p. 164°/12 mm.

Ethylisopropylsuccinic acid, m. p. 96°, crystallises in cubes; the calcium salt, $C_9H_{14}O_4Ca, H_2O$, forms long needles.

Dihydroxytoluquinones are best prepared by the action of methylamine on toluquinone and hydrolysis of the tetra-acetate of this, when the resulting tetrahydroxytoluene is rapidly oxidised by air to the dihydroxytoluquinone.

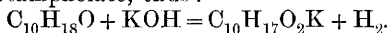
Di-p-methylaminotoluquinone, $NHMe \cdot C_6H_3(O_2Me)_2 \cdot NHMe$, forms a brown, crystalline powder, m. p. 235°. The *tetra-acetate*,

$C_6HMe(OAc)_4$, crystallises in needles, m. p. 198°. This tetra-acetate differs from the dialkylated compounds in that its alkaline solution does not become colourless even on prolonged boiling; the product is a black, syrupy mass, from which a crystalline acid could not be isolated. G. Y.

Preparation of $\alpha\beta$ -Dihydroxyanthraquinones and $\alpha\beta$ -Hydroxyanthraquinonesulphonic Acids. R. WEDEKIND & Co. (D.R.-P. 195874).—The 1:6- and 1:7-anthraquinonesulphonic acids when heated under pressure with water, calcium hydroxide, potassium nitrate, and calcium chloride yield a mixture of 1:6- and 1:7-dihydroxyanthraquinones and an intermediate hydroxy-anthraquinonesulphonic acid. G. T. M.

Preparation of Halogen Derivatives of Benzanthrone, BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 193959. Compare Abstr., 1907, i, 324).—A *bromobenzanthrone*, yellow needles or leaflets, m. p. 170°, is obtained by brominating benzanthrone in acetic acid solution. Chlorination of benzanthrone in the same medium leads to the formation of two dichlorobenzanthrones, which are separated by fractional crystallisation from acetic anhydride, glacial acetic acid, or nitrobenzene; these isomerides crystallise in yellow needles, and melt respectively at 269° and 218°. By chlorinating benzanthrone with potassium chlorate and hydrochloric acid in 50% acetic acid, a *chlorobenzanthrone* is obtained, golden-yellow needles m. p. 176°. *Bromobenzanthronequinoline*, golden-yellow needles, m. p. 298°, is produced by brominating benzanthronequinoline. These products differ from those obtained by condensing the halogenated anthraquinones with glycerol in containing the halogen in the anthrone ring. On oxidation, they furnish anthraquinone-1-carboxylic acid, whereas the former series give rise to the halogen derivatives of this acid. G. T. M.

Direct Transformation of Borneol into Campholic and *iso*Campholic Acids. MARCEL GUERBET (*Compt. rend.*, 1908, 147, 70—72. Compare Abstr., 1901, i, 307.)—When borneol is heated at 250—280° in sealed tubes with recently-fused potassium hydroxide, it is almost completely transformed into a mixture of potassium campholate and *iso*-campholate, thus:



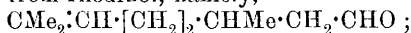
This is probably to be explained by the rupture of one of the rings in borneol in two different ways, one giving campholic, and the other *iso*-campholic, acid. The two acids are readily separated, since the former

is precipitated from its alkaline solutions by carbon dioxide, and, moreover, it is not esterified by hydrochloric acid and alcohol.

The campholic acid obtained has $\alpha + 46.6^\circ$, differing somewhat from the value $+49.8^\circ$ obtained by Montgolfier (Abstr., 1878, 891). From 36 grams of borneol, 26.5 grams of crude campholic acid, 1.10 grams of *isocampholic acid*, 3.30 grams of borneol, and some neutral oily products are obtained. E. H.

Compounds of the Citronella Series. CARL D. HARRIES and ALFRED HIMMELMANN (*Ber.*, 1908, 41, 2187—2199. Compare this vol., i, 714).—An investigation of the ozonides of citronellaldehyde, citronellol, and citronellic acid. These compounds decompose when treated with water, yielding acetone and β -methyladipic acid, except in the case of the ozonide of citronellol, when acetone, but not β -methyladipic acid, is obtained. The quantities obtained are 21, 32, and 52% of acetone, and 0, 35, and 58% of β -methyladipic acid respectively.

The quantities of acetone obtained closely correspond with those of β -methyladipic acid. From these results, the authors consider it highly probable that compounds of the citronella series which have hitherto been regarded as simple substances are mixtures of compounds of the citronella series, $\text{CH}_2\text{:CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\text{R}$, with those of the isomeric rhodina series, $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CH}_2\text{R}$. For example, ordinary citronellaldehyde is probably a mixture of a compound having the formula assigned by Barbier (Abstr., 1897, i, 537) and Harries (Abstr., 1901, i, 730) to citronellaldehyde, namely, $\text{CH}_2\text{:CMe}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$, with a substance having the constitution assigned by Bouveault (Abstr., 1900, i, 452) to the aldehyde derived from rhodinol, namely,



the latter formula was originally given by Tiemann and Schmidt to citronellaldehyde (Abstr., 1897, i, 198). From the quantities of acetone obtained from the various ozonides, it follows that ordinary citronellol contains about 20% of rhodinol, citronellaldehyde about 40% of rhodinaldehyde, whilst citronellic acid contains about 60% of rhodinic acid.

The ketonic substances which would result from the ozonides of the citronella series ($\text{CH}_2\text{:CMe}\cdot\text{CH}_2\ldots$) on treatment with water, namely, $\text{X}\cdot\text{CH}_2\cdot\text{OH}$ from citronellol, $\text{X}\cdot\text{CHO}$ from citronellaldehyde, and $\text{X}\cdot\text{CO}_2\text{H}$ from citronellic acid, where $\text{X} = \text{Me}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2-$, were not isolated.

This assumption explains why Tiemann and Schmidt (*loc. cit.*) obtained only 50% of *isopulegol* on treating the aldehyde with acetic anhydride, and why only one-half of the citronellaldimethylacetal when oxidised with potassium permanganate is converted into the dimethylsemiactal of β -methyladipic acid (Harries and Schauwecker, Abstr., 1901, i, 448).

The compound obtained by acting on citronellaldehyde with ozone is an *ozonide peroxide*, $\text{C}_{10}\text{H}_{18}\text{O}_5$ (compare Langheld, Abstr., 1906, i, 226); it is converted by sodium hydrogen carbonate solution into the normal *ozonide*, $\text{C}_{10}\text{H}_{18}\text{O}_4$. The *ozonide*, $\text{C}_{10}\text{H}_{18}\text{O}_6$, obtained by passing

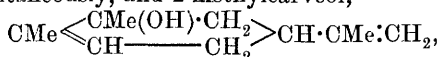
ozone into a solution of the aldehyde in carbon tetrachloride, is a non-explosive, colourless, syrupy liquid with an unpleasant odour.

An *ozonide peroxide* of citronellic acid, $C_{10}H_{18}O_6$, is formed when ozone is passed into a solution of the acid in carbon tetrachloride until the solution no longer decolorises a solution of bromine in acetic acid. It is a slightly explosive, colourless, viscid liquid, which, when treated with water, yields an *ozonide*, $C_{10}H_{18}O_5$. An *ozonide*, $C_{10}H_{18}O_7$, is obtained by passing ozone into the solution in carbon tetrachloride until the latter becomes blue; it is similar in properties to the ozonide peroxide. An *ozonide* of citronellol, $C_{10}H_{20}O_6$, is obtained by passing ozone into a solution of citronellol in carbon tetrachloride; it is a non-explosive, colourless, viscid liquid.

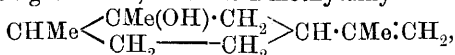
W. H. G.

A Hydrocarbon from *iso*Pulegone. HANS RUPE and A. EBERT (*Ber.*, 1908, 41, 2067—2071).—The action of magnesium methyl iodide on *isopulegone* leads to the formation of a tertiary alcohol which loses water with moderate ease. It has been found previously (*Abstr.*, 1906, i, 374; this vol., i, 433, 556) that the stability of tertiary alcohols of this series depends on the relative position in the molecule of the carbinol group and an ethylene linking, the loss of water taking place the more readily the nearer these are together.

Thus 3-methylpulegol, $CHMe \begin{smallmatrix} \text{CH}_2 \cdot CMe(OH) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} > C : CMe_2$, and 2-methylcarvenol, $CHMe \begin{smallmatrix} CMe(OH) \cdot CH \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} > CPr^3$, cannot be isolated, as they lose water spontaneously, and 2-methylcarveol,



loses water with great ease, whereas 2-methyldihydrocarveol,



and homothujyl alcohol, $CHMe \begin{smallmatrix} CMe(OH) \cdot CH_2 \\ CH \text{---} CH_2 \end{smallmatrix} > CPr^3$, which does not contain an ethylene linking, are stable, and lose water only with great difficulty. Hence it is considered that the new tertiary alcohol is

3-methylisopulegol, $CHMe \begin{smallmatrix} CH_2 \cdot CMe(OH) \\ CH_2 \text{---} CH_2 \end{smallmatrix} > CH \cdot CMe : CH_2$. The

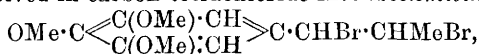
hydrocarbon formed from this by loss of water must be 3-methyl- $\Delta^{2,8(9)}$ -menthadiene, $CHMe \begin{smallmatrix} CH : CMe \\ CH_2 \text{---} CH_2 \end{smallmatrix} > CH \cdot CMe : CH_2$, as the molecular refraction approximates closely to the calculated, which excludes the possibility of the presence of conjugated ethylene linkings. The substances described may, however, be mixtures of isomerides (compare Wallach, this vol., i, 402).

3-Methylisopulegol, $C_{11}H_{20}O$, is a mobile oil, b. p. 93—94°/12 mm., D^{20}_D 0.9108, n_D^{20} 1.4699, $[\alpha]^{20}_D$ 19.54°, has an odour resembling geraniol, and, on treatment with phosphorus trichloride in ethereal solution, yields 3-chloro-3-methyl- $\Delta^{8(9)}$ -menthene, $C_{11}H_{19}Cl$, which is obtained as a mobile, colourless oil, b. p. 92—93°/10 mm., gradually decomposing at the ordinary temperature.

3-Methyl- $\Delta^{2,8(9)}$ -menthadiene, $C_{11}H_{18}$, prepared by heating the preceding chloro-compound with potassium acetate in alcoholic solution, or by converting the tertiary alcohol into its *acetyl* derivative and distilling this under the ordinary pressure and again over sodium, forms a mobile liquid having a slight odour of menthene. Of the following physical constants, the first series is those obtained with the hydrocarbon prepared from the chloro-compound, and the second with that from the acetyl derivative, b. p. 180—185°/750 mm. or 95—97°/12 mm., D^{20}_D 0.8401, n^{20}_D 1.4734, $[\alpha]^{20}_D + 29.00^\circ$; b. p. 182—184°/750 mm. or 95—97°/12 mm., D^{20}_D 0.8400, n^{20}_D 1.4724, $[\alpha]^{20}_D + 46.27^\circ$.

G. Y.

Components of Ethereal Oils. Establishment of the Constitutional Formulæ of Elemicin and *iso*Elemicin. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 2183—2187).—Elemicin (compare this vol., i, 557) is definitely shown to be 3:4:5-trimethoxy-1-allylbenzene; *isoelemicin* is therefore 3:4:5-trimethoxy-1-propenylbenzene. Elemicin, obtained by fractional distillation from the ethereal oil, has been further purified by treatment with concentrated formic acid; it then has b. p. 144—147°/10 mm., D^{20}_D 1.063, n_D 1.52848. *iso*Elemicin, obtained from elemicin purified in this manner, has b. p. 153—156°/10 mm., D^{20}_D 1.073, n_D 1.54679. It is converted by bromine dissolved in carbon tetrachloride into *isoelemicin dibromide*,



forming crystals, m. p. 89—90°.

W. H. G.

Preparation of Santalyl Camphorate. J. D. RIEDEL (D.R.-P. 193960).—*Santalyl camphorate*, yellow oil, D 0.9945/24°, is produced by heating methyl camphorate with 2 to 4 parts of santalol, or the corresponding amount of sandal-wood oil at 150—200° for several hours. The excess of santalol, or oil, is expelled in steam, and the new ester is obtained from the residue.

G. T. M.

Reduction of Aliphatic Terpene Compounds. C. J. ENKLAAR (*Ber.*, 1908, 41, 2083—2087).— $\beta\zeta$ -Dimethyloctane (Willstätter and Mayer, this vol., i, 383) is obtained by reduction of ocimene (van Romburgh, *Abstr.*, 1901, i, 220), geraniol, or linalool with hydrogen in presence of nickel at 130°. When reduced with sodium and alcohol, and thereafter treated with bromine, ocimene and myrcene yield the same *dihydro-ocimene tetrabromide*, m. p. 88°. Hence ocimene, *allo-ocimene*, and myrcene are derivatives of the same decane. A comparison of the properties of $\beta\zeta$ -dimethyloctane obtained with those of Willstätter and Mayer's preparation shows that, whilst ocimene does not contain cyclic terpenes, myrcene cannot be freed from these.

Reduction of geraniol with limited amounts of hydrogen leads to the formation of decanol (Willstätter and Mayer, *loc. cit.*), together with a cyclic alcohol, $C_{10}H_{20}O$, D^{15}_D 0.906, which yields a *phthalate*, m. p. 169—170°, and is therefore not identical with *r*-menthol or thymomenthol, and considerable amounts of a *product*, $C_{31}H_{57}O$, b. p. 192—194°/22 mm., D^{15}_D 0.8500, n^{19}_D 1.4564.

G. Y.

Phellandrene from Water Fennel Oil. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1908, [ii], 78, 42—46).—It has been shown previously that the so-called natural phellandrene, obtained from water fennel oil, consists of a mixture of a phellandrene and at least 20% of pinene, which, on treatment with hydrogen chloride, forms *d*-bornyl chloride, dipentene dihydrochloride, and a mixture of liquid hydrochlorides. These when treated with alcoholic potassium hydroxide yield Kindt's camphor and a hydrocarbon containing small amounts of dipentene (Abstr., 1907, i, 329, 712, 713). These various products have now been further investigated. It is found that, on treatment with hydrogen chloride in various solvents, natural phellandrene yields *d*-bornyl chloride, with or without small amounts of dipentene dihydrochloride, formed from pinene, and an unsaturated monohydrochloride, sometimes together with a stable, liquid dihydrochloride, formed from the phellandrene. An optically inactive hydrocarbon, b. p. 177—182°, D^{15}_D 0.848, n_D 1.47877, containing possibly traces of camphene and dipentene, is obtained from the monohydrochloride and from the stable dihydrochloride. This hydrocarbon resinifies rapidly on exposure to air, and forms a liquid nitrite, liquid bromide, and liquid dihydrochloride. As the hydrochlorides of pinene have smaller rotatory powers than the hydrocarbon, and as natural phellandrene yields bornyl chloride with $[\alpha]^{17.5}_D + 28.3^\circ$, the pinene contained in natural phellandrene must have a rotatory power not less than 35° , whilst the hydrocarbon, ψ - or β -phellandrene, must boil above 173° , have a density less than 0.858, and be optically inactive. The constitutions of α - and β -phellandrene remain to be determined.

G. Y.

Ethereal Oils. HEINRICH HAENSEL (*Chem. Zentr.*, 1908, i, 1837; from *Geschäftsber.*, October, 1907, March, 1908).—*Acaroid resin oil* is reddish-brown in colour, and in odour resembles tolu- and peru-balsam, D^{20} 0.9600, $\alpha_D \pm 0^\circ$, acid number 4.7, ester number 37.5. *Birch-leaf oil*, yellow in colour and solid at the ordinary temperature, D^{80} 0.8683, acid number 30, ester number 81, and from which a paraffin was obtained crystallising in leaflets, m. p. 49—50°. *Coriander oil* free from terpene has D^{15} 0.8786, $\alpha_D + 9.5^\circ$, ester number 13.3. *Oil of Cubebs*, obtained from cubeben, D 0.941, $\alpha_D - 13.55^\circ$. *Guaiacum resin oil* is a dark brown, aromatic-smelling oil, which is not completely soluble in 96% alcohol, D^{15} 0.9417, acid number 77, ester number 13.8, and when warmed with ammoniacal silver solution gives a silver mirror. *Rock-rose oil*, obtained from the dried plant, is dark brown and has an unpleasant odour, D^{21} 0.9296, acid number 0, ester number 111; it contains neither aldehyde nor ketone. *Laurel-leaf oil* has D 0.9361, $\alpha_D - 15.95^\circ$, and, besides *l*-pinene, probably contains some phellandrene. *Celandine oil*, from the dry plant, is brown and has a pleasant odour; it solidifies at 30° , and has D^{40} 0.9374. *Oil of Frankincense*, $D^{17.5}$ 0.8810, $\alpha_D + 22.08^\circ$, acid number 2, ester number 15.5, contains an alcohol, $C_{26}H_{44}O$. *Olibanol*, which is a thick, yellow oil, b. p. 205—212°, D^{20} 0.9570, $\alpha_D - 65.05^\circ$.

J. V. E.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Zentr.*, 1908, i, 1838—1840; from *Geschäftsber.*, April 1908. Compare Abstr., 1907, i, 782—783).—Ayapana oil has D^{15} 0.9806, $\alpha_D + 2.92^\circ$, acid number 5.5, ester number 5.9; the yield of this oil from the leaves of *Eupatorium triplinerva* from Ceylon, 1.14%. A fraction obtained from camphor oil, b. p. 175.5—177°/763 mm., D^{15} 0.8470, $\alpha_D + 39.77^\circ$, contained a considerable quantity of *d*-limonene with dipentene. Oil of lemon from Java may occasionally be dextrorotatory up to $+1.77^\circ$; an oil not differing in properties from Java oil of lemon had D^{15} 0.9058, $\alpha_D + 0.17^\circ$, a total content of 79.7% ($C_{10}H_{18}O$), and was soluble in 1 vol. 80% alcohol. Oil of bergamot from Ischia Island does not differ from the ordinary commercial oil from Messina; it is brownish-green in colour and strong smelling, D^{15} 0.8828, $\alpha_D + 13^\circ$, acid number 1.8, ester number 96.4, and corresponds with 33.7% linalyl acetate; non-volatile residue, 5.2%. A small quantity of oil (yield, 2.94%) distilled from the seeds of *Heracleum giganteum* had the following constants: D^{15} 0.8738, $\alpha_D + 1^\circ$, n_D^{20} 1.42402, acid number 3.7, ester number 281.9, after acetylation 311.8, and dissolved in 1.2 vols. 80% alcohol. Kobuschi oil from the young twigs and leaves of *Magnolia Kobus* had D^{15} 0.9451, $\alpha_D - 1.5^\circ$, acid number 0.7, ester number 4.3, and contained citral and cineol together with about 16% anethole and probably also methylchavicol.

Oil from *Lavandula stoechas* contains *d*-fenchone and *d*-camphor. A sample of *Niaouli* oil (from *Melaleuca viridiflora*) obtained from New Caledonia was pale lemon-yellow in colour, smelling strongly like eucalyptol, and had D^{15} 0.9284, $\alpha_D - 1.17^\circ$; it contained about 40% cineol. Oil of Savin does not contain pinene, thus enabling any adulteration with turpentine oil to be detected.

Canadian Snakeroot oil, from the air-dried disintegrated root of *Asarum canadense* (Indian ginger root, wild ginger), yields 3.36% of a yellowish-brown aromatic oil, D^{15} 0.9508, $\alpha_D - 22^\circ$, n_D^{20} 1.48537, acid number 3.7, ester number 115.9, after acetylation 140.1, soluble in 2.7 vols. and more of 70% alcohol. The oil obtained from the root without the fibre (yield, 3.83%) is purer yellow in colour, and has D^{15} 0.9516, $\alpha_D - 2.83^\circ$, n_D^{20} 1.48508, acid number 3.7, ester number 117.6, after acetylation 137.2, and it dissolves in 2.3 vols. 70% alcohol. The oil from the fibre of the root (yield, 1.20%) had D^{15} 0.9659, $\alpha_D - 39.66^\circ$, n_D^{20} 1.50280, acid number 2.2, ester number 39.2, after acetylation 110.2, and is not soluble in 10 vols. 70% alcohol, but soluble in 0.9 vols. 80% alcohol.

The residue obtained from the purification of American turpentine oil gives, when fractionated, portions which are rich in β -pinene, especially the fraction, b. p. 164—166°.

American Wormseed oil (from *Chinopodium ambrosioides* var. *anthelminticum*) has D 0.96—0.98, and dissolves in 10 vols. 70% alcohol to a clear solution; oils have, however, for some time been met with having D 0.93—0.95, which are only soluble in 80% alcohol, the difference in properties being caused by a slow distillation process. It is advised to distil at a moderate rate and to employ only the seeds of the plant; the plant free from seeds gives no oil. A careful investigation of this oil showed D^{15} 0.9768, $\alpha_D - 4.5^\circ$, n_D^{20} 1.47850, acid number

0, saponification number 8.4, after acetylation 280.1, and it was soluble in 4 vols. 70% alcohol. The acetylated oil was heavier than water, and had a strong scent similar to spearmint. Small quantities of a terpene, probably silvestrene, *p*-cymene, and also *d*-camphor have been found in the oil; the chief constituent, however, is a repugnant-smelling substance, *ascaridol*, $C_{10}H_{16}O_2$, b. p. $83^{\circ}/4-5$ mm., D^{15}_D 1.0079, $\alpha_D - 4.25^{\circ}$, n^{20}_D 1.47431. Towards reagents which show alcoholic, aldehydic, ketonic, or phenolic characters, this substance is quite indifferent only with 50% resorcinol solution does it give, at the ordinary temperature, an unstable liquid compound, which when heated to $130-150^{\circ}$ decomposes with explosive violence. It appears that at 150° a transformation takes place; the product purified by vacuum distillation had b. p. $98.5-99.5^{\circ}/4.5$ mm., D^{15}_D 1.0266, $\alpha_D \pm 0^{\circ}$, n^{20}_D 1.46545, and had a similar composition to that given above. Ascaridol reacts violently with concentrated formic acid, giving cymene, but less readily with alcohol, potassium hydroxide, or zinc chloride; zinc dust and acetic acid give cymene and probably also carvenone. Oxidation with potassium permanganate (1% solution) gives an acid mixture in which, besides formic, acetic, and isobutyric acids, a higher boiling liquid acid is obtained ($C_{10}H_{16}O_4$), b. p. $80-81^{\circ}/5$ mm., D^{15}_D 1.0641, $\alpha_D \pm 0^{\circ}$, n^{20}_D 1.44388, which when heated to $120-130^{\circ}$ gives methylheptenone. The transformation product of ascaridol decomposes when boiled with water, and gives with zinc dust and acetic or formic acid no cymene, but with the latter a ketone, $C_8H_{14}O$, semicarbazone, m. p. $194-195^{\circ}$. Normal American oil (D^{15}_D 0.9708) contains 62-65% of ascaridol and about 22% of cymene, but light oil (D^{15}_D 0.9426), only 45-50% of ascaridol.

Hyssop oil, from dried flowering plants, had D^{15}_D 0.9377, $\alpha_D - 22.5^{\circ}$, acid number 1.8, ester number 5.8, after acetylation 44, and is soluble in about 6 vols. 80% alcohol with separation of paraffin. From withered flowering plants, the oil had D^{15}_D 0.9322, $\alpha_D - 22.4^{\circ}$, acid number 1.3, ester number 3.6, after acetylation 37.3, n^{20}_D 1.48315, and is soluble in about 8 vols. 80% alcohol with separation of paraffin. Very faded flowering plants yielded an oil, D^{15}_D 0.9336, $\alpha_D - 20.43^{\circ}$, n^{20}_D 1.48441, acid number 1.8, ester number 3.1, and is soluble in about 7 vols. 80% alcohol with separation of paraffin; the last oil appears to contain β -pinene, *l*-pinocamphone, and a very small quantity of an alcohol, b. p. $221-222^{\circ}$. The higher boiling portions of this oil are probably sesquiterpenes. A beautiful crystalline *dibromide* has been obtained from *l*-pinocamphone, m. p. $93-94^{\circ}$, which gives in alcohol solutions an alcohol of camphor-like odour, m. p. $67-68^{\circ}$, b. p. $217-218^{\circ}$. When reduced or oxidised, it yields *l*-pinonic acid, $C_{10}H_{16}O_8$, m. p. $69.5-70.5^{\circ}$, but when oxidised by sulphuric acid, *l*-menthoethylheptanonolide, m. p. $46-47^{\circ}$, is produced.

The following oils from Mayotte are described for the first time: Two *Basilicum* oils, one of which contains eugenole, whilst the other, from *B. canum* (*Ocimum canum*), contains a considerable quantity of *d*-camphor; also an oil from Mexico from the leaves of *Schinus molle*, a colourless oil, D^{15}_D 0.8583, $\alpha_D + 44.83^{\circ}$, ester number 7.2; that from the fruit was pale yellow, D^{15}_D 0.8600, $\alpha_D + 42.5^{\circ}$, ester number 25.2, after acetylation 56.5; both these oils give strong phellandrene reactions.

Oil from the leaves and flowers of Buddleia perfoliata from Mexico : a pleasant, although peculiar, smelling pale yellow oil, $D_{20}^{25} 0.8862$, $n_D^{25} - 25^\circ$, acid number 0.6, ester number 8.1.

Oil from Vitex agnus castus.—The leaves of this plant give 0.48% of a brown oil, which has an odour resembling hyssop, $D_{20}^{25} 0.9010$, $n_D^{25} 7.92^\circ$, acid number 6.4, ester number 18.3, after acetylation 58.4; it contained cineol and probably sabinene. J. V. E.

Transformations of Chlorophyll under the Influence of Acids. LAD. HILDT, LEON MARCHLEWSKI, and J. ROBEL (*Bull. Acad. Sci. Cracow*, 1908, 261—296. Compare Willstätter and Hocheder. Abstr., 1907, i, 784).—The conclusion is drawn that chlorophyllan, phaeophytin, and phyllogen are identical. The two last are obtained by the action of acids on chlorophyll at low temperatures and as a rule contain no phyllocyanin or other decomposition product which is not extracted from the ethereal solution by 15% hydrochloric acid. Phaeophytins containing strongly basic products have been obtained, for example, from Acacia leaves. Chlorophyllan is usually obtained at higher temperatures, and can therefore contain decomposition products, but phyllogens have been prepared which react with 15% hydrochloric acid in exactly the same manner as chlorophyllans, and thus the chief difference between the two groups is removed. J. J. S.

Conversion of Phyllotaonin into Phytorhodins. T. KOŹNIEWSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 247—261; *Biochem. Zeitsch.*, 1908, 10, 472—485).—It is shown by means of spectroscopic measurements that allophyllotaonin is converted, under the influence of acids at high temperatures, into substances which are identical with Willstätter and Mieg's phytorhodins (Abstr., 1907, i, 69). The conversion of alkachlorophyll into these compounds thus takes place in two stages, the intermediate product being allophyllotaonin. Phyllotaonin and allophyllotaonin are much more closely related to alkachlorophyll than are the phytorhodins.

A very marked difference exists in the behaviour of phyllotaonin and the phytorhodins towards alkalis at high temperatures. Phyllotaonin is the best source for the preparation of phylloporphyrin, whereas phytorhodins do not yield this compound when heated with alkali at 200° under pressure. J. J. S.

Phaeophytin and Chlorophyllan with some Concluding Remarks on Phylloxanthin. M. TSVETT (*Biochem. Zeitsch.*, 1908, 10, 404—413).—The dark green precipitate which is formed from chlorophyll solutions by the addition of organic acids or of traces of hydrochloric acid (Tschirsch's chlorophyllan, Willstätter's phaeophytin) is a mixture of the immediate products formed by the action of acid on chlorophyll, that is, a mixture, according to the author, of the already described α - and β -chlorophyllans; at any rate, it can by the absorption-analysis method be separated into constituents with the same spectroscopic properties and chemical reactions. By throwing it into Frémy's diphasic ethyl ether hydrochloric acid mixture, it gives the so-called phylloxanthin, which is apparently unchanged

β -chlorophyllan and remains in ethereal solution, and the so-called phyllocyanin, which is not unchanged α -chlorophyllan, but a mixture that can be resolved into its components by Willstätter's method of acid fractionation. S. B. S.

The Nature of the So-called Crystallisable Chlorophyll ("Metachlorophyllin"). M. TSVETT (*Biochem. Zeitsch.*, 1908, 10, 414—425).—The so-called "crystallisable chlorophyll" (α -metachlorophyllin) is not a natural constituent of chlorophyll, but an artifact, which is formed by the slow extraction of plants, and is formed from the genuine chlorophyllin under the influence of some unknown factor in the cell mechanism. Chlorophyll extracts immediately after preparation are free from this substance. In its spectrum, it combines the bands of both chlorophyllins (α and β), and must be considered as derived from both. S. B. S.

A New System of the So-called Chlorophyll Derivatives. M. TSVETT (*Biochem. Zeitsch.*, 1908, 10, 426—429).—According to this system there are two main constituents of chlorophyll extract, namely, α -chlorophyllin and β -chlorophyllin. By the action of alkalis at low temperatures they yield respectively α - and β -chlorophyllic acids. The former of these, on treatment with alkali at 200°, yields Willstätter's rhodophyllin (from which by the action of acids alloporphyrin is obtained), whereas the latter under the same conditions yields phylloporphyrin. On treatment with weak acids, α -chlorophyllin yields chlorophyllan, from which, by the action of strong acids, Schunck's phyllocyanin is obtained. This on further treatment by acid, yields Willstätter's phytochlorins and phytorhodins. β -Chlorophyllin, on treatment with weak acids, yields β -chlorophyllan (Tschirch and Schunck's phylloxanthin), from which by more energetic hydrolysis the phytochlorins and phytorhodins are obtainable. These latter substances are obtainable directly from chlorophyllic acid by energetic hydrolysis. S. B. S.

Theory of Mordant Dyes. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2245—2246).—Polemical. A reply to Liebermann (this vol., i, 441). W. R.

Theory of Mordant Dyes. ALFRED WERNER (*Ber.*, 1908, 41, 2383—2386).—A reply to Liebermann (this vol., i, 441). G. Y.

Blue Erythrosin Silver. LÜPPO-CRAMER (*Zeitsch. Chem., Ind. Kolloide*, 1908, ii, 325—326).—When silver nitrate is added to an excess of a dilute solution of erythrosin, a much more intensely coloured colloidal solution of the silver salt of erythrosin is obtained. The colour of the colloidal solution is distinctly more blue than the original. On boiling or on keeping for some time, the solution becomes opalescent, and the erythrosin silver compound, which has a pure blue colour, gradually separates.

The same thing can be observed in the presence of silver bromide or

chloride, which act as protective colloids. The separated erythrosin silver compound when shaken up with water forms a very fine suspension, which can be filtered through paper without leaving a residue.

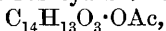
Fluorescein, dibromofluorescein, eosin, and tetraiododichlorofluorescein behave differently from erythrosin; the colloidal solutions of the silver salts in presence of colloidal silver bromide appear to be quite stable.

H. M. D.

Rosocyanin. LATHAM CLARKE and C. LORING JACKSON (*Amer. Chem. J.*, 1908, **39**, 696—719).—Rosocyanin, the red colouring matter produced in the well-known test for boric acid with turmeric paper, has been studied by Schlumberger (*Bull. Soc. chim.*, 1866, [ii], **5**, 194) and by Ivanow-Gajewski (this Journ., 1873, 504, 760).

In the present investigation, the rosocyanin was prepared by heating an alcoholic solution of curcumin with boric and sulphuric acids, and was obtained as a purple powder with a yellowish-green metallic lustre. It does not melt, but decomposes at 200—230°. The statement of Schlumberger and Ivanow-Gajewski that the substance does not contain boron is confirmed. Rosocyanin has the composition $C_{14}H_{14}O_4$, and is thus isomeric with curcumin. It yields only mono-salts with the alkalis, whereas curcumin gives both mono- and di-salts. It is evident, therefore, that the former substance only contains one hydroxyl group. The *ammonium*, *potassium*, and *barium* salts are blue. The *acetyl* derivative forms a brownish-red powder. The *methyl ether* is obtained as a purple powder resembling rosocyanin itself.

When a mixture of curcumin, boric acid, and alcohol is left for eight hours, a red solution is obtained, from which ether precipitates a red powder, which is decomposed by water into rubrocurcumin and boric acid. If a mixture of curcumin, boric acid, and alcohol in certain proportions is left for some hours and then poured into water, *rubrocurcumin*, $C_{14}H_{14}O_4$, is obtained as a vermilion-coloured powder; it is unstable, gradually changing into curcumin, and, when heated at 200—240°, is converted into rosocyanin. *Acetylrubrocurcumin*,



m. p. 245°, forms orange-yellow, prismatic needles.

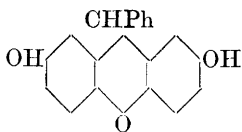
Curcumin methyl ether, $C_6H_3(OMe)_2 \cdot C_7H_7O_2$, m. p. 145°, forms small, orange-yellow needles, and, on oxidation with potassium permanganate, yields veratric acid.

Protocurcumin, $C_6H_3(OH)_2 \cdot C_7H_7O_2$, formed by the removal of a methyl group from curcumin, gives a crimson coloration when treated with boric acid, sulphuric acid, and alcohol, which is turned blue by alkali hydroxides. This substance will be described in a future paper.

E. G.

Condensation Products of Quinol. RICHARD MEYER and KARL WITTE (*Ber.*, 1908, **41**, 2453—2459).—A condensation product differing from that described by Schorygin (*Abstr.*, 1907, i, 1031) is obtained by adding small quantities of benzaldehyde to a solution of quinol in dilute sulphuric acid. From its chemical behaviour and

from the results of analysis and mol.-wt. determinations, the compound so formed is evidently 2:7-dihydroxyphenylxanthen, annexed formula.



It crystallises in glittering, slender, colourless needles, m. p. 259° (decomp.); the *acetate*, $C_{19}H_{12}O(OAc)_2$, crystallises in glistening, slender, white needles, m. p. 200° (decomp.); the *benzoate*, $C_{19}H_{12}O(OBz)_2$, forms slender needles, m. p. 237°; the *dimethyl ether*, $C_{19}H_{12}O(OMe)_2$, forms small, colourless crystals, m. p. 132°; the *diethyl ether*, $C_{19}H_{12}O(OEt)_2$, crystallises in slender, white needles, m. p. 100—101°; the *dibenzyl ether*, $C_{19}H_{12}O(O\cdot CH_2Ph)_2$, forms stellate groups of small needles, m. p. 190°.

The acetate is oxidised by chromic acid, yielding the *carbinol*, $O\langle \begin{smallmatrix} C_6H_3(OAc) \\ C_6H_3(OAc) \end{smallmatrix} \rangle CPh\cdot OH$, m. p. 171—172°; the corresponding *benzoate*, $C_{19}H_{12}O_2(OBz)_2$, has m. p. 209°.

Condensation products of quinol with formaldehyde, acetaldehyde, chloral, &c., could not be isolated in a pure state.

Succinic anhydride (1 mol.) when heated with quinol (2 mols.) yields a *succinein*, $CO\langle \begin{smallmatrix} C_2H_4 \\ O \end{smallmatrix} \rangle C\langle \begin{smallmatrix} C_6H_3(OH)_2 \\ C_6H_3(OH)_2 \end{smallmatrix} \rangle$; it crystallises in slender, white needles, m. p. 217°. The *acetate*, $C_{16}H_{10}O_3(OAc)_2$, forms small, white crystals, m. p. 161—162°. The corresponding benzoate could not be obtained; in all cases, quinol dibenzoate was formed. Attempts to prepare the dihydroxy-compound corresponding with the acetate were also unsuccessful.

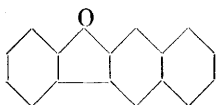
W. H. G.

Pyronone Syntheses by means of the "Tertiary Bases Reaction." I. EDGAR WEDEKIND and JOHANNES HAEUSSERMANN (*Ber.*, 1908, 41, 2297—2302).—The term "tertiary bases reaction" is used to denote the condensation of acyl halides by means of tertiary bases, a reaction which led to the production of dehydracetic acid from acetyl chloride (Wedekind, *Abstr.*, 1902, i, 739, compare also Wedekind and Weisswange, *Abstr.*, 1906, i, 437). The authors have now studied the action of tripropylamine on propionyl chloride, and have obtained a product the molecular weight of which is three times that of monomethylketen (which may be formed as an intermediate compound, compare Staudinger and Klever, this vol., i, 318), but it is not identical with trimethylphloroglucinol. The substance is probably formed by loss of 2HCl from 3 mols. of propionyl chloride, forming the compound $COEt\cdot CHMe\cdot CO\cdot CHMe\cdot COCl$, which is partly transformed into the enolic modification, and loses hydrogen chloride, thus: $CO\langle \begin{smallmatrix} CHMe\cdot COCl \\ CMe\cdot CEt\cdot OH \end{smallmatrix} \rangle \rightarrow CO\langle \begin{smallmatrix} CHMe\cdot CO \\ CMe\cdot CEt \end{smallmatrix} \rangle O$, giving 3:5-dimethyl-2-ethyl-4:6-pyronone. This separates from glacial acetic acid in monoclinic crystals, m. p. 151°. On heating with alkalis under pressure, it is decomposed into propionic acid and diethyl ketone, and an acetic acid solution absorbs bromine.

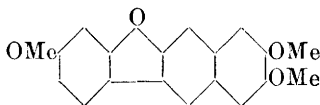
J. C. C.

Brazen from Naphthalene. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, 41, 2373—2377).—The constitution (I)

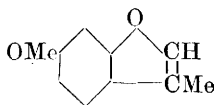
for brazan suggested by Kostanecki and Lloyd (Abstr., 1903, i, 645) is supported by the following facts: (1) Those transformation products which in the brazilin series yield brazan, in the hæmatoxylin series form naphthalene. (2) 2:7:8-Trimethoxybrazan (II) behaves towards concentrated sulphuric acid in the same manner as its analogue, 5-methoxy-2-methylcoumarone (III).



(I.)

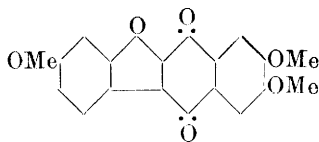


(II.)

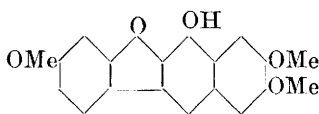


(III.)

(3) 2:7:8-Trimethoxybrazanquinone (IV), obtained from 5- or 10-hydroxy-2:7:8-trimethoxybrazan (V), behaves as a *p*-quinone.



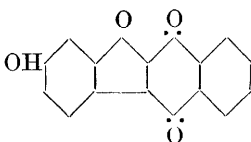
(IV.)



(V.)

Hence, brazan contains a naphthalene and a coumarone nucleus, and is a $\beta\beta$ -derivative of naphthalene. The constitution of brazan has now been confirmed by syntheses.

Liebermann (Abstr., 1899, i, 523) prepared anhydro- α -naphthaquinonerescinol (2-hydroxybrazanquinone, annexed formula) from 2:3-dichloro- α -naphthaquinone. The

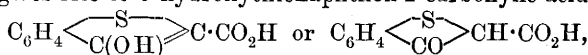


2-hydroxy-compound crystallises in orange-yellow needles, m. p. 320°, gives a bluish-green coloration with concentrated sulphuric acid, and is converted by methyl sulphate and alkalis into 2-methoxybrazanquinone, $C_{17}H_{10}O_4$, crystallising in golden leaflets, m. p. 290°. This resembles 2:7:8-trimethoxybrazan in that it distills unchanged when carefully heated and behaves like the hydroxy-compound towards concentrated sulphuric acid. When heated with hydriodic acid, 2-methoxybrazanquinone yields 2-hydroxybrazan, $C_{16}H_{10}O_2$, which forms white crystals, m. p. 255°, gives a green coloration with alcoholic ferric chloride, and dissolves in sodium hydroxide to a colourless solution with blue fluorescence. 2-Acetoxybrazan, $C_{18}H_{12}O_3$, white needles, m. p. 196—197°, has a slight blue fluorescence in alcoholic solution. 2-Methoxybrazan, $C_{17}H_{12}O_2$, prepared by the action of methyl sulphate and alkalis on the hydroxy-compound, crystallises in white leaflets, m. p. 205—206°, and gives colorations with ferric chloride and sulphuric acid. Brazan, m. p. 202°, is obtained when 2-hydroxybrazan or 2-hydroxybrazanquinone is distilled with zinc dust.

G. Y.

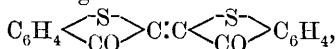
Preparation of a Red Colouring Matter of the Thionaphthen Series. KALLE & Co. (D.R.-P. 194237 and 194254).—Phenylthioglycol-*o*-carboxylic acid, when treated with condensing agents or when

heated, gives rise to 3-hydroxythionaphthen-2-carboxylic acid,



and 3-hydroxythionaphthen, $\text{C}_6\text{H}_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{array} \text{CH}$ or $\text{C}_6\text{H}_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH}_2$.

When either of these compounds is oxidised with ferric chloride or potassium dichromate in the presence of alkali and the solution then acidified, a red colouring matter is precipitated. This product probably has the following constitution:



and resembles indigotin in its chemical properties; it furnishes a colourless leuco-derivative, which is again converted into the colouring matter by aerial oxidation. The red colouring matter is also produced on warming 3-hydroxythionaphthen with sulphur or by adding milk of sulphur to an alkaline solution of 3-hydroxythionaphthen-2-carboxylic acid. In the latter case, the dye is precipitated with acid.

G. T. M.

Indigoid Dyes. I. PAUL FRIEDLÄNDER (*Monatsh.*, 1908, 29, 359—374. Compare Abstr., 1906, i, 378; 1907, i, 334; this vol., i, 200, 371).—The author has prepared further members of this class of dyes (compare also following abstracts), of which a general account is given. In addition to the work previously published (compare also Bezdzik, Friedländer, and Koeniger, this vol., i, 200), the following is new. “Leucothioindigotin” (Abstr., 1907, i, 335) forms a *diacetyl* derivative, $\text{C}_{16}\text{H}_8\text{O}_2\text{S}(\text{COMe})_2$, colourless, glistening needles, m. p. 240°. “2:3-Bisthionaphthenindigotin” (thioindirubin) [2:3'-bisoxythionaphthen], $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C} : \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{S}$, formed by condensing hydroxythionaphthen with thionaphthenquinone in glacial acetic acid solution with addition of a little hydrochloric acid, crystallises in red needles, m. p. 205—207°.

J. C. C.

Indigoid Dyes. II. A. BEZDZIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1908, 29, 375—386. Compare preceding abstract).—A detailed account of work previously published (Friedländer, this vol., i, 371, 372). The following is new:

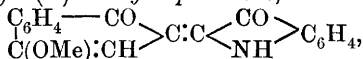
“3-Thionaphthen-2-indole-indigotin” [2'-indoxyl-3-thionaphthen-2'-one], $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} : \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{S}$, prepared by heating indoxyl with thionaphthenquinone in glacial acetic acid solution, crystallises from xylene in violet-black needles, m. p. 247—250°, which sublime at a higher temperature.

“2-Thionaphthen-3-indole-indigotin” [3'-indoxyl-2-thionaphthen-3-one], $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C} : \text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{NH}$, prepared similarly from isatin and hydroxythionaphthen, crystallises from nitrobenzene in small, red needles, which do not melt at 270°, and sublime at a higher temperature. The dye (thioindigo-scarlet) forms a pale yellow *leuco*-compound,

from which textile fibres are dyed scarlet. An improved method of preparing 2'-indoxyl-3-thionaphthen-2'-one consists in condensing isatin chloride and hydroxythionaphthen in benzene solution in presence of phosphoryl chloride. It is also formed by heating together α -isatinanilide and hydroxythionaphthen either in petroleum or in acetic anhydride. 1-Oxy-2:(2')-indoxyl-naphthalene is best prepared by condensing α -isatinanilide with α -naphthol in acetic anhydride solution. When prepared from isatin chloride (this vol., i, 372), an isomeric *dye*, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}:\text{CH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is also formed, which crystallises from glacial acetic acid in compact prisms, resembling potassium permanganate. It forms a brownish-yellow *acetyl* derivative, crystallising from glacial acetic acid in compact, glistening needles. When isatin chloride is condensed with 2-chloro- α -naphthol, a *dye*, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH}:\text{CCl} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained, which crystallises from glacial acetic acid in brassy, dark prisms.

1-Oxy-2:(3')-indoxyl-naphthalene, $\text{CH} \begin{smallmatrix} \text{CH}\cdot\text{CO} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing isatin chloride with β -naphthol in benzene solution, crystallises from xylene in blackish-violet, glistening needles.

4-Methoxy-1-oxy-2-(2')indoxyl-naphthalene,



prepared by condensing 4-methoxy- α -naphthol with α -isatinanilide in acetic anhydride solution, forms bluish-black, glistening needles.

8-Oxy-7-indoxylacenaphthene, $\begin{smallmatrix} \text{CO} \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is

obtained by condensing indoxyl with acenaphthenequinone in glacial acetic acid solution. It forms coppery needles; from the *leuco*-compound, reddish-violet shades on textile fibres are obtained. The *sulphonic acid* of the dyestuff gives a reddish-violet solution in water.

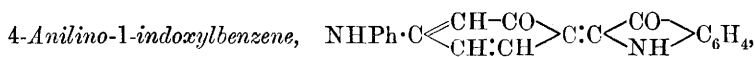
8-Oxy-7-oxythionaphthenylacenaphthene, $\begin{smallmatrix} \text{CO} \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$,

prepared by condensing hydroxythionaphthen with acenaphthenequinone in glacial acetic acid solution, crystallises from nitrobenzene in brick-red, glistening needles. By the use of the *leuco*-compound, textile fibres are dyed red.

J. C. C.

Indigoid Dyes. III. PAUL FRIEDLÄNDER and R. SCHULOFF (*Monatsh.*, 1908, 29, 387—393. Compare preceding abstracts).—

4-Hydroxy-1-indoxylbenzene, $\text{HO}\cdot\text{C} \begin{smallmatrix} \text{CH}\cdot\text{CO} \\ \text{CH}:\text{CH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by condensing isatin chloride with resorcinol in benzene solution, crystallises from alcohol in bronzy, dark violet needles. It forms a *sulphonic acid*. 4-Methoxy-1-indoxylbenzene, similarly obtained from resorcinol monomethyl ether, forms brownish-violet needles, m. p. 162°. The *sulphonic acid* is red. On warming with dilute sodium hydroxide the dye yields *o*-hydroxyanisaldehyde.



prepared by condensing isatin chloride with *m*-hydroxydiphenylamine in benzene solution, forms violet needles.

3-Hydroxy-1-indoxylbenzene, similarly prepared from catechol, forms violet-black needles, m. p. 245° (decomp.). It dyes iron- and chrome-mordanted cotton in greenish-blue shades. *3:4-Dihydroxy-1-indoxylbenzene*, obtained from pyrogallol, forms blackish-violet needles and gives bluish-violet shades on iron- and chrome-mordanted cotton. The *sulphonic acid* is red. J. C. C.

Constitution of Neosine. D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1908, 56, 220—222).—Neosine, $\text{C}_6\text{H}_{17}\text{O}_9\text{N}$, from meat-extract, yields on distillation with baryta, trimethylamine, and is perhaps a homologue of choline. G. B.

Tropine. ERNST SCHMIDT and A. KIRCHER (*Chem. Zentr.*, 1908, i, 1467; from *Pharm. Post.*, 1907, 40, 771—772).—The authors show that the tropine bromide prepared directly from tropine is identical with α -tropidine hydrobromide, $(\text{C}_8\text{H}_{14}\text{BrN}, \text{HBr})$; it forms colourless, needle-shaped crystals, m. p. 216—217°, and gives an *aurichloride*, $\text{C}_8\text{H}_{14}\text{BrN}, \text{HAuCl}_4$, which crystallises in yellow needles, m. p. 170°, and a *platinichloride*, $(\text{C}_8\text{H}_{14}\text{BrN})_2, \text{H}_2\text{PtCl}_6$, which crystallises in long, red needles, blackening at 210°, and m. p. 215—216°. Silver nitrate decomposes the bromide, removing hydrogen bromide; the product gives a crystalline, anhydrous *platinichloride*, $(\text{C}_8\text{H}_{13}\text{N})_2, \text{H}_2\text{PtCl}_6$, m. p. 160—161° (decomp.), and is not identical with that obtained from tropidine. J. V. E.

Synthesis of Amino-acids. VII. Proline (Pyrrolidine-2-carboxylic Acid). SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1908, 56, 236—249. Compare Abstr., 1903, i, 833; 1905, i, 600, 749; Willstätter, 1900, i, 405; Fischer, 1901, i, 745).—A good yield of pyrrolidine-2-carboxylic acid is obtained by boiling ethyl γ -bromopropylphthaliminomalonate with alcoholic sodium hydroxide and evaporating the product with hydrochloric acid. The acid is isolated and purified by means of its copper salt.

Proline is not formed when arginine is hydrolysed with barium hydroxide solution. Under suitable conditions, the amount of ornithine obtained during the hydrolysis is 64% of that required by Schultze and Winterstein's equation: $\text{NH}_2\text{C}(\text{NH}_2)\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H} + \text{CO}(\text{NH}_2)_2$. J. J. S.

New Method of Preparing Bromoacetonitrile and its Addition to Tertiary Bases. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2113—2123. Compare this vol., i, 625).—The interaction of cyanogen bromide and tertiary bases according to the equation $\text{RR}'\text{NR}'' + \text{BrCN} = \text{RR}'\text{N}\cdot\text{CN} + \text{R}''\text{Br}$, has hitherto been applied chiefly to the preparation of secondary bases (compare Abstr., 1904, i, 344, 687; this vol., i, 626, 684, and Sachs and Weigert, Abstr., 1907, i, 1046), but it also affords

a means of preparing alkyl bromides that are not readily obtained directly, provided that the tertiary base is readily accessible and has been prepared by some other method than the alkylation of a primary or secondary amine by an alkyl halide.

The use of dimethyl-, diethyl-, or dipropyl-aminoacetonitrile is not suitable for the ready preparation of pure bromoacetonitrile, and from his former researches (Abstr., 1907, i, 960) the author was led to employ piperidylacetonitrile, which was found to give good results. Bromoacetonitrile, being thus readily obtainable, has been employed in a number of reactions; in the present paper, its action towards tertiary aromatic amines and alkaloids is described. Whilst with tertiary aliphatic amines and cyclic bases, bromoacetonitrile yields normal additive products, with bases such as dimethylaniline it yields, for example, phenyltrimethylammonium bromide. The additive products which are formed with alkaloids, for example, atropine, codeine, strychnine, &c., although containing two new poisonous factors (quaternary character and cyanogen group), in addition to that inherent in the alkaloid, are relatively harmless.

When piperidylacetonitrile (200—300 grams) is mixed with 1 mol. of cyanogen bromide and, after twenty-four hours, heated on the water-bath, dicyanomethylpiperidinium bromide, $C_5NH_{10}(CH_2 \cdot CN)_2Br$, is formed. This is extracted with ether, the ethereal solution evaporated, and the residue distilled. The fraction distilling at 50—90°/15 mm. contains the bromoacetonitrile, which can be purified by redistillation. The following homologues of piperidinoacetonitrile were prepared: *α*-Piperidyl-*n*-butyronitrile, $C_5NH_{10} \cdot CHEt \cdot CN$ (from piperidine and propaldehyde cyanohydrin or propaldehyde potassium cyanide and sodium hydrogen sulphite), colourless liquid, b. p. 88—91°/7 mm. *α*-Piperidyl-*n*-hexonitrile, $C_5NH_{10} \cdot CH(C_4H_9) \cdot CN$ (from piperidine and valeraldehyde), colourless liquid with a weak odour of valeraldehyde, b. p. 123°/12 mm. *α*-Piperidyl-*n*-octonitrile, $C_5NH_{10} \cdot CH(C_6H_{13}) \cdot CN$ (from piperidine and heptaldehyde) is a colourless, viscous oil with a weak odour of heptaldehyde, b. p. 158—159°/9 mm. When these homologues of piperidylacetonitrile are treated with cyanogen bromide in the cold, only the hydrobromides of the compounds are formed; with water they are decomposed into the parent aldehyde, hydrogen cyanide, and piperidine hydrobromide. *α*-Piperidyl-*n*-octonitrile hydrobromide has m. p. 155°.

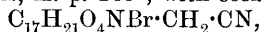
Bromoacetonitrile forms with triethylamine a compound,
 $NEt_3Br \cdot CH_2 \cdot CN$,
 m. p. 202° (decomp.), with tripropylamine a compound,
 $NPr^a_3Br \cdot CH_2 \cdot CN$,
 m. p. 167° (decomp.), with phenylpiperidine a compound,
 $C_5NH_{10}PhBr \cdot CH_2 \cdot CN$,
 m. p. 171°, with pyridine a compound, $C_5NH_5Br \cdot CH_2 \cdot CN$, m. p. 160°,
 giving with alkalis a yellow precipitate, probably $\begin{matrix} CH \cdot CH \cdot CH \cdot OH \\ | \\ CH \cdot CH \cdot N \cdot CH_2 \cdot CN \end{matrix}$
 which is converted on warming into a greyish-green, amorphous powder, softening at 120°, m. p. 150°, corresponding with the composition $C_{14}H_{14}ON_4$, but which may be a mixture. With isoquinoline, bromoacetonitrile gives a compound, $C_9NH_7Br \cdot CH_2 \cdot CN$, m. p. 195°, yielding

a red *precipitate* with alkalis, which is at once partly converted into a reddish-yellow *powder*, softening at 150° , m. p. 160° .

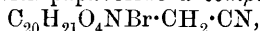
Bromoacetonitrile gives with tropine a *compound*,



blackening at 215° , m. p. 225° , with atropine a very hygroscopic *compound*, the *platinichloride* of which, $(\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}\cdot\text{CH}_2\cdot\text{CN})_2\text{PtCl}_6$, forms small, red crystals, m. p. 215° , with cocaine a *compound*,

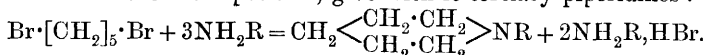


m. p. 169° (decomp.), with papaverine a *compound*,

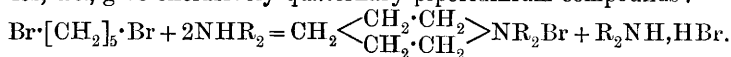


m. p. 204° , with codeine a *compound*, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{NBr}\cdot\text{CH}_2\cdot\text{CN}$, m. p. 189° , and with strychnine a *compound*, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\text{Br}\cdot\text{CH}_2\cdot\text{CN}$, m. p. 275° .
J. C. C.

Characterisation of Primary, Secondary, and Tertiary Bases by the Aid of α -Dibromo-*n*-pentane. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2156—2165).—The author shows that α -dibromo-*n*-pentane is an excellent agent for characterising the three classes of amines. Primary amines, in which the nitrogen is attached to an open chain, a hydrogenised carbon ring, a heterocyclic ring, or a benzene ring not substituted in the ortho-position, give with it tertiary piperidines:



When a benzene ring contains one or two ortho-substituents, pentamethylenediamine derivatives are formed (Scholtz and Wassermann, *Abstr.*, 1907, i, 339). Secondary amines of the aliphatic or piperidine series, &c., give exclusively quaternary piperidinium compounds:



In the case of secondary aromatic bases, small amounts of tertiary pentamethylenediamine bases are also formed, and when the benzene ring contains an ortho-substituent, the latter constitute the sole product.

Tertiary amines, either aliphatic or aromatic, yield diammonium bromides, $\text{Br}\cdot[\text{CH}_2]_5\cdot\text{Br} + 2\text{NR}_3 = \text{NR}_3\text{Br}\cdot[\text{CH}_2]_5\cdot\text{NR}_3\text{Br}$, but they are readily characterised only when they consist of tertiary cyclic bases, such as pyridine, methylpiperidine, &c., for the derivatives of the tertiary aliphatic amines are usually very hygroscopic, and those of the aromatic bases are formed only very slowly.

The formation of tertiary piperidines by the aid of dibromopentane has already been the subject of several investigations (compare *Abstr.*, 1904, i, 841; 1907, i, 960; Luft, *Abstr.*, 1906, i, 118; Scholtz and Wassermann, *loc. cit.*), and the author now describes *camphylpiperidine*, $\text{C}_{10}\text{H}_{17}\cdot\text{NC}_5\text{H}_{10}$, b. p. $134\text{--}135^{\circ}/10\text{ mm.}$, obtained by warming 3 mols. of camphylamine and 1 mol. of dibromopentane, the excess of the base being removed by means of benzenesulphonyl chloride, whereby *camphylamine benzenesulphonate*, a red, viscid oil, is formed. *Camphylpiperidine picrate*, $\text{C}_{15}\text{H}_{27}\text{N}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, has m. p. 117° .

Diethylpiperidinium bromide, $\text{C}_5\text{NH}_{10}\text{Et}_2\text{Br}$, forms white, glistening leaflets, m. p. 257° , decomposing at this temperature into ethyl bromide

and ethylpiperidine. The *platinichloride* forms small, reddish-yellow crystals, m. p. 240°.

Diisoamylpiperidinium bromide forms silvery, hygroscopic leaflets, m. p. 115°; the *aurichloride* has m. p. 177°, and the *platinichloride* blackens at 212° and has m. p. 216°.

With dibromopentane, methylaniline forms mostly *phenylmethylpiperidinium bromide*, $C_5NH_{10}PhMeBr$, m. p. 170°, with a small quantity of *s-diphenyldimethylpentamethylenediamine*,



m. p. 38°, b. p. 244—245°/8 mm., the *picrate* of which is described, and some phenylpiperidine. Ethylaniline gives, under the same conditions, *phenylethylpiperidinium bromide*, $C_5NH_{10}PhEtBr$, m. p. 217°, and *s-diphenyldiethylpentamethylenediamine*, $NPhEt \cdot [CH_2]_5 \cdot NPhEt$, a pale yellow, viscous liquid, b. p. 257—259°/7 mm. Methyl-*o*-toluidine and dibromopentane yield only *s-di-o-tolyldimethylpentamethylenediamine*, $C_6H_4Me \cdot NMe \cdot [CH_2]_5 \cdot NMe \cdot C_6H_4Me$, a viscous liquid, b. p. 229°/9 mm.; the *platinichloride* is a viscid, red oil, and the *picrate* has m. p. 184°.

From tetrahydroquinoline is obtained *s-bistetrahydroquinolylpentamethylenediamine*, $C_9NH_{10} \cdot [CH_2]_5 \cdot C_9NH_{10}$, glistening crystals, m. p. 76°. The *picrate* softens at about 70°, and has m. p. below 90°.

Triethylamine and dibromopentane condense to a very hygroscopic compound, of which the *platinichloride* has m. p. 235°. Similar compounds are obtained from tripropyl-, tributyl-, and triamyl-amine.

1-Phenylpiperidine gives a pale red, hygroscopic compound; the *platinichloride*, $\{(C_5NH_{10}Ph)_2[CH_2]_5\}PtCl_6$, is a red, crystalline powder, m. p. 216°. Quinoline yields a yellowish-red, crystalline powder, $C_9NH_7Br \cdot [CH_2]_5 \cdot C_9NH_7Br$, m. p. 200°, with previous sintering. Tropine gives a white compound, $C_{21}H_{40}O_2N_2Br_2$, m. p. 282°, and strychnine a white compound, $C_{47}H_{54}O_6N_4Br_2$, which does not melt at 300°.

J. C. C.

Stereoisomerism of Compounds Containing Asymmetric Carbon and Asymmetric Quinquevalent Nitrogen Atoms. MAX SCHOLTZ (*Ber.*, 1908, 41, 2005—2009).—The addition of an alkyl haloid to an active *N*-alkylated conine, conhydrine (*Abstr.*, 1904, i, 1044; 1905, i, 296), or 2-phenyl-6-methylpiperidine (Scholtz and Wassermann, *Abstr.*, 1907, i, 340) results in the formation of two stereoisomeric quaternary ammonium compounds; active alkaloids, excepting the preceding, yield only one. Such isomerides have been obtained only from piperidine derivatives having a large substituent in position 2, and the theory is obvious that the existence of two stereoisomeric quaternary compounds is due to the influence of this substituent, which confers stability on the groups attached to the neighbouring nitrogen atom. To test the validity of the theory, α - and β -pipercoline have been converted into the *N*-ethyl derivatives, and, after resolution by tartaric acid, the *l*-forms of the tertiary base have been treated with benzyl bromide or iodide. In neither case have two isomerides been obtained. Moreover, the author showed some years ago (*Abstr.*, 1901, i, 749) that active amyl iodide and 1-methyl-2-pipercoline yield only one additive product. Hence it appears that a methyl group, whether directly attached to the asymmetric nitrogen

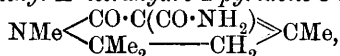
atom or in the α -position in the piperidine ring, cannot exert sufficient stabilising influence to ensure the formation of two stable stereo-isomeric quaternary compounds.

Hohenemser and Wolfenstein resolved 1-ethyl-2-pipecoline by means of the hydrogen tartrate, and found that the salt of the *d*-base separated first (Abstr., 1899, i, 936); the author, using the same method, obtained the salt of the *l*-base first. The discrepancy is attributed to the influence of temperature. 1-1-Benzyl-1-ethyl-2-pipecolinium iodide, m. p. 230°, has $[\alpha]_D - 52.5^\circ$ in 10% alcoholic solution; the corresponding bromide, m. p. 237°, has $[\alpha]_D + 20^\circ$ in the same solvent. The bromide of the inactive base has m. p. 204°.

1-Ethyl-3-pipecoline, b. p. 145.5—146.5°, was resolved by tartaric acid, and the active base so obtained had $D^{17} 0.8095$ and $[\alpha]_D - 3.2^\circ$. 1-1-Benzyl-1-ethyl-3-pipecolinium iodide, m. p. 174°, crystallises in colourless needles. C. S.

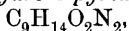
Hydrolysis of Oxyhydropyridine Nitriles. GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1908, 43, 547—558. Compare this vol., i, 51).—The nitriles described in the former paper are not attacked by hydrochloric acid below 120°. The hydrolysis can be arrested before the elimination of the carboxyl group by employing 95—96% sulphuric acid at 150° as the hydrolysing agent. The amide is thus obtained, and may be converted into the acid by alkalis.

1 : 4 : 6 : 6-Tetramethyl- Δ^3 -tetrahydro-2-pyridone-3-carboxylamide,



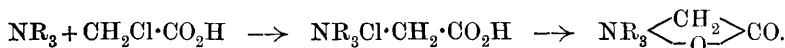
crystallises from alcohol in brilliant, colourless rosettes, or from water in large, monoclinic prisms, m. p. 195—196°. Its solution in water is neutral, but it dissolves readily in acids, and is precipitated by the usual reagents for alkaloids. Boiling with 50% sodium hydroxide solution is necessary to remove the NH_2 group. The corresponding carboxylic acid, $\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$, may be obtained by heating the nitrile with hydrochloric acid, $D 1.19$, for several hours at 120—125°, or by boiling the amide with 20% sulphuric acid, some decomposition of the acid occurring in the latter case, or best by the action of nitrous acid on the amide. It forms colourless prisms, m. p. 125—126° if rapidly, 118—120° (decomp.) if slowly, heated. The salts are readily soluble.

4 : 6 : 6-Trimethyl- Δ^3 -tetrahydro-2-pyridone-3-carboxylamide,

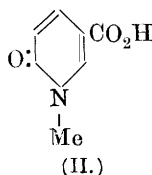
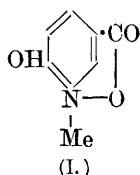


forms large, colourless prisms, m. p. 199—200° (corr.). Nitrous acid converts it into the carboxylic acid, $\text{C}_9\text{H}_{13}\text{O}_3\text{N}$, crystallising from water in long, colourless prisms, m. p. 116—117° (corr.). The sodium salt, $\text{C}_9\text{H}_{12}\text{O}_3\text{NNa} \cdot 2\text{H}_2\text{O}$, and the barium salt, $(\text{C}_9\text{H}_{12}\text{O}_3\text{N})_2\text{Ba} \cdot 3\text{H}_2\text{O}$, are described. C. H. D.

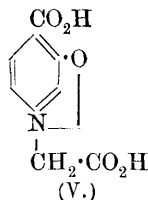
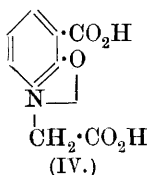
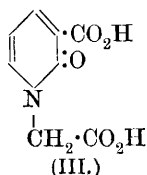
New Betaines of the Pyridine Series. ALFRED KIRPAL (*Monatsh.*, 1908, 29, 471—484).—According to Liebreich (*Ber.*, 1869, 2, 12), betaines are formed when tertiary bases are heated with chloroacetic acid and the products shaken with silver oxide:



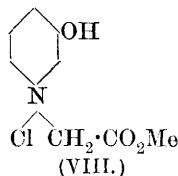
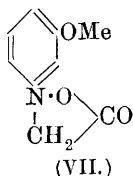
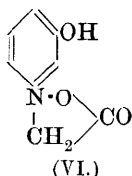
It is found now that, when heated with chloroacetic acid and treated with sulphuric acid, hydroxypyridinecarboxylic acids yield products which, according to the above scheme, should be the corresponding betaines, $\text{CO}_2\text{H} \cdot \text{C}_5\text{NH}_3(\text{OH}) \langle \text{CH}_2 \rangle \text{CO}$. This structure, however, appeared doubtful, as on titration the products behaved as dibasic acids. Meyer has shown (Abstr., 1906, i, 108) that the action of methyl iodide on 6-hydroxynicotinic acid in alkaline solution leads to the formation, not of the expected betaine (I), but of the *N*-methyl derivative of the keto-acid (II).



In analogy to this, the product obtained from 2-hydroxynicotinic acid and chloroacetic acid might have the formula (III) or (IV), there being, similarly, two possibilities for the constitution of the product from 4-hydroxynicotinic acid, but that from 3-hydroxyisonicotinic acid, if not a betaine, can have only the formula (V).



It has been found, however, that 3-hydroxypyridinebetaine (VI) acts towards alkalis as a monobasic acid, and forms a silver salt, which with methyl iodide yields a methyl derivative; this does not react with ammonia, and must therefore be the ether (VII) (this vol., ii, 436). In agreement with this, it is found that the additive compound of 3-hydroxypyridine and methyl chloroacetate (VIII), on treatment with silver oxide, yields the betaine (VI), and not a chlorine-free methyl ester.



The products obtained from the hydroxypyridinecarboxylic acids are therefore considered to be betaines, the second mol. of alkali being neutralised by the hydroxyl.

In connexion with the formation of methyl iodide when pyridine betaine is treated according to the Herzig-Meyer method (this vol., ii, 436), it is observed that von Gerichten found that pyridinebetaine hydrochloride, when heated at 200°, decomposes, forming pyridine, carbon dioxide, and methyl chloride (Abstr., 1882, 1109).

The *additive* compound of 3-hydroxypyridine and chloroacetic acid, $\text{OH} \cdot \text{C}_5\text{NH}_4\text{Cl} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_5\text{NH}_4(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises in colourless needles, m. p. 185° (decomp.). 3-Hydroxypyridinebetaine, $\text{C}_7\text{H}_7\text{O}_3\text{N} \cdot \text{H}_2\text{O}$, crystallises in colourless, rhombic plates, m. p. 182° (decomp.). The silver salt, $2\text{C}_7\text{H}_6\text{O}_3\text{N} \cdot \text{Ag} \cdot 3\text{H}_2\text{O}$, was analysed. The methyl ester, $\text{C}_8\text{H}_9\text{O}_3\text{N}$, forms needles, m. p. 160° (decomp.).

The *additive* compound of 3-hydroxypyridine and methyl chloroacetate, $\text{C}_8\text{H}_{10}\text{O}_3\text{NCl}$, forms colourless plates, m. p. 155° (decomp.); the *platinchloride*, $(\text{C}_8\text{H}_9\text{O}_3\text{N})_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, crystallises in orange-yellow plates, m. p. 205°.

2-Hydroxynicotinic acid betaine (*2-hydroxy-3-carboxypyridinebetaine*), $\text{C}_8\text{H}_7\text{O}_5\text{N}$, crystallises in needles, m. p. 240°.

3-Hydroxy-4-carboxypyridinebetaine, prepared from 3-hydroxyisonicotinic acid, crystallises in needles, m. p. 200° (decomp.).

4-Hydroxy-3-carboxypyridinebetaine, prepared from 4-hydroxynicotinic acid, forms plates, m. p. 220° (decomp.). G. Y.

Quinoline-2-carboxyl Chloride. EMIL BESTHORN (*Ber.*, 1908, 41, 2003—2004).—The difference between Meyer (Abstr., 1905, i, 155, 666) and Besthorn and Ibele (Abstr., 1905, i, 612; 1906, i, 605) as to the physical properties of quinoline-2-carboxyl chloride is due to the fact that Kahlbaum's thionyl chloride contains a not inconsiderable amount of stannic chloride, which reacts with quinoline-2-carboxylic acid to form a substance insoluble in organic solvents. When thionyl chloride, free from tin, reacts with quinoline-2-carboxylic acid, the chloride, m. p. 97—98°, is obtained, the molecular weight of which, determined in benzene by the cryoscopic method, agrees with the formula $\text{C}_{10}\text{H}_6\text{ONCl}$. Meyer's chloride probably contained tin.

The presence of tin chloride in thionyl chloride is detected by the yellow colour produced by triphenylmethyl chloride, or by the splendid red coloration produced by *p*-tri-iodotriphenylmethyl chloride. A coloration is not produced in either case if pure thionyl chloride is used. C. S.

2-Quinolyl Phenyl Ketone. EMIL BESTHORN (*Ber.*, 1908, 41, 2001—2003).—The reaction between quinoline-2-carboxyl chloride and aluminium chloride in dry benzene leads to the formation of *2-quinolyl phenyl ketone*, $\text{C}_9\text{NH}_6 \cdot \text{COPh}$, m. p. 110—111°, in good yield. The substance is colourless, and shows no tendency to yield dyes; consequently, it is doubtful whether the red substance, $\text{C}_{19}\text{H}_{12}\text{ON}_2$, obtained by Besthorn and Ibele (Abstr., 1904, i, 527) is 2:2'-di-quinolyl ketone. C. S.

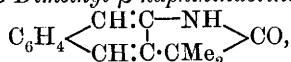
Indolinones. D. LIEBER (*Monatsh.*, 1908, 29, 421—429).—Brunner has shown that the phenylhydrazides of fatty acids, or phenyl-substituted fatty acids, are converted into indolinones when heated with calcium oxide (Abstr., 1907, i, 240). This reaction has

now been applied to the formation of indolinones from the α - and β -naphthylhydrazides of isobutyric acid.

isoButyryl- α -naphthylhydrazide, $C_{10}H_7 \cdot NH \cdot NH \cdot C_4H_7O$, is obtained in a 86.3% yield by the action of isobutyric anhydride on α -naphthylhydrazine in benzene solution and extraction with water of the α -naphthylhydrazine isobutyrate, which is simultaneously formed. When heated with calcium oxide at 230° , it yields 3:3-dimethyl-

α -naphthindolinone, $\begin{array}{c} C_6H_4 - C - NH \\ | \quad | \quad | \\ CH : CH : C \cdot CMe_2 \end{array} > CO$, which separates from dilute alcohol in white crystals, m. p. 201° , and forms solutions with reddish-blue fluorescence. The *methyl ether*, $C_{15}H_{15}ON$, m. p. 78.5° , is formed by the action of sodium and methyl iodide on the indolinone in methyl-alcoholic solution. The *acetyl* derivative, $C_{16}H_{15}O_2N$, forms a crystalline mass, m. p. 106.5° . With mercuric chloride in concentrated alcoholic or aqueous solution, the indolinone yields a mixture of the *mercurichloride* and the free base; the salt is hydrolysed by excess of water.

isoButyryl- β -naphthylhydrazide is prepared in the same manner as the α -compound. 3:3-Dimethyl- β -naphthindolinone,



forms white crystals, m. p. 145.5° . The *methyl ether*, m. p. 155.5° . The *acetyl* derivative, m. p. 139.5° . G. Y.

Tetrahydroacridine and a New Synthesis of Acridine. WILHELM BORSCHÉ [with H. TIEDTKE and W. ROTTSIEPER] (*Ber.*, 1908, 41, 2203—2208).—The hitherto unknown tetrahydrodibenzopyridines may be prepared by the following three methods: (1) Condensation of α -acyl cyclohexamethylene ketones with aniline and its homologues, and intramolecular condensation of the anilino-compounds initially formed. By this method, a mixture of the isomeric tetrahydroacridine and tetrahydrophenanthridine compound is obtained. (2) Condensation of aromatic *o*-amino-aldehydes or ketones with hydroaromatic ketones containing a methylene group ortho to the carbonyl group. (3) The hydroaromatic ketone is treated with isatin and strong aqueous alkali, whereby tetrahydroacridine-5-carboxylic acid is formed. The latter, when heated, is converted into tetrahydroacridine with the evolution of carbon dioxide.

[With W. ROTTSIEPER].—*Tetrahydroacridine*, $C_6H_4 < \begin{array}{c} CH \\ \diagup \quad \diagdown \\ N \end{array} > C_6H_8$, is formed by heating *o*-aminobenzaldehyde with cyclohexanone at 130° , or by treating a solution of these substances in alcohol with a few drops of aqueous sodium hydroxide; it forms small, colourless plates, m. p. 54.5 — 55° . The *picrate* crystallises in small, yellow needles, m. p. 208 — 209° ; the *methiodide*, $C_{14}H_{16}NI$, is a yellow, crystalline powder, which sinters and then melts at 202 — 204° ; the *platinichloride*, $(C_{13}H_{13}N)_2 \cdot H_2PtCl_6$, crystallises in small, brownish-yellow needles, m. p. 233 — 235° ; the *aurichloride*, $(C_{13}H_{13}N)_3 \cdot HCl \cdot 2HAuCl_4$, is a yellow, crystalline powder, m. p. 156 — 158° .

Tetrahydroacridine-5-carboxylic acid, $C_6H_4 \begin{smallmatrix} \swarrow C(CO_2H) \\ \searrow N \end{smallmatrix} C_6H_5$, crystallises in small, colourless leaflets, m. p. 284—286° (decomp.); the *hydrochloride*, $C_{14}H_{13}O_2N \cdot HCl$, crystallises in long, colourless needles, m. p. 233°. The *silver*, *lead*, and *calcium* salts are obtained as white precipitates from aqueous solutions of the *ammonium* salt; the *copper* salt is obtained as a green precipitate.

Acridine may be prepared from tetrahydroacridine or its carboxylic acid by distilling with litharge and passing the vapour over heated litharge (compare this vol., i, 365). W. H. G.

9:10-Phenanthraquinoline. FRIEDRICH HERSCHMANN (*Ber.*, 1908, 41, 1998—2000).—Skraup's synthesis has for the first time been applied in the phenanthrene series. The interaction of 9-amino-phenanthrene, nitrobenzene, glycerol, and concentrated sulphuric acid at 145—150° for four to five hours leads to the formation of a quinoline which must be 9:10-*phenanthraquinoline*, since ring-closure in the 9:8-positions would give a seven-membered ring. The compound forms long, colourless needles, and has m. p. 174°. The *nitrate*, m. p. 240°, *hydrochloride*, m. p. 248°, darkening at 245°, *sulphate*, *platinichloride*, and *picrate* are mentioned. The reaction with 2-amino-phenanthraquinone did not yield a pure product. C. S.

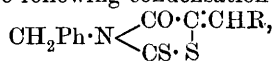
Substituted Rhodanic Acids and their Aldehyde Condensation Products. VII. RUDOLF ANDREASCH (*Monatsh.*, 1908, 29, 399—419. Compare *Abstr.*, 1907, i, 233).—The substituted rhodanic acids derived from *m*-toluidine, benzylamine, hydrazine, and glycine are now described in amplification of the previous papers on this subject.

3-m-Tolylrhodanic acid, $C_6H_4Me \cdot N \begin{smallmatrix} \swarrow CO \cdot CH_2 \\ \searrow CS \cdot S \end{smallmatrix}$, formed together with *ethyl m-tolyldithiocarbaminacetate*, $C_6H_4Me \cdot NH \cdot CS \cdot S \cdot CH_2 \cdot CO_2Et$, transparent prisms, m. p. 77°, from ammonium *m*-tolyldithiocarbamate and ethyl chloroacetate, crystallises in microscopic prisms, m. p. 148°.

The following *condensation products*, $C_6H_4Me \cdot N \begin{smallmatrix} \swarrow CO \cdot C \cdot CHR \\ \searrow CS \cdot S \end{smallmatrix}$, of *3-m-tolylrhodanic acid* with aldehydes are described.

$R = Ph$: yellow needles, m. p. 124°; $R = \cdot C_6H_4 \cdot OH$ (*o*): yellow leaflets, becomes red at 190°, m. p. 220°; $R = \cdot C_6H_4 \cdot OAc$ (*o*): greyish-white scales, m. p. 231°; $R = \cdot C_6H_4 \cdot NO_2$ (*m*): chrome-yellow, microscopic needles, m. p. 234°; $R = \cdot C_6H_4 \cdot NMe_2$ (*p*): scarlet, crystalline powder, m. p. 140°, dyes wool, silk, and skin orange-yellow; $R = \cdot C_6H_3 \cdot O_2 \cdot CH_2$: chrome-yellow, crystalline powder, m. p. 178°; $R = \cdot CH \cdot CHPh$: yellowish-brown powder, m. p. 145—146°.

3-Benzylrhodanic acid, $CH_2Ph \cdot N \begin{smallmatrix} \swarrow CO \cdot CH_2 \\ \searrow CS \cdot S \end{smallmatrix}$, prepared from benzylamine, carbon disulphide, and ethyl chloroacetate, crystallises in white leaflets, m. p. 83°. The following *condensation products*,

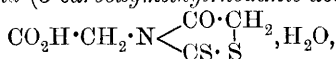


with aldehydes are described.

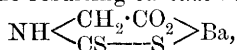
R = Ph: golden needles, m. p. 219° ; R = $\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (*m*): yellow needles, m. p. 183° , becomes superficially colourless on prolonged exposure to light; R = $\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (*p*): red needles with blue lustre, m. p. 177° .

The action of ethyl chloroacetate on hydrazine dithiocarbazate (Curtius and Heidenreich, Abstr., 1894, i, 166) leads to the formation of 3-aminorhodanic acid, $\text{NH}\cdot\text{N} < \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CS}\cdot\text{S} \end{smallmatrix}$, which crystallises in slightly yellow needles, m. p. 92° , together with a crystalline substance, $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2\text{S}_3$, m. p. 60° . 3-Aminorhodanic acid forms condensation products with *m*-nitrobenzaldehyde, $\text{NH}_2\cdot\text{N} < \begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \\ \text{CS}\cdot\text{S} \end{smallmatrix}$, yellow needles, m. p. $175\text{--}176^{\circ}$, and *p*-dimethylaminobenzaldehyde, $\text{C}_3\text{H}_2\text{ON}_2\text{S}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, red, microscopic plates, commences to decompose at 200° , m. p. 266° .

Rhodaninacetic acid (3-carboxymethylrhodanic acid),



is formed as the *barium* salt by the action of carbon disulphide and baryta on glycine (compare Siegfried, Abstr., 1905, ii, 332; 1906, i, 324) and treatment of the resulting *barium dithiocarbamate*,



with ethyl chloroacetate. The rhodaninacetic acid crystallises in needles or leaflets, loses H_2O at 100° , or partially in a vacuum, m. p. 145° , and forms a white *lead* and green *copper* salt; the red *silver* salt rapidly decomposes. The condensation products with benzaldehyde, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{N} < \begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{CHPh} \\ \text{CS}\cdot\text{S} \end{smallmatrix}$, yellow needles, commence to decompose at 200° , m. p. 240° ; *m*-nitrobenzaldehyde, $\text{C}_{12}\text{H}_8\text{O}_3\text{N}_2\text{S}_2$, yellow needles, commences to decompose at 200° , m. p. $270\text{--}280^{\circ}$, and *p*-dimethylaminobenzaldehyde, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2\text{S}_2$, orange-red plates, m. p. 235° (decomp.), are described.

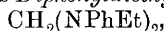
Rhodanic acids are obtained also from other amino-acids, such as alanine and aminobenzoic acid; that from asparagine yields a crystalline *benzylidene* derivative. Analogous substances are formed from the hydrolysis products of gelatin and from Witte's peptone. G. Y.

Action of Formaldehyde on Secondary Aromatic Amines.

JULIUS VON BRAUN (*Ber.*, 1908, 41, 2145—2156).—When formaldehyde acts on methylaniline or its aliphatic homologues in neutral or alkaline solution, condensation readily occurs with production of derivatives of methylenediamine. In the case of methyl-*o*-toluidine, however, the reaction is more sluggish, and still more so with methyl-*p*-toluidine. On boiling diphenyl-, dimethyl-, or diethyl-methylenediamine with acids or by treating methyl- or ethyl-aniline (2 mols.) with formaldehyde (1 mol.) in acid solution, the product is in each case the same; it consists of a mixture of the original secondary base, the diphenylmethane derivative, and a more complex substance containing about $1\frac{1}{2}$ mols. of the formaldehyde residue to 2 mols. of the base.

The latter is formed in larger amount when a greater excess of formaldehyde is employed; it is formed probably from a further condensation of formaldehyde with the diphenylmethane base, involving the elimination of the hydrogen atom in the ortho-position to the nitrogen and the condensation of a further amount of methylaniline. This explanation is confirmed by the fact that methyl-*o*- and -*p*-toluidines furnish only very small amounts of these complex substances, the diphenylmethane bases derived from them containing only half as many *o*-hydrogen atoms as in the case of that derived from methylaniline.

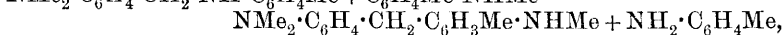
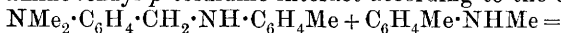
s-Diphenyldimethylmethylenediamine, $\text{CH}_2(\text{NPhMe})_2$, prepared from methylaniline and formaldehyde in presence of alkali, forms a mass of white crystals, m. p. 35° . *s*-Diphenyldiethylmethylenediamine,



forms white, glistening needles, m. p. 79° , b. p. $205^\circ/9$ mm. Diethyldiaminodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NHEt})_2$, prepared from formaldehyde and ethylaniline in presence of hydrochloric acid, is a pale yellow liquid, b. p. $255^\circ/10$ mm.; the nitroso-derivative has m. p. 83° , and the phenylthiocarbamide, white leaflets, has m. p. 153° . For investigating the action of formaldehyde on methyl-*o*-toluidine, the latter was prepared by the action of cyanogen bromide on dimethyl-*o*-toluidine in the same way as described for methyl-*p*-toluidine (this vol., i, 626). The *o*-tolylmethylcyanamide produced in the reaction has b. p. $135\text{--}136^\circ/8$ mm., and, on boiling with 30% sulphuric acid for twenty hours, yields methyl-*o*-toluidine and a small amount of dimethyldiaminodi-*o*-tolylmethane. *o*-Tolylecyanamide in contrast to this furnishes *o*-toluidine and *o*-tolylcarbamide.

s-Di-*o*-tolylldimethylmethylenediamine, $\text{CH}_2(\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me})_2$, has b. p. $212\text{--}215^\circ/18$ mm.; it yields dimethyldiaminodi-*o*-tolylmethane when boiled with acids. *s*-Di-*p*-tolylldimethylmethylenediamine forms white crystals, m. p. 68° . Dimethyldiaminodi-*p*-tolylmethane is a tough, gummy substance; the nitroso-derivative is a yellow, crystalline powder, m. p. 123° .

The difference exhibited by methylaniline and methyl-*o*-toluidine in their behaviour towards formaldehyde is also shown in the conversion of aminobenzyl bases into diphenylmethane bases by boiling with amines in acid solution. Thus, whilst methyl-*o*-toluidine and dimethylaminobenzyl-*p*-toluidine interact according to the equation

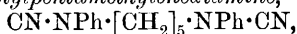


methylaniline furnishes a complex substance similar to that obtained in the formaldehyde condensation, together with *p*-toluidine and trimethyldiaminodiphenylmethane, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$, b. p. $245\text{--}246^\circ/9$ mm., m. p. 57° , the nitroso-derivative of which forms small, yellow crystals, m. p. $96\text{--}97^\circ$. J. C. C.

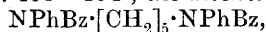
Synthesis of *s*-Diphenylcadaverine. [*s*-Diphenylpentamethylenediamine]. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2165—2168).—*s*-Diphenylpentamethylenediamine has been prepared in two ways, namely, (1) aniline is converted by means of $\alpha\epsilon$ -dibromo-*n*-pentane into 1-phenylpiperidine, this with cyanogen bromide gives

phenyl- ω -bromoamylcyanamide (Abstr., 1907, i, 960), which is condensed with aniline, forming cyanodiphenylpentamethylenediamine, this being hydrolysed finally. (2) Methylaniline is converted into *s*-diphenyldimethylpentamethylenediamine (this vol., i, 678), which is treated with cyanogen bromide, and the resulting *s*-dicyanodiphenylpentamethylenediamine is hydrolysed.

Cyanodiphenylpentamethylenediamine, $\text{CN}\cdot\text{NPh}\cdot[\text{CH}_2]_5\cdot\text{NHPh}$, forms small, colourless crystals, m. p. 67° ; the *hydrochloride* has m. p. 101° . *Dicyanodiphenylpentamethylenediamine*,



forms white, bushy needles, m. p. 76° . *s*-Diphenylpentamethylenediamine, $\text{NHPh}\cdot[\text{CH}_2]_5\cdot\text{NHPh}$, has m. p. 45° , b. p. $260\text{--}265^\circ/10\text{ mm.}$; the *hydrochloride*, m. p. $193\text{--}194^\circ$, the *dibenzoyl* derivative,



hard, glistening crystals, m. p. 124° , and the *dinitroso*-derivative, $\text{NO}\cdot\text{NPh}\cdot[\text{CH}_2]_5\cdot\text{NPh}\cdot\text{NO}$, m. p. 60° , are described. J. C. C.

Coloured Salts of Schiff's Bases. II. Hydrochlorides of Bases formed by Condensing Phenyl-*p*-phenylenediamine with Aromatic Aldehydes. FORRIS J. MOORE and R. G. WOODBRIDGE, JUN. (*J. Amer. Chem. Soc.*, 1908, 30, 1001—1004).—Moore and Gale (this vol., i, 368) have shown that the bases obtained by condensing *p*-phenylene-*as*-dimethyldiamine with aromatic aldehydes unite with hydrogen chloride in two proportions, forming dark red hydrochlorides and yellow dihydrochlorides.

It is now found that phenyl-*p*-phenylenediamine behaves in a similar manner, but that the dihydrochlorides are formed less readily. All the dihydrochlorides, however, with the exception of that of phenylcinnamylidene-*p*-phenylenediamine, are so stable as to retain their 2 mols. of hydrogen chloride when dried over sodium hydroxide in a vacuum desiccator. The dihydrochloride of the cinnamylidene compound, under these conditions, gradually darkens and loses 1 mol. of hydrogen chloride.

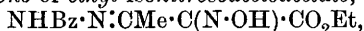
The *mono*- and *di*-hydrochlorides of the following bases have been prepared: benzylidene- and salicylidene-phenyl-*p*-phenylenediamines (Hencke, Abstr., 1889, 609); phenylpiperonylidene-*p*-phenylenediamine, m. p. 116° ; phenylanisylidene-*p*-phenylenediamine, m. p. 105° , which forms silver-grey, pearly scales, and phenylcinnamylidene-*p*-phenylenediamine, m. p. 145° , which crystallises in brilliant yellow scales. E. G.

Isomeric Modifications of *p*-Tolildioxime and their Behaviour as to Formation of Complexes. LEO A. TSCHUGAEFF and L. SPIRO (*Ber.*, 1908, 41, 2219—2221).—The conclusion previously drawn that only the *sym*-forms of 1:2-dioximes give complex metallic compounds with nickel, cobalt, or ferrous salts (this vol., i, 554) is further supported by the behaviour of the *p*-tolildioximes; the *amphi*- and *anti*-compounds give negative results, whereas the *syn*-modifications give with nickel salts a red precipitate, with ammonium palladium chloride and pyridine an orange-red precipitate, and with ferrous sulphate and pyridine a reddish-violet coloration.

The *syn*- and *anti*-*p*-tolildioximes have already been prepared by Stierlin (Abstr., 1889, 513); the *amphi*-compound was obtained as follows: On oxidising *p*-tolualdoxime by Beckmann's method (Abstr., 1899, 980), *p*-tolualdoxime peroxide, $(C_6H_4Me \cdot CH:N)_2O_2$, is obtained as glistening needles, m. p. 108°. It is insoluble in alkali, and is reduced by ammonium sulphide to aldoxime. By passing nitrous fumes into an ethereal suspension of the peroxide, or, better, into a solution of the aldoxime until almost complete solution of the crystals has occurred, *p*-tolildioxime peroxide, $C_{16}H_{14}O_2N_2$, is obtained, separating from light petroleum in crystals, m. p. 142°. *amphi-p*-Tolildioxime, $C_{16}H_{16}O_2N_2$, obtained by reducing the peroxide in alcoholic solution with zinc dust and acetic acid, forms white needles, which contain 1 mol. of chloroform of crystallisation when this solvent is used. The chloroform-free substance melts on placing it in a bath at 200°, immediately resolidifies, and then has m. p. 229—230°, a phenomenon also characteristic of γ -benzildioxime. It is readily converted into the β -modification at 200°.

W. R.

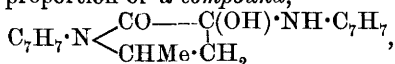
The Benzoylhydrazone of Ethyl *iso*Nitrosoacetoacetate and its Fission Products. CARL BÜLOW and FRITZ SCHAUB (*Ber.*, 1908, 41, 2181—2183).—When the benzoylhydrazone of ethyl *isonitroso*-acetoacetate is evaporated with aqueous ammonia or allowed to remain with concentrated sulphuric acid for eight hours, or boiled with alcohol for seventy-one hours, it is decomposed into ethyl alcohol, benzoic acid, and 4-*isonitroso*-3-methylpyrazolone (compare Knorr, Abstr., 1903, i, 660; Betti, Abstr., 1904, i, 533; Wolff, *ibid.*, 722). The benzoylhydrazone of ethyl *isonitroso*acetoacetate,



sinters at 164.5°, and is completely decomposed at 173°. The properties of 4-*isonitroso*-3-methylpyrazolone are correctly given by Betti, and the m. p. is 230—231° (Betti gives 230°).

J. C. C.

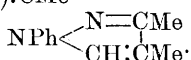
The Mechanism of the Synthesis of Cyclic Nitrogen Compounds [Quinoline Derivatives]. LOUIS J. SIMON (*Compt. rend.*, 1908, 146, 1400—1402).—In view of the results obtained in the condensation of ethyl oxalacetate with primary amines (Simon and Conduché, Abstr., 1907, i, 963; Simon and Mauguin, this vol., i, 296), the author has repeated his work on the action of pyruvic acid on *p*-toluidine (Abstr., 1898, i, 152) when molecular proportions are mixed in chloroform solution in the cold. The chief product is a very unstable compound, which is readily changed by the action of solvents or heat, or even after some time. This is not *p*-tolilpyruvic acid (*loc. cit.*), but a more complex substance, probably of the constitution $CO_2H \cdot CMe(NH \cdot C_7H_7) \cdot CH_2 \cdot C(OH)(NH \cdot C_7H_7) \cdot CO_2H$, which when treated with boiling water yields *p*-toluidine and 2:6-dimethylquinoline-4-carboxylic acid, decomposing at 265° and furnishing 2:6-dimethylquinoline. The ethyl ester has m. p. 74°. In the same reaction is also produced a small proportion of a compound,



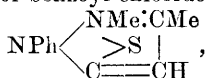
which with alcoholic hydrogen chloride gives 1-*tolyl-2-methyl-4:5-diketo-pyrrolidine*, $C_7H_7 \cdot N \begin{smallmatrix} \text{CO} \text{---} \text{CO} \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix}$. The production of these compounds is in accord with the author's views on the mechanism of the synthesis of quinoline derivatives (Abstr., 1907, i, 241). J. C. C.

Preparation of 4-Sulphonamino-1-phenyl-2:3-dimethyl-5-pyrazolone. EMIL SCHEITLIN (D.R.-P. 193632).—4-*Sulphonamino-1-phenyl-2:3-dimethyl-5-pyrazolone* results from the action of sodium hydrogen sulphite on 4-nitroso-1-phenyl-2:3-dimethyl-5-pyrazolone in aqueous solution. It is first produced in the form of its alkali salt, and is precipitated from the aqueous solution of this substance by hydrochloric acid. It is a monobasic acid, and is readily neutralised either by organic bases or alkali carbonates. G. T. M.

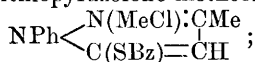
Thiopyrazolones. AUGUST MICHAELIS (*Annalen*, 1908, 361, 251—301).—Since azo-derivatives of thiopyrazolone (Abstr., 1905, i, 392) and of thiopyrines and antipyrines (Abstr., 1901, i, 52; 1904, i, 780) have been described, it seemed of interest to study the parent substances, the thiopyrazolones. Attempts to prepare these by fission of methyl from thiopyrines or ψ -thiopyrines were unsuccessful, as the methyl-sulphur linking is mostly too stable. Whilst antipyrine hydriodide, when heated, decomposes into methyl iodide and phenylmethylpyrazolone, the thiopyrine hydriodides under the same conditions are transformed into the salts of the corresponding ψ -thiopyrines, which are stable towards concentrated hydrochloric acid at 200°. Glacial acetic acid and 48% hydrobromic acid (Stoermer, this vol., i, 190) are also without action. Some ψ -thiopyrines are attacked by hydrogen haloids, but these lose sulphur; thus ψ -methylthiopyrine, $NPh \begin{smallmatrix} N \text{---} CMe \\ C(SMe) \cdot CMe \end{smallmatrix}$, forms phenyldimethylpyrazole,



It was, however, found possible to prepare 5-thio-1-phenyl-3-methylpyrazolone by the action of benzoyl chloride on thiopyrine,



which forms the benzoylthiopyrazolone methochloride,



this, when heated, loses methyl chloride, and the resulting benzoylthiopyrazolone, $NPh \begin{smallmatrix} N \text{---} CMe \\ C(SBz) \cdot CH \end{smallmatrix}$, on hydrolysis with hydrochloric

acid, yields 5-thio-1-phenyl-3-methylpyrazolone, $NPh \begin{smallmatrix} N \text{---} CMe \\ C(SH) \cdot CH \end{smallmatrix}$ (Abstr., 1904, i, 780). The derivatives of this thiopyrazolone, of its 4-benzoyl derivative, and of 5-thio-1-*p*-tolyl-3-methylpyrazolone, which has been prepared in the same manner, are now described.

Thiopyrazolones resemble pyrazolones in the following points. They condense with benzaldehyde in molecular proportions, forming benzylidene derivatives. These are colourless in the thiopyrazolone, but intensely red in the pyrazolone, series. Pyrazolones and thiopyrazolones condense with ketones in the molecular proportions 1:1 and 1:2, in the latter case with loss of hydrogen sulphide and formation of a tricyclic nucleus. Thiopyrazolones, like pyrazolones, form coloured azo-compounds. Both series have basic, as well as acid, properties; the thiopyrazolones are the more strongly acid, and, in correspondence with the great affinity of sulphur for mercury, readily form mercaptides. On the other hand, the thiopyrazolones and pyrazolones show the following differences. With alkyl iodides, the pyrazolones form antipyrines; the thio-compounds, not the corresponding thiopyrines, but ψ -thiopyrines. The azo-compounds of the pyrazolones are antipyrines; those of the thio-series are azo- ψ -thiopyrines. The pyrazolones form stable *isonitroso*-compounds; the thiopyrazolones, unstable nitroso-compounds, which rapidly change into disulphides. Oxidation of the pyrazolones leads to the formation of bispyrazolones; of the thiopyrazolones, to disulphides or sulphonic acids. On further oxidation, the bispyrazolones form pyrazole-blue, in which two pyrazole nuclei are united by a double linking; the disulphides form colourless compounds, in which two thiopyrazolone groups are united by a sulphur and by a carbon linking.

5-Thio-1-phenyl-3-methylpyrazolone and its Derivatives.—[With ROBERT PANDER.]—The *hydrochloride*, $C_{10}H_{10}N_2S \cdot HCl$, m. p. 145° , *platinichloride*, $(C_{10}H_{10}N_2S)_4 \cdot H_4PtCl_6$, yellow powder, m. p. 175° , the *silver salts*, $C_{10}H_9N_2S \cdot Ag$ and $C_{10}H_9N_2S \cdot Ag \cdot AgNO_3 \cdot H_2O$, the *mercuric salt*, $(C_{10}H_9N_2S)_2 \cdot Hg$, m. p. 70° , and the *mercurichloride*, $C_{10}H_9N_2S \cdot HgCl$,

white crystals, m. p. 196° , of 5-thio-1-phenyl-3-methylpyrazolone are described. The action of methyl iodide on the thiopyrazolone leads to the formation of ψ -thiopyrine hydriodide.

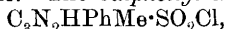
The benzoyl derivative, m. p. 93° (Abstr., 1904, i, 780), reacts with bromine in glacial acetic acid solution, forming the 4-bromo-derivative,

$$NPh \begin{cases} N \equiv CMe \\ C(SBz) \cdot CBr \end{cases}$$
 which crystallises in white needles, m. p. 116° .

The action of benzenesulphonyl chloride on the thiopyrazolone in alkaline solution leads to the formation of the 5-benzenesulphonylthio-compound, $C_{10}H_9N_2 \cdot S \cdot SO_2Ph$, which is obtained as a yellow oil. With diazobenzene chloride in alkaline solution, the thiopyrazolone forms 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene (Abstr., 1905, i, 392). When treated with sodium nitrite in acid solution and with iodine in presence of potassium iodide, the thiopyrazolone forms the *disulphide*, $S_2(C_{10}H_9N_2)_2$, which is obtained as a yellow, viscid oil, and gives with platinum tetrachloride a yellow, with mercuric chloride a white, precipitate. On treatment with iodine in alcoholic solution, the thiopyrazolone yields the *disulphide* of an iodo-derivative, $S_2(C_{10}H_8N_2I)_2$, as a white, crystalline precipitate.

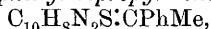
1-Phenyl-3-methylpyrazole-5-sulphonic acid, $C_{10}H_9N_2 \cdot SO_3H$, formed by oxidation of the thiopyrazolone with hydrogen peroxide in very dilute alkaline solution, separates in white crystals, m. p. 235° , and

when heated with concentrated hydrochloric acid at 150° is decomposed, forming sulphuric acid and 1-phenyl-3-methylpyrazole. The sodium, $C_{10}H_9N_2 \cdot SO_3Na$, and barium, ($+ H_2O$), salts were analysed. On treatment with bromine water, the sulphonic acid yields 4-bromo-1-phenyl-3-methylpyrazole-5-sulphonic acid, m. p. 225° , which yields sulphuric acid and 4-bromo-1-phenyl-3-methylpyrazole when heated with an excess of bromine. The sulphonyl chloride,



formed by heating the sulphonic acid with phosphorus pentachloride, crystallises in white needles, m. p. 101° , and is hydrolysed by hot water, forming the acid. The sulphonamide, $C_{10}H_9N_2 \cdot SO_2 \cdot NH_2$, prepared by shaking the sulphonyl chloride with ammonium carbonate, crystallises in white prisms, m. p. 243° , and is soluble in aqueous sodium hydroxide. The anilide, $C_{10}H_9N_2 \cdot SO_2 \cdot NHPh$, crystallises in needles, m. p. 127° .

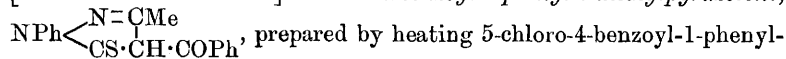
The thiopyrazolone reacts with benzaldehyde when heated, forming the 4-benzylidene derivative, $C_{10}H_8N_2S : CHPh$, which crystallises in white needles, m. p. $183-184^{\circ}$. On prolonged heating, the thiopyrazolone and benzaldehyde yield an amorphous product, m. p. 191° . The action of acetone on thiopyrazolone leads to the formation of (a) the 4-isopropylidene derivative, $C_{10}H_8N_2S : CMe_2$, which crystallises in needles, m. p. 204° , is sparingly soluble in alcohol, and when treated with permanganate in acetic acid solution yields a crystalline substance, m. p. 150° , and (b) a product, formed from 2 mols. of the thiopyrazolone and 1 mol. of acetone, $C_{10}H_8N_2 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ CMe_2 \end{smallmatrix} C_{10}H_8N_2$, which forms stout crystals, m. p. 176° , and is more soluble in alcohol and ether than the preceding condensation product. With acetophenone, the thiopyrazolone forms a 4-phenylisopropylidene derivative,



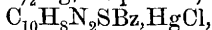
crystallising in yellow needles, m. p. $135-136^{\circ}$.

When heated with alkalis or concentrated acids, 4-bromo-5-benzoylthio-1-phenyl-3-methyl-4:5-dihydropyrazole is converted into bis-5-thio-1-phenyl-3-methylpyrazolone, $N \begin{smallmatrix} \diagup \quad \diagdown \\ NPh \cdot C \cdot S_2 \cdot C \cdot NPh \\ | \quad | \\ CMe \cdot C \quad C \cdot CMe \end{smallmatrix} N$, which crystallises in white needles, m. p. 198° , is stable towards oxidising and reducing agents, and forms a methiodide, $C_{20}H_{16}N_4S_2, MeI$, crystallising in white needles, m. p. 198° , losing methyl iodide.

5-Thio-4-benzoyl-1-phenyl-3-methylpyrazolone and its Derivatives.—[With ERICH LEHMANN.]—5-Thio-4-benzoyl-1-phenyl-3-methylpyrazolone,



prepared by heating 5-chloro-4-benzoyl-1-phenyl-3-methylpyrazole with sodium hydrogen sulphide in alcoholic solution, crystallises in dark yellow needles with red lustre, m. p. 112° , and forms an unstable hydrochloride, crystallising in needles. The mercuric salt, $(C_{10}H_8N_2SBz)_2Hg$, m. p. 201° , and the mercurichloride,

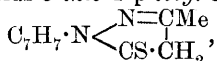


white needles, m. p. 223° , were analysed. If the 5-chloropyrazole is heated with alcoholic sodium hydrogen sulphide in a sealed tube at 150° , it forms a substance, m. p. 174° . When oxidised with hydrogen

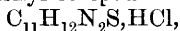
peroxide in alkaline solution, the thiopyrazolone yields 4-benzoyl-1-phenyl-3-methylpyrazole-5-sulphonic acid, which is amorphous, and is hydrolysed by concentrated hydrochloric acid, forming hydrochloric acid and 1-phenyl-4-benzoyl-3-methylpyrazole. One oxidation of the thiopyrazolone with hydrogen peroxide led to the formation of a crystalline substance, m. p. 84°. Oxidation of the thiopyrazolone with iodine in alkaline solution leads to the formation of the disulphide, $(C_{10}H_8N_2Bz)_2S_2$, which is obtained as a by-product in the preparation of the thiopyrazolone from the 5-chloropyrazole; it crystallises in yellow plates, m. p. 156°, and dissolves in concentrated hydrochloric acid.

5-Methylthiol-4-benzoyl-1-phenyl-3-methylpyrazole (4-benzoyl- ψ -thiopyrpyrine), $COPh \cdot C_3N_2PhMe \cdot SMe$, formed by the action of methyl iodide on the thiopyrazolone in alkaline solution, crystallises in white needles, m. p. 78°, and on oxidation with permanganate in glacial acetic solution yields the sulphone, $COPh \cdot C_3N_2PhMe \cdot SO_2Me$, crystallising in colourless plates, m. p. 167°. The 5-ethylthiol compound, $COPh \cdot C_3N_2PhMe \cdot SEt$, colourless plates, m. p. 98°, is formed by the action of ethyl iodide on the thiopyrazolone in alkaline solution, or by the action of mercaptan and sodium ethoxide on the 5-chloropyrazole. The ethylsulphone, $C_{18}H_{18}O_3N_2S$, crystallises in colourless needles, m. p. 122°. The 5-phenylthiol compound, $COPh \cdot C_3N_2PhMe \cdot SPh$, cannot be prepared from the thiopyrazolone, but is obtained by heating the 5-chloropyrazole with thiophenol and sodium ethoxide; it crystallises in colourless needles, m. p. 104°, and yields sulphuric acid when heated with nitric acid only at 300°. The sulphone, $C_{23}H_{18}O_3N_2S$, forms colourless needles, m. p. 125°, and when heated with phenylhydrazine is reduced to the phenylthiol compound. The benzyl ether, $COPh \cdot C_3N_2PhMe \cdot S \cdot CH_2Ph$, is formed from benzyl chloride and the thiopyrazolone; it crystallises in needles, m. p. 116°. The 5-benzoyl derivative, $C_{10}H_8N_2SBz_2$, prepared by shaking the thiopyrazolone with benzoyl chloride in alkaline solution, crystallises in needles, m. p. 107°. The carboxymethyl ether, $COPh \cdot C_3N_2PhMe \cdot S \cdot CH_2 \cdot CO_2H$, formed from the thiopyrazolone and chloroacetic acid, is obtained in colourless crystals, m. p. 124°, and is soluble in dilute alkalis.

5-Thio-1-p-tolyl-3-methylpyrazolone and its Derivatives. — [With ERICH DULK.]—p-Tolylthiopyrpyrine, m. p. 212°, which will be described later, is converted into 5-benzoylthio-1-p-tolyl-3-methylpyrazolone, b. p. 190–200°/15 mm., in the same manner as that employed with the phenyl compound. On hydrolysis with alcoholic potassium hydroxide, the benzoyl compound yields 5-thio-1-p-tolyl-3-methylpyrazolone,



which is also formed from 1-p-tolyl-3-methylpyrazolone by Stoermer and Johannsen's method (Abstr., 1907, i, 966); it is obtained in large, rhombic crystals, m. p. 135°, and behaves towards alkalis and acids in the same manner as the phenyl compound. The hydrochloride,



colourless plates; the mercuric salt, $(C_{11}H_{11}N_2S)_2Hg$, needles, m. p. 142°; the mercurichloride, $C_{11}H_{11}N_2S \cdot HgCl$, prisms, m. p. 208. The methiodide, $C_{11}H_{12}N_2S \cdot MeI$, formed by the action of methyl iodide on

the thiopyrazole, has m. p. 175° , and is converted by water into the liquid methyl ether. The benzoyl derivative, $C_{11}H_{11}N_2 \cdot SBz$, crystallises in white needles, m. p. 114° , and forms a 4-bromo-derivative, $C_{11}H_{10}N_2Br \cdot SBz$, which crystallises in prisms, m. p. 104° , yields benzoic acid and hydrogen bromide when heated with concentrated hydrochloric acid, and appears to form 4-bromo-1-*p*-tolyl-3-methylpyrazolone when treated with alkalis. The disulphide, $S_2(C_{11}H_{11}N_2)_2$, forms a yellowish-green mass, m. p. 74° , and is soluble in concentrated hydrochloric acid, being reprecipitated unchanged by water. The 5-sulphonic acid, $C_{11}H_{11}N_2 \cdot SO_3H$, crystallises in white prisms, m. p. 246° ; the barium salt, $(C_{11}H_{11}O_3N_2S)_2Ba$, forms small prisms. The sulphonyl chloride, $C_{11}H_{11}N_2 \cdot SO_2Cl$, white needles, m. p. 77° . The sulphonamide, $C_{11}H_{11}N_2 \cdot SO_2 \cdot NH_2$, prisms, m. p. 227° . The sulphonanilide, $C_{11}H_{11}N_2 \cdot SO_2 \cdot NHPh$,

needles, m. p. 118° .

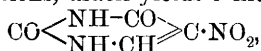
The 4-benzylidene derivative, $C_{11}H_{10}N_2S:CHPh$, crystallises in white needles, m. p. 212° . When heated with the calculated amount of acetone, the thiopyrazolone yields the 4-isopropylidene compound,

$C_{11}H_{10}N_2S:CM_e_3$, crystallising in colourless needles, m. p. 206° , but if with an excess of acetone and alcohol or a large excess of acetone alone, it forms the condensation product, $C_{11}H_{10}N_2 \langle \begin{smallmatrix} S \\ CM_e_2 \end{smallmatrix} \rangle C_{11}H_{10}N_2$, which crystallises in needles, m. p. 186° . The 4-phenylethylidene derivative,

$C_{11}H_{10}N_2S:CPhMe$, formed from the thiopyrazolone and acetophenone, crystallises in colourless needles, m. p. 106° . G. Y.

Pyrimidines. VIII. Separation of Thymine from Uracil. TREAT B. JOHNSON (*J. Biol. Chem.*, 1908, 4, 407—418).—When thymine is dissolved in cold fuming nitric acid (D 1.5) and evaporated, crystals of nitrohydroxyhydrothymine, $CO \langle \begin{smallmatrix} NH & CO \\ NH \cdot CH(OH) \end{smallmatrix} \rangle CMe \cdot NO_2$, are formed, which generally melt with effervescence at 183 — 185° (α -variety), but sometimes at 230 — 235° (efferv.); on keeping, the latter modification is spontaneously transformed into the former. Both modifications when reduced yield the original thymine.

Under the same conditions, uracil yields 5-nitrouracil,

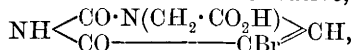


which requires 800 to 900 parts of cold alcohol for complete solution, and can be reduced to amino-uracil. Since nitrohydroxyhydrothymine is very soluble in cold alcohol, a separation of the two substances can be readily effected by nitration. One gram of the mixture is dissolved in 10 c.c. of nitric acid (D 1.5); after evaporation of the solution below 60° , the residue is extracted with 15 c.c. of cold alcohol. The nitro-compounds can be purified by crystallisation from hot water and alcohol. C. B.

Pyrimidines. XXXI. Synthesis of Uracil-3-acetic Acid. HENRY L. WHEELER and LEONARD M. LIDDLE (*J. Amer. Chem. Soc.*, 1908, 30, 1152—1156).—Johnson and Heyl (Abstr., 1907, i, 728) have

found that when 2-ethylthiol-6-pyrimidone is treated with methyl iodide in presence of potassium hydroxide, 2-ethylthiol-1-methyl-6-pyrimidone is produced. When, however, 2-ethylthiol-6-pyrimidone is treated with ethyl chloroacetate and alkali hydroxide, alkylation takes place in the 3-position with formation of *ethyl 2-ethylthiol-6-pyrimidone-3-acetate*, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CH}$, m. p. 129°, which crystallises in long, colourless prisms. The corresponding *acid*, m. p. 208—209°, forms slender prisms, and can be prepared either by the hydrolysis of the ester or by heating 2-ethylthiol-6-pyrimidone with potassium chloroacetate. When the acid is warmed with hydrochloric acid, mercaptan is evolved and uracil-3-acetic acid is produced.

Uracil-3-acetic acid, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CH}$, m. p. 285° (decomp.), prepared by heating an alkaline solution of uracil with chloroacetic acid, forms small tablets; its *potassium*, *copper*, and *barium* salts are described. The *methyl* ester melts partly at about 177°, and completely at about 216°. The 5-bromo-derivative,

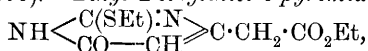


m. p. 244° (decomp.), forms colourless needles. The corresponding 5-nitro-derivative, m. p. 264—265° (decomp.), crystallises in colourless prisms.

1-Methyluracil-3-acetic acid, $\text{NMe} \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CH}$, m. p. 239—240°, prepared by the action of potassium chloroacetate on methyluracil or by treating uracil-3-acetic acid with methyl iodide in presence of potassium hydroxide, crystallises in needles or prisms.

E. G.

Pyrimidines. XXXII. Synthesis of Uracil-4-acetic Acid.
HENRY L. WHEELER and LEONARD M. LIDDLE (*J. Amer. Chem. Soc.*, 1908, 30, 1156—1160).—*Ethyl 2-ethylthiol-6-pyrimidone-4-acetate*,

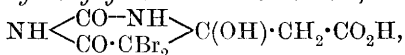


m. p. 131°, prepared by the action of ethyl acetonedicarboxylate on an alkaline solution of the ethyl bromide additive product of thiocarbamide, forms long, colourless, silky needles. The corresponding *acid*, m. p. 155° (decomp.), crystallises in colourless needles, and when heated at 170° is converted into 2-ethylthiol-4-methyl-6-pyrimidone. When this acid is warmed with strong hydrochloric acid, mercaptan is evolved and uracil-4-acetic acid is produced.

Uracil-4-acetic acid, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 340° (decomp.), crystallises in flat prisms and is soluble in about 8 parts of boiling water and in 30 parts of cold water; its *potassium* salt is described. The *ethyl* ester, m. p. 187—189°, crystallises with 1H₂O. The *methyl* ester has m. p. 216—218°. 5-Nitrouracil-4-acetic acid, m. p. 153° (decomp.), forms minute cubes.

By the action of bromine on an aqueous solution of uracil-4-acetic

acid, 5-dibromo-4-hydroxyhydrouracil-4-acetic acid,



m. p. 240° (decomp.), is produced, which forms colourless plates, probably containing $\frac{1}{2}\text{H}_2\text{O}$. E. G.

α -Chloro- β -iminazolypropionic Acid. ADOLF WINDAUS and W. VOGT (*Beitr. chem. Physiol. Path.*, 1908, 11, 406—408).—By employing the method already given by Fränkel (*Abstr.*, 1906, i, 547) for preparing chlorohistidinecarboxylic acid by treating histidine hydrochloride with nitrous acid and subsequent treatment of the crude product so obtained with zinc dust and glacial acetic acid, the authors have succeeded in obtaining only β -iminazolypropionic acid. The chlorohistidinecarboxylic acid was, however, obtained by the following method. Histidine was treated with hot potassium nitrate in concentrated hydrochloric acid; the crude hydrochloride of chlorohistidinecarboxylic acid was then esterified by 10% alcoholic hydrogen chloride, and the hydrochloride of the ester thus obtained was precipitated from alcoholic solution by means of ether. This was converted into the oxalate, m. p. 161°. The free ester is an oil, from which, by saponification, pure chlorohistidinecarboxylic acid can be obtained. This melts at 191° (decomp.).

β -Iminazolypropionic acid, on the other hand, which agrees in properties with the substance described by Fränkel as chlorohistidinecarboxylic acid, has m. p. 80°, and when heated loses H_2O .

S. B. S.

Hydroxyquinoxalines. OTTO HINSBERG (*Ber.*, 1908, 41, 2031—2033).—Five compounds, $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$, have been prepared; these have been termed: 1. Dihydroxyquinoxaline (Bladin, *Abstr.*, 1885, 785); 2. Dihydroxyethylenephenylenediamine (Aschan, *ibid.*, 1886, 147); 3. Dihydroxyquinoxaline (Hinsberg and Pollak, *ibid.*, 1896, i, 394); 4. Phenyleneoxamide (Seeliger and Meyer, *ibid.*, 1897, i, 45); 5. Phenyleneoxamide (Motylowski, this vol., i, 371). Compounds 2 to 5 are shown to be identical. Although compounds 1 and 3 were previously stated to be identical, it is now shown that they are different substances. Hinsberg and Pollak's compound, unlike Bladin's, does not combine with water of crystallisation.

Motylowski's oxidation product of hydroxydihydroquinoxaline is probably identical with 2-hydroxyquinoxaline.

J. J. S.

Synthesis of Phenylquinoxalines. OTTO FISCHER and FRITZ RÖMER (*Ber.*, 1908, 41, 2350—2353).—Fischer and Schindler described recently (this vol., i, 221) the formation of 2- and 3-phenylnaphthaquinoxalines from diketo-*s*- $\alpha\beta$ -naphthazine and diketo-*as*- $\alpha\beta$ -naphthazine respectively. As these phenylnaphthaquinoxalines were previously unknown, and in their properties differed markedly from Feist and Arnstein's phenylnaphthaquinoxaline prepared from β -naphthaquinone and phenylethylenediamine (*Abstr.*, 1895, i, 258), it was advisable to confirm their constitution by synthesis. For this purpose, the authors employed Hinsberg's method for the preparation of phenylquinoxalines from bromoacetophenone and *o*-diamines, and

found that the action of bromoacetophenone on 1 : 2-diaminonaphthalene leads to the formation of the two products described by Fischer and Schindler, but in small yields and accompanied by much resin. Better yields are obtained by employing isonitrosoacetophenone, which reacts more smoothly than does bromoacetophenone with *o*-diamines, and with *o*-phenylenediamine gives good yields of phenylquinoxaline (Hinsberg, Abstr., 1897, i, 120).

Fischer and Schindler's phenylnaphthaquinoxalines are formed when isonitrosoacetophenone and 1 : 2-diaminonaphthalene are boiled in molecular proportions in methyl-alcoholic solution. The 2-phenyl-compound is now found to be white. Both quinoxalines are volatile with steam, and give with zinc dust and acetic acid a transient red coloration. If boiled in ethyl-alcoholic solution, isonitrosoacetophenone and 1 : 2-diaminonaphthalene form, together with the quinoxalines, a substance, which separates from pyridine in red crystals, and gives green and blue colorations with concentrated sulphuric acid. This red substance is not formed in presence of small amounts of hydroxylamine hydrochloride.

The repetition of Feist and Arnstein's experiment shows that these authors could not have obtained a single substance. The action of ethylenediamine, which oxidises more easily than phenylethylenediamine, on β -naphthaquinone leads to the formation of naphthaquinoxaline (Hinsberg, Abstr., 1890, 972). The *picrate*, $C_{18}H_{11}O_7N_5$, crystallises in yellow needles, m. p. 171°. G. Y.

Preparation of Isatin and its Methyl Derivative. RUDOLPH BAUER (D.R.-P. 193633).—It has been found that isatin and its methyl derivatives can be produced by the action of warm concentrated sulphuric acid on substituted iminochlorides having the general formula $RN:CCl:CCl:NR$, where R is a phenyl or tolyl group. Diphenyloxaliminochloride, m. p. 115°, di-*o*-tolylloxaliminochloride, m. p. 131°, di-*m*-tolylloxaliminochloride, yellow prisms, m. p. 72°, and di-*p*-tolylloxaliminochloride, yellow leaflets, m. p. 107°, were employed in this synthesis. *o*-Methylisatin, which is fully described for the first time, yields a *phenylhydrazone*, golden needles, m. p. 242°, and *oxime*, yellow needles, m. p. 235°. G. T. M.

Preparation of Stable Chloroindigotins. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193971).—A stable chloroindigotin, $C_{16}H_9O_2N_2Cl$, is obtained by passing chlorine into a mixture of finely-powdered indigotin and nitrobenzene. A vigorous reaction occurs, and the chloro-derivative is produced in a crystalline form. When reduced with alkaline hyposulphite, this substance furnishes a light yellow leuco-derivative, which has valuable tinctorial properties. G. T. M.

Preparation of Halogen Derivatives of β -Naphthindigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193970).—*Bromo- β -naphthindigotin* is prepared by successively brominating β -naphthisatin, converting the bromo-derivative into the chloride, reducing the latter with hydriodic acid or some other suitable reducing agent, and finally oxidising the product with air in the presence of sodium hydroxide. The product is a dark green, crystalline

powder, which furnishes a reddish-brown leuco-derivative giving fast shades of blue on cotton. G. T. M.

Transformation of *s*-Phenyldiphenylhydrazine by Hydrogen Chloride in Benzene Solution. MIECISŁAS DZIURZYŃSKI (*Bull. Acad. Sci. Cracov*, 1908, 401—408).—When *s*-phenyldiphenylhydrazine is dissolved in benzene and the solution saturated with hydrogen chloride, intramolecular change takes place with formation of a semidine base and a diphenylene base, which are separated by means of their different solubilities in aqueous alcohol.

The semidine base, which is probably 3-amino-4-anilinodiphenyl, $\text{NHPh} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{C}_6\text{H}_5$, crystallises in silvery scales, m. p. 141° . The *acetyl* derivative forms white needles, m. p. 165° . The *hydrochloride* and the *sulphate* are described. With nitrous acid, the base yields an *azimino*-derivative, $\text{NPh} \begin{smallmatrix} \diagup \text{C}_6\text{H}_3\text{Ph} \\ \diagdown \text{N}_2 \end{smallmatrix}$, m. p. 82.5° , with benzil a compound,



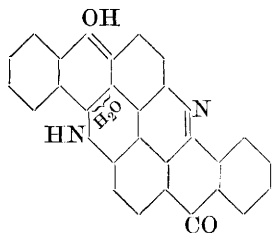
of which the free base gives a yellowish-green fluorescence in alcoholic solution, and with carbon disulphide a compound, $\text{C}_6\text{H}_3\text{Ph} \begin{smallmatrix} \diagup \text{NH} \\ \diagdown \text{NPh} \end{smallmatrix} \text{CS}$, yellowish-white scales, m. p. 150° .

The diphenylene base, which is probably 2:4'-diamino-*p*-diphenylbenzene, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, is a dark oil, crystallising after some months. The *diacetyl* derivative forms small, hard crystals, m. p. 223° .

The *dihydrochloride* is blue, and the *sulphate* crystallises from alcohol in white needles. In the filtrate from the precipitated bases, 4-benzeneazodiphenyl was recognised. J. C. C.

Indanthren and Flavanthren, X. Products of Reduction of Flavanthren and the Relation between their Colour and Constitution. ROLAND SCHOLL (*Ber.*, 1908, 41, 2304—2328. Compare Abstr., 1907, i, 540).—By the reduction of flavanthren, the author has prepared seven compounds, namely, dihydroflavanthren, α - and β -tetrahydroflavanthrens, α - and β -hexahydroflavanthrens, flavantrine, and flavantrinol, of which the fourth and the last will be described in a later paper.

[With KARL HOLDERMANN].—*Dihydroflavanthren hydrate* is prepared by reducing flavanthren with alkaline sodium hyposulphite in an atmosphere of hydrogen. On cooling, bronzy needles of the *sodium*

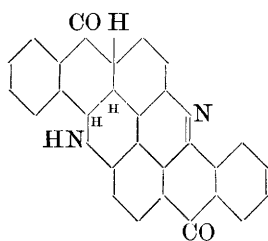


salt (annexed formula, in which the OH and H_2O groups are replaced by ONa and NaOH respectively) crystallise out, and are treated with acetic acid. Dark bluish-green, coppery crystals are obtained, which are fairly stable at the ordinary temperature, but are readily oxidised to flavanthren at 100° , or when moist; when heated for a few hours at 150 — 170° in a stream of carbon dioxide, water is lost and *dihydroflavanthren* is formed. This

is a green powder, which is not so readily oxidised by the air as is the hydrate. It is also the chief product when flavanthren is heated with hydriodic acid and red phosphorus at 125°. Although flavanthren is of a very weakly basic character, dihydroflavanthren hydrate readily forms salts with mineral acids. *Dihydroflavanthren hydrochloride* probably contains the acid united with the nitrogen atom.

o-Benzoyldihydroflavanthren is a reddish-brown powder, m. p. 220° (decomp.).

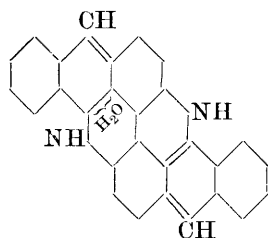
α-Tetrahydroflavanthren hydrate could not be isolated, but the sodium salt is stated to be formed when flavanthren is reduced by zinc dust and sodium hydroxide. On acidification, a mixture of dihydro-



flavanthren hydrate with a small amount of *α*-hexahydroflavanthren hydrate results.

β-Tetrahydroflavanthren (annexed formula), prepared by treating flavanthren with hydriodic acid and red phosphorus at 170°, is a green powder. It forms salts with acids and alkalis, in the latter case passing into the red enolic modification. The *dibenzoyl* derivative forms microscopic, lemon-yellow prisms. The authors consider that *β*-hexahydroflavanthren

is formed when the red alkaline solution of *β*-tetrahydroflavanthren is reduced with zinc dust, but the compound could not be isolated from the resulting yellow solution. By reducing



flavanthren with hydriodic acid and red phosphorus at 207–210°, *flavanthrine hydrate*, annexed formula, is formed as a greenish-brown powder, which on heating to 240° loses water and yields *flavanthrine*. This forms large, brown needles with a green, metallic lustre, and sinters at 380°, m. p. about 390°. It is readily oxidised to flavanthren.

The relation between the colour and constitution of these reduction products of flavanthren is discussed.

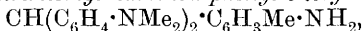
J. C. C.

Influence of Methyl Groups on the Tinctorial Properties of the Basic Dyes derived from Triphenylmethane. JEAN BIELECKI and ALEXANDRE KOLENIEW (*Bull. Acad. Sci. Cracow*, 1908, 296–318).—It is well known that the presence of such substituents as SO_3H , Cl , Br , NO_2 , OH , and CO_2H in the ortho-position to the methane-carbon atom of basic triphenylmethane dyes belonging to the malachite-green and magenta series renders them more resistant towards alkalis. The authors have now examined the effect of introducing the methyl group, not only in the ortho-position (where any increased fastness to alkalis might be assigned to steric hindrance of the change of the quinonoid to the carbinol structure under the influence of alkalis), but also in the meta- and para-positions to the methane carbon-atom. It is found that, in all three positions, the presence of the methyl group increases the fastness to alkalis, whilst with regard to the shade produced, its influence is similar to

that exerted by the acidic groups cited above; in the meta-position no change in colour is evident, whilst in the ortho- and para-positions the change is marked; thus *o*-methylated malachite-green is bluish-green and the *p*-methylated derivative is yellowish-green.

The dyes were prepared by condensing tetramethyldiaminodiphenyl-carbinol with 1 mol. of an amine (mostly homologues of dimethylaniline). When the operation is effected in presence of dilute hydrochloric acid, the amine usually attaches itself to the methane-carbon atom at the position para to the amino-group, but when concentrated sulphuric acid is used, the point of union is in the meta-position (compare Noetling, Abstr., 1892, 187).

4-Amino-4':4''-tetramethyldiaminodiphenyl-*o*-tolylmethane,



prepared by condensing the carbinol with *o*-toluidine in dilute hydrochloric acid, has m. p. 184°, and is readily oxidised to a *dye*, which dyes tannin-mordanted cotton in violet-blue shades. When sulphuric acid is used as condensing agent, there is formed 3-amino-4':4''-tetramethyldiaminodiphenyl-*o*-tolylmethane, m. p. 146°, which on oxidation yields a green *dye*. 4:4':4''-Hexamethyltriaminodiphenyl-*o*-tolylmethane, prepared from dimethyl-*o*-toluidine by condensing it with the carbinol in dilute hydrochloric acid, separates from ether as a pale yellow, microcrystalline powder, m. p. 144°. On oxidation, it yields a violet-blue *dye*. When sulphuric acid is used as the condensing agent, 3:4':4''-hexamethyltriaminodiphenyl-*o*-toluidine, m. p. 113°, is obtained, which on oxidation gives a yellowish-green *dye*.

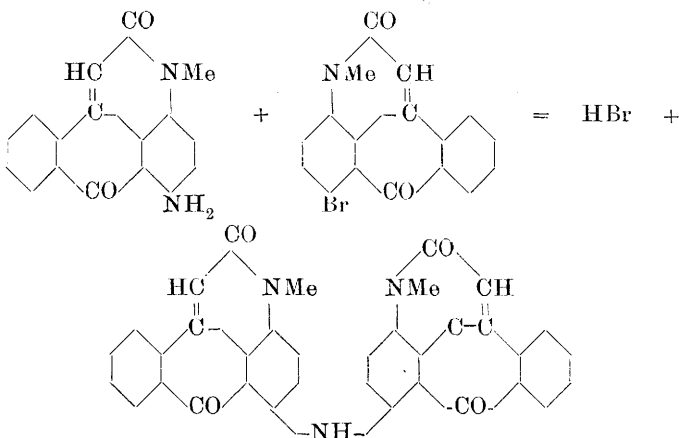
4:4':4''-Hexamethyltriaminodiphenyl-*m*-tolylmethane is prepared by condensing the carbinol with dimethyl-*m*-toluidine in presence of either dilute hydrochloric or concentrated sulphuric acid. It crystallises from methyl alcohol in colourless prisms, m. p. 118°, and on oxidation yields a violet-blue *dye*. 2:4':4''-Hexamethyltriaminodiphenyl-*p*-tolylmethane, prepared from the carbinol, dimethyl-*p*-toluidine, and dilute hydrochloric acid, crystallises from methyl alcohol in pale yellow flocks, m. p. 107°. The corresponding *dye* is violet-blue. When 100% sulphuric acid is used as the condensing agent, 3:4':4''-hexamethyltriaminodiphenyl-*p*-tolylmethane, white prisms, m. p. 113°, is obtained (Noetling, Abstr., 1892, 190, gives 100°). The corresponding dye is bluish-green (compare L. Cassella & Co., Abstr., 1904, i, 804).

2:4':4''-Hexamethyltriaminodiphenyl-*m*-xylylmethane, prepared by condensing the carbinol with dimethyl-*m*-4-xylidine in dilute hydrochloric acid, crystallises from methyl alcohol in yellow flocks, m. p. 115°. The corresponding *dye* is blue. When 100% sulphuric acid is the condensing agent, 3:4':4''-hexamethyltriaminodiphenyl-*m*-xylylmethane, prisms, m. p. 135°, is obtained. The corresponding *dye* is greenish-blue. 4:4':4''-Hexamethyltriaminodiphenyl-*p*-xylylmethane is prepared from the carbinol and dimethyl-*p*-xylidine by the aid of either dilute hydrochloric or 100% sulphuric acid. It crystallises from methyl alcohol in long needles, m. p. 150°. The corresponding *dye* is violet-blue. 2:4':4''-Hexamethyltriaminodiphenyl-*o*-xylylmethane, prepared from the carbinol and dimethyl-*o*-4-xylidine in presence of dilute hydrochloric acid, has m. p. 164°. This base could not be oxidised

either by tetrachloro-*p*-benzoquinone or lead peroxide. 3:4':4''-Hexamethyltriaminodiphenyl-o-xylylmethane is obtained when 100% sulphuric acid is used as the condensing agent in the preceding reaction. It crystallises from methyl alcohol in leaflets, m. p. 185°. The corresponding dye is deep blue. J. C. C.

Preparation of Anthracene Derivatives Containing Nitrogen.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 194253. Compare this vol., i, 456).—By condensing 1:4-aminoanthrapyridone with 4-bromoanthrapyridone by means of dry sodium acetate and copper chloride in the presence of naphthalene, a compound crystallising in dark violet needles is obtained, which is formed in accordance with the following equation :



A similar compound containing one anthrapyridone and one anthraquinone residue is obtained by condensing 1:4-bromoanthrapyridone and 4-aminoanthraquinone. Several substances of the same type are described in the patent. G. T. M.

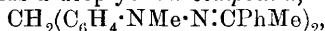
Constitution and Colour. FRIEDRICH KEHRMANN (*Ber.*, 1908, 41, 2340—2345).—Partly a criticism of Willstätter and Piccard's views as to the constitution of Wurster's dyes (this vol., i, 475). The author shows that change of colour can take place in two ways, namely, (1) without change in constitution of the chromophoric group: this occurs when an auxochromic group is introduced; and (2) accompanied by change in constitution of the chromophore, as when colourless bases yield coloured salts and *vice versa*. Quinhydrones are more strongly coloured than quinones, owing to the presence of the auxochromic hydroxyl group, and the compounds to which Willstätter and Piccard have assigned a special constitution do not differ in kind, but only in degree, from ordinary quinhydrones, and are therefore to be regarded as having a constitution similar to these. J. C. C.

Dihydrazines. I. 4:4'-Bismethylhydrazinodiphenylmethane, a Reagent for the Characterisation of Aldehydes. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2169—2181).—4:4'-Bismethylhydrazinodiphenylmethane, obtained by reducing dinitrosodimethyldiaminodiphenylmethane (Braun and Kayser, *Abstr.*, 1904, i, 687) with zinc and acetic acid, reacts instantly with aliphyl and aryl aldehydes, forming condensation products which are readily characterised. It reacts very slowly with ketones, so that a convenient method is afforded of distinguishing between the two. An exception to this rule is displayed by α -keto-carboxylic acids, which react as if they were aldehydes. Aldehydic sugars, such as mannose and galactose, condense immediately, but dextrose reacts only very slowly.

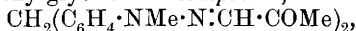
4:4'-Bismethylhydrazinodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}_2)_2$, has m. p. 102° ; the *hydrochloride*, m. p. 190° (decomp.), and *sulphate* are described. The *semicarbazide*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, is a white powder, m. p. 232° ; the *phenylthiosemicarbazide* has m. p. 211° , and the *benzoyl* derivative softens at 176° and has m. p. 181° .

4:4'-Bismethylhydrazinodiphenylmethane condenses to hydrazones of the type $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{N}\cdot\text{CH}\cdot\text{R})_2$ with the following aldehydes, the figures in brackets being the m. p.: formaldehyde (137°), acetaldehyde (114°), butaldehyde (71°), heptaldehyde (57°), citral ($107\text{--}108^\circ$), benzaldehyde (220° , softening at 214°), cuminaldehyde (169°), anisaldehyde (195°), *p*-dimethylaminobenzaldehyde (209°), salicylaldehyde (200° with previous sintering), opianic acid (220°), cinnamaldehyde (203°), furfuraldehyde (201°).

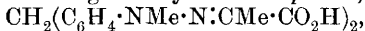
Acetophenone yields a deep yellow compound,



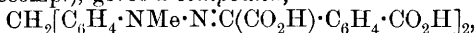
m. p. 105° ; the compound from benzophenone is deep yellow, sintering at 120° , m. p. 152° ; glyoxal yields a compound, $\text{C}_{17}\text{H}_{18}\text{N}_4$, decomp. $280\text{--}282^\circ$, and methylglyoxal the compound,



m. p. 185° . Pyruvic acid gives a yellow compound,



m. p. 100° (decomp.), and phenylpyruvic acid behaves similarly. Phthalonic acid, the *phenylmethylhydrazone* of which is yellow and has m. p. 140° (decomp.), gives a compound,



softening at 60° , m. p. 78° , and decomposing at 90° .

J. C. C.

Disulphides with Neighbouring Double Linkings. III. EMIL FROMM (*Annalen*, 1908, 361, 302—352. Compare *Abstr.*, 1906, i, 656, 714; 1907, i, 982).—It has been shown that all disulphides with neighbouring double linkings, $\text{X}\cdot\text{CR}\cdot\text{S}\cdot\text{S}\cdot\text{C}\cdot\text{Y}$, are decomposed by alkalis and amines with liberation of sulphur and formation of new compounds. Thus perthiocyanic acid reacts with phenylhydrazine, forming sulphur, phenyldithiourazole, 3-amino-5-thion-1-phenyldihydrotriazole, and anilthiuret. Similarly, the thiurets, $\text{NH}\begin{smallmatrix} \text{C}(\text{NH})\cdot\text{S} \\ \text{C}(\text{NR})\cdot\text{S} \end{smallmatrix}$, react with phenylhydrazine, forming two products, considered to have the formulæ $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NHPh}$ and $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NPh}\cdot\text{NH}_2$.

Fromm and Vetter (Abstr., 1907, i, 982) obtained only one product from the interaction of aniline and phenylthiuret, which was considered to have the formula $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NHPh}$. In continuing the investigation, it has now been found that the action of aromatic amines on thiurets gives rise to two products; thus, with aniline and *p*-tolylthiuret, there are formed phenylguanido-*p*-tolylthiocarbamide, $\text{C}_7\text{H}_7\cdot\text{N}:\text{C}(\text{SH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NHPh}$, and phenyl-*p*-tolylguanidothiocarbamide, $\text{C}_7\text{H}_7\cdot\text{N}:\text{C}(\text{NHPh})\cdot\text{NH}\cdot\text{C}(\text{SH})\cdot\text{NH}$.

The action of aniline or phenylhydrazine on thiurets, which are derived from secondary amines, is found to lead to the substitution of the anilino- or phenylhydrazino-group for the secondary amine residue.

The phenyldithiourazole described by Fromm and Schneider (Abstr., 1906, i, 714) has been re-studied, and in connexion with it a number of new dithiobiurets and their derivatives have been prepared.

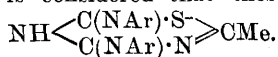
Action of Aromatic Amines and Hydrazines on p-Tolylthiuret.—[With ARNOLD WELLER.]—*p*-Tolylthiuret hydrochloride, $\text{C}_9\text{H}_{10}\text{N}_2\text{S}_2\text{Cl}$, is formed by boiling *p*-tolylthiurets with ferric chloride and hydrochloric acid; it is obtained as a yellow, amorphous powder, m. p. 194°, and, when boiled with 2 mols. of aniline in alcoholic solution, forms two products: (a) *Phenylguanido-p-tolylthiocarbamide*, $\text{C}_{15}\text{H}_{16}\text{N}_4\text{S}$, separates from the hot alcoholic solution and crystallises in white leaflets, m. p. 182°. Its *hydrochloride*, $\text{C}_{15}\text{H}_{16}\text{N}_4\text{S}\cdot\text{HCl}$, forms white needles, m. p. 214° (? 244°). (b) *Phenyl-p-tolylguanidothiocarbamide* is isolated from the alcoholic filtrate as the *hydrochloride*, $\text{C}_{15}\text{H}_{16}\text{N}_4\text{S}\cdot\text{HCl}$, which crystallises in needles, m. p. 158°. When boiled with benzyl chloride and alcoholic sodium hydroxide, the base from (a) yields *phenylguanido-p-tolyl-ψ-benzylthiocarbamide*, $\text{C}_{22}\text{H}_{11}\text{N}_4\text{S}$, which crystallises in white leaflets, m. p. 176°, whereas, under the same conditions, the base from (b) is converted into *phenyl-p-tolyldicyanodiamide*, which crystallises in white leaflets, m. p. 186°.

The action of *p*-toluidine on phenylthiuret leads to formation of only one product, which is identical with the phenyl-*p*-tolylguanidothiocarbamide described above.

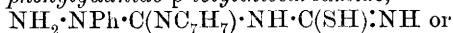
p-Tolylguanido-p-tolylthiocarbamide, $\text{C}_{16}\text{H}_{18}\text{N}_4\text{S}$, formed by the action of *p*-toluidine on *p*-tolylthiuret, crystallises in white needles, m. p. 170—180°; the *ψ-benzyl* derivative forms yellow needles, m. p. 199°.

The arylguanidoarylthiocarbamides are readily acetylated by means of acetic anhydride, whilst the diarylguanidothiocarbamides, on the other hand, do not form acetyl derivatives.

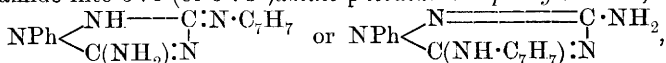
Acetylphenylguanido-p-tolylthiocarbamide, $\text{C}_{17}\text{H}_{18}\text{ON}_4\text{S}$, crystallises in needles, m. p. 225°. When it is heated with sodium hydroxide and benzyl chloride, the latter does not enter into reaction, but the alkali converts the acetyl compound into an *anhydro*-derivative, $\text{C}_{17}\text{H}_{16}\text{N}_4\text{S}$, which crystallises in white needles, m. p. 185°, and when heated with concentrated aqueous sodium hydroxide yields acetic acid and phenylguanido-*p*-tolylthiocarbamide. *Acetyl-p-tolylguanido-p-tolylthiocarbamide*, $\text{C}_{18}\text{H}_{20}\text{ON}_4\text{S}$, crystallises in white needles, m. p. 194°. The *anhydro*-derivative, $\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}$, forms needles, m. p. 206°. It is considered that these anhydro-derivatives have the constitution



Action of Phenylhydrazine on p-Tolylthiuret.—When treated with 2 mols. of phenylhydrazine, *p*-tolylthiuret hydrochloride yields *amino-phenylguanido-p-tolylthiocarbamide*,



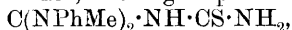
$\text{NH}_2 \cdot \text{NPh} \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{C}(\text{NC}_7\text{H}_7) \cdot \text{SH}$, which crystallises in white leaflets, m. p. 168°, and forms a *benzylidene* derivative, $\text{C}_{22}\text{H}_{21}\text{N}_5\text{S}$, greenish-yellow powder, decomp. 110°. Alcoholic sodium hydroxide converts aminophenylguanido-*p*-tolylthiocarbamide into 3:5-(or 5:3)-*amino-p-toluidino-1-phenyltriazole*,



which crystallises in white needles, m. p. 148°, is stable towards boiling acids or alkalis, and forms crystalline salts with acids. The *hydrochloride*, $\text{C}_{15}\text{H}_{15}\text{N}_5\text{HCl}$, white needles, m. p. 172°. The *acetyl* derivative, $\text{C}_{17}\text{H}_{17}\text{ON}_5$, m. p. 115°.

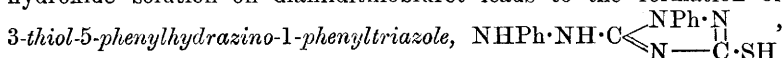
Action of Aromatic Amines and Hydrazines on Phenylmethylthiuret and Phenylethylthiuret.—[With H. BAUMHAUER.]—*Phenylethylthiobiuret*, $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$, formed by heating perthiocyanic acid with ethyl-aniline, separates from alcohol in crystals, m. p. 119·5°, and when boiled with dilute hydrochloric acid and ferric chloride yields *phenylethylthiuret hydrochloride*, $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2\text{HCl}$, m. p. 230°.

When boiled with aniline in alcoholic solution, phenyl-, methyl-, or phenylethyl-thiuret yields phenylguanidophenylthiocarbamide, sulphur, and methyl- or ethyl-aniline. Methylphenylthiuret reacts with methylaniline at 120—125°, forming sulphur and the *compound*,

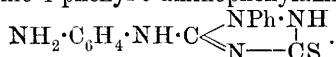


m. p. 90°, which cannot be benzylated with benzyl chloride and sodium hydroxide, but forms lead sulphide when heated with sodium plumbate.

When boiled with 2 mols. of phenylhydrazine, phenylmethylthiuret yields sulphur, methylaniline, 3-amino-5-thiol-1-phenyltriazole, m. p. 234°, and *dianildithiobiuret*, $\text{NH}(\text{CS} \cdot \text{NH} \cdot \text{NHPh})_2$, which crystallises from alcohol in needles, m. p. 178°. The action of cold potassium hydroxide solution on dianildithiobiuret leads to the formation of



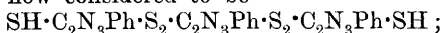
which forms yellowish-red crystals, m. p. 177°, and is oxidised by sulphur in boiling alkaline, or by iodine in boiling alcoholic, solution, forming the *benzeneazotriazole*, $\text{NPh} \cdot \text{N} \cdot \text{C}_2\text{N}_3\text{Ph} \cdot \text{SH}$, which is obtained in brownish-red crystals, m. p. 218°, and is soluble in aqueous alkalis. The action of acetic anhydride on dianildithiobiuret leads to the formation of a *substance*, which has m. p. 218°, but is not identical with the preceding azo-compound, as when boiled with aqueous potassium hydroxide and reprecipitated by an acid it yields the hydrazino-compound, m. p. 177°. When boiled with hydrochloric acid, dianildithiobiuret yields the preceding azo-compound, m. p. 218°, and a *base*, $\text{C}_{14}\text{H}_{13}\text{N}_5\text{S}$, which crystallises in white needles, m. p. 180·5°, and is probably 3-thio-1-phenyl-5-aminophenylaminotriazole,



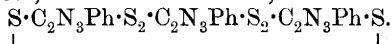
This forms a diacetyl derivative, $C_{18}H_{17}O_2N_5S$, crystallising in colourless needles, m. p. 106° , and a *dibenzylidene* derivative, $C_{28}H_{21}N_5S$, m. p. 195° .

The action of phenylhydrazine on phenylmethyldithiobiuret in boiling alcoholic solution leads to the formation of 3-amino-5-thiol-1-phenyltriazole, m. p. 244° , and 3:5-dithiol-1-phenyltriazole, m. p. 193° .

Oxidation Products of 3:5-Dithiol-1-phenyltriazole.—[With H. BAUMHAUER.]—The oxidation of 3:5-dithiol-1-phenyltriazole by means of iodine in alcoholic solution leads to the formation of two products: the one, m. p. 181° , previously (Abstr., 1906, i, 714) given as $C_{16}H_{10}N_6S_4$, is now considered to be



the other, m. p. 163° , has the constitution,



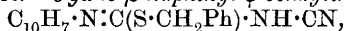
Both oxidation products, when boiled with alkalis, yield the parent dithiolphenyltriazole and small amounts of 3-(or 5-)thiol-1-phenyltriazole, $C_2N_3H_2SPh$, which crystallises in colourless needles, m. p. 178° , and forms a benzyl derivative, $C_{15}H_{13}N_3S$, m. p. 64° .

New Dithiobiurets and their Derivatives.—[With A. WELLER.]— β -Naphthylthiobiuret, $C_{12}H_{11}N_3S_2$, formed from perthiocyanic acid and β -naphthylamine, is obtained as a white powder, m. p. 245° .

Dimethylaminophenyldithiobiuret hydrochloride, $C_{10}H_{14}N_4S_2 \cdot HCl$, formed from perthiocyanic acid and aminodimethylaniline, crystallises in white needles, m. p. 205° . The free base forms yellow needles, m. p. 168 — 169° .

β -Naphthylthiurethiuret hydrochloride, $C_{12}H_{10}N_3S_2Cl$, formed by boiling the dithiobiuret with ferric chloride and hydrochloric acid, separates from dilute hydrochloric acid in crystals, m. p. above 300° . *Dimethylaminophenyldithiurethiuret hydriodide*, $C_{10}H_{12}N_4S_2 \cdot 2HI \cdot C_2H_6O$, formed by adding iodine to the dithiobiuret in alcoholic solution, crystallises in yellow needles, decomp. 175° .

Formation of Cyanoamides.—The action of benzyl chloride and sodium hydroxide on dithiobiurets leads to the formation of cyano- ψ -benzylthiocarbamides. *Cyano- β -naphthyl- ψ -benzylthiocarbamide*,



crystallises in white leaflets, m. p. 201° . *Cyanodimethylaminophenyl- ψ -benzylthiocarbamide*, $C_{17}H_{18}N_4S$, formed from dimethylaminophenyldithiobiuret, crystallises in white needles, m. p. 193° . Cyano-*p*-tolyl- ψ -benzylthiocarbamide (Abstr., 1906, i, 656) is now found to be formed when *p*-tolylthiobiuret is heated with benzyl chloride and concentrated ammonia added.

G. Y.

Preparation of Hydroxyalkyl Derivatives of Xanthine Bases. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 193799. Compare this vol., i, 475).—The xanthine bases condense with alkylene oxides to form hydroxyalkyl derivatives. 1:3-Dimethyl-7-hydroxyethylxanthine is thus obtained by heating theophylline and ethylene oxide at 130° . Dehydrating agents, such as zinc or hydrogen chloride, may be employed, and theobromine, 3-methylxanthine, and other bases may be similarly condensed with propylene and trimethylene oxides.

G. T. M.

Physico-chemical Researches on the Behaviour of Urates in Solution. F. GUDZENT (*Zeitsch. physiol. Chem.*, 1908, 56, 150—179).—Urates, in which both acidic hydrogen atoms are replaced by a metal, are hydrolysed in solution to monatomic salts; of these, monosodium urate crystallises with $1\text{H}_2\text{O}$, and monopotassium and monoammonium urate crystallise anhydrous. On continued shaking, the amount of these salts dissolved passes through a maximum, and then diminishes somewhat, this ultimate diminution being 4—5 times greater for the ammonium salt than for the sodium and potassium salts. The diminution is not explicable, and is not due to hydrolysis or to a change in size of the particles, or to hydration of the excess of solid salt with which the solution is shaken. The maximum solubilities are: 1 part of potassium, of sodium, and of ammonium urate requires respectively at 18° , 653, 1201, and 2415, and at 37° , 370, 665, and 1352 parts of water. G. B.

Position of Entrance of the Diazo-group in the Formation of Azo-dyes. WASSILI SCHARWIN and KALJANOFF (*Ber.*, 1908, 41, 2056—2060).—The rule that the diazo-group enters the ortho-position in a para-substituted amine or phenol does not always hold good. Thus, when the auxochrome is a dialkylamino-group, either no combination takes place (probably owing to steric hindrance) or the *p*-substituent is displaced with formation of the corresponding dye. The authors show that when *p*-diazobenzenesulphonic acid acts on dimethyl-*p*-toluidine, *p*-bromodimethylaniline, dimethylsulphanilic acid, *p*-dimethylaminodiphenylmethane, tetramethylbenzidine, or *N*-dimethyl- β -naphthylamine, no dye is formed. *N*-Dimethyl- α -naphthylamine, as was to be expected, forms 4-*p*-sulphobenzeneazo-1-dimethylnaphthylamine, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_8\cdot\text{NMe}_2$, crystallising from water in violet, glistening needles. The sodium salt forms golden-yellow leaflets. The authors confirm Pinnow's observation (*Abstr.*, 1895, i, 98) that helianthin is formed when diazobenzenesulphonic acid acts on tetramethyldiaminodiphenylmethane, and show that the reaction proceeds according to the equation

$$2\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OH} + \text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2 =$$

$$2\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O}.$$

A similar reaction takes place when *p*-nitrodiazobenzene is used (compare Noelting, *Abstr.*, 1888, 270; Bamberger, *Abstr.*, 1895, i, 351).

When diazobenzenesulphonic acid acts on *p*-dimethylaminobenzoic acid, the carboxyl group is eliminated and helianthin is formed (compare Limpricht, *Abstr.*, 1891, 1036) without any other product (compare Grandmougin and Freimann, *Abstr.*, 1907, i, 986). By treating *m*-phenylenetetramethyldiamine with diazobenzenesulphonic acid, 4-*p*-sulphobenzeneazo-*m*-phenylenetetramethyldiamine (Pinnow and Wegner, *Abstr.*, 1898, i, 185) was prepared. This forms microscopic, Bordeaux-red needles; the alkali salts are orange-coloured. J. C. C.

Ethyl Arylazoacetoacetateacylhydrazones and their Conversion into Derivatives of 4-Arylazo-3-methyl-5-pyrazolones with an Acid Radicle Attached to the Primary Nitrogen Atom. CARL BÜLOW and FRIEDRICH SCHAUB (*Ber.*, 1908, 41,

2355—2366. Compare Abstr., 1907, i, 301; this vol., i, 579; Curtius, Darapsky, and Müller, Abstr., 1907, i, 451).—A number of 4-arylaazo-1-acyl-3-methylpyrazolones, $\text{COR} \cdot \text{N} \begin{smallmatrix} \text{N}=\text{CMe} \\ | \\ \text{CO} \cdot \text{CH} \cdot \text{N}_2\text{R}' \end{smallmatrix}$, have been prepared from 1:2-acylhydrazones of ethyl arylazoacetoacetates, $\text{COR} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CH}(\text{N}_2\text{R}') \cdot \text{CO}_2\text{Et}$. Contrary to the statements of Curtius and Struve (Abstr., 1895, i, 34), therefore, pyrazolones can be formed from the acylhydrazones of α -substituted ethyl acetoacetates. On hydrolysis, the acyl-pyrazolone yields the corresponding 4-arylaazo-3-methyl-5-pyrazolone, $\text{NH} \begin{smallmatrix} \text{N}=\text{CMe} \\ | \\ \text{CO} \cdot \text{CH} \cdot \text{N}_2\text{R}' \end{smallmatrix}$, which can be synthesised from the ethyl arylazoacetoacetates, $\text{CMe} \cdot \text{CH}(\text{N}_2\text{R}') \cdot \text{CO}_2\text{Et}$.

The benzoylhydrazones of ethyl arylazoacetoacetates are formed from the ethyl arylazoacetoacetate and benzoylhydrazide in cooled acetic acid solution, and can be recrystallised only under certain conditions, as intramolecular ring condensation, followed in some cases by fission of the benzoyl group, takes place with great ease.

The *benzoylhydrazone* of ethyl phenylazoacetoacetate, $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_4$, crystallises in canary-yellow needles, m. p. 156° , and, when dissolved in cold dilute alkali hydroxides and precipitated immediately by means of carbon dioxide, is regained unchanged. When heated with aqueous sodium hydroxide or acetate on the water-bath, it condenses to 4-benzeneazo-3-methyl-5-pyrazolone, $\text{C}_{10}\text{H}_{10}\text{ON}_4$, which crystallises in orange-red leaflets, m. p. $199.5\text{--}200^\circ$ (197° : Rothenburg, 1895, i, 686).

Ethyl o-tolylazoacetoacetate, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$, formed by the action of diazotised *o*-toluidine on ethyl acetoacetate in presence of sodium acetate, crystallises in lemon-yellow needles, m. p. 67° . The *benzoylhydrazone* crystallises in yellow needles, m. p. $145\text{--}149^\circ$, and on recrystallisation forms 4-*o*-tolueneazo-3-methylpyrazolone, $\text{C}_{11}\text{H}_{12}\text{ON}_4$, orange leaflets, m. p. $224\text{--}225^\circ$, and its 1-benzoyl derivative, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_4$, scales, m. p. 209° .

The *benzoyl* derivative of ethyl *p*-tolylazoacetoacetate, formed from diazotised *p*-toluidine and ethyl acetoacetate, crystallises in yellow needles, m. p. 165° . 4-*p*-Tolueneazo-3-methyl-5-pyrazolone forms orange leaflets, m. p. 196° .

Ethyl m-xyllylazoacetoacetate, $\text{C}_{14}\text{H}_{18}\text{O}_3\text{N}_2$, crystallises in yellow needles, m. p. 121° . The *benzoylhydrazone*, $\text{C}_{21}\text{H}_{24}\text{O}_3\text{N}_4$, m. p. $145\text{--}149^\circ$. 4-*m*-Xyleneazo-1-benzoyl-3-methyl-5-pyrazolone, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_4$, orange-red needles, m. p. $171\text{--}172^\circ$. 4-*m*-Xyleneazo-3-methyl-5-pyrazolone, $\text{C}_{12}\text{H}_{14}\text{ON}_4$, m. p. $190\text{--}191^\circ$.

The *benzoylhydrazone* of ethyl α -naphthylazoacetoacetate, $\text{C}_{23}\text{H}_{22}\text{O}_3\text{N}_4$, forms brownish-yellow threads, m. p. $165\text{--}167^\circ$ (decomp.). 4- α -Naphthaleneazo-1-benzoyl-3-methyl-5-pyrazolone, $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_4$, yellowish-red needles, m. p. 212° . 4- α -Naphthaleneazo-3-methyl-5-pyrazolone, $\text{C}_{14}\text{H}_{12}\text{ON}_4$, brownish-red crystals, m. p. 247° .

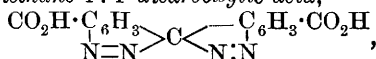
The *benzoylhydrazone* of ethyl β -naphthylazoacetoacetate, $\text{C}_{23}\text{H}_{22}\text{O}_3\text{N}_4$, forms canary-yellow crystals, m. p. $160\text{--}164^\circ$ (decomp.). 4- β -Naphthaleneazo-1-benzoyl-3-methyl-5-pyrazolone, $\text{C}_{21}\text{H}_{16}\text{O}_2\text{N}_4$, orange crystals, m. p. 224° . 4- β -Naphthaleneazo-3-methyl-5-pyrazolone forms

red crystals, m. p. 237—238°, and yields a *sodium* salt, which is decomposed by carbon dioxide or boiling alcohol.

Ethyl carboxyphenylazoacetate, $C_{13}H_{14}O_5N_2$, formed from diazotised anthranilic acid, is obtained in yellow crystals, m. p. 162—163°. The *benzoylhydrazone*, yellow crystals, m. p. 244—245°. *4-Carboxybenzeneazo-3-methyl-5-pyrazolone*, $C_{11}H_{10}O_3N_4$, crystallises in orange needles, m. p. above 280° (decomp.). G. Y.

Bisazo-compounds. HENRI DUVAL (*Compt. rend.*, 1908, 146, 1407—1409).—Continuing his recent work (*Abstr.*, 1907, i, 663), the author finds that nitrous acid acts on the di-*o*-amino-derivatives of diphenylmethane-4 : 4'-dicarboxylic acid, of 4 : 4'-dicyanodiphenylmethane, and of 4 : 4'-diacetyldiphenylmethane to produce bisazo-compounds, whilst with the di-*o*-amino-derivatives of diphenylmethane and of 4 : 4'-diacetyldiaminodiphenylmethane, nitrous acid gives a mixture of the corresponding phenol and the bisazo-compound.

Bisazodiphenylmethane-4 : 4'-dicarboxylic acid,



can be obtained by hydrolysing its ethyl ester (*loc. cit.*), but is best prepared as described above. It melts above 300°. 4 : 4'-*Dicyano-bisazodiphenylmethane* melts above 350°. 4 : 4'-*Diacetylbisazodiphenylmethane* separates from pyridine in bright yellow crystals, decomp. at about 300°. 4 : 4'-*Diacetyldiaminobisazodiphenylmethane* forms red crystals, m. p. above 300°. The conclusion is drawn that the presence of an electronegative substituent in the diphenylmethane nucleus favours the formation of bisazo-compounds of the above type.

J. C. C.

Aminoazo-compounds. ARTHUR HANTZSCH (*Ber.*, 1908, 41, 2435—2437).—Reply to Hewitt (this vol., i, 581). C. S.

Protein Constitution. New Method of Hydrolysis by Means of Hydrofluoric Acid. L. HUGUNENQ and ALBERT MOREL (*Compt. rend.*, 1908, 146, 1291—1293).—It is claimed that hydrofluoric acid is superior to other acids as a reagent for the hydrolysis of proteins. Far less of the humin substances are formed; the acid can be readily removed after completion of the reaction by calcium carbonate, and the amino- and diamino-acids formed can be obtained in a state of great purity. Commercial hydrofluoric acid (50%) diluted with about five times its volume of water is employed. The mixture with proteins is heated in lead vessels on a water-bath for from forty-eight to one hundred hours, until the biuret reaction disappears. S. B. S.

Calorimetric Investigation on Protein Precipitation. AMEDEO HERLITZKA (*Biochem. Zeitsch.*, 1908, 11, 481—492).—During the process of salting-out protein with ammonium sulphate, or during the converse process of re-solution due to dilution, there is no development of heat. In the precipitation process, only protein, and not any salt, is precipitated. In precipitation with silver nitrate, the precipitate

contains both protein and silver, and heat is developed. If, however, the precipitate contains much silver, heat production is negative, due to adsorption of silver by the protein. The heat developed is 4.18 calories per gram of protein. If adsorption occurs, the calorific value is -16.67 cal. per gram of silver nitrate. W. D. H.

The Diffusion of Colloids. II. REGINALD O. HERZOG and H. KASARNOWSKI (*Biochem. Zeitsch.*, 1908, 11, 172—176).—The diffusion coefficients of various colloidal substances were determined. The coefficient can be regarded as a physical constant. By its means it can be determined whether a given product is a mixture; trypsin, for example, was found to consist of a mixture of ferments. By means of the diffusion constant, from the equation $M = 59.2/K^2$, the molecular weight of a solution can be determined.

The results agree well with those obtained by other methods. For ovalbumin, the molecular weight found was 17,000; for ovomucoid, 30,000; for pepsin, 13,000; for invertin, 54,000, and for emulsin, 45,000. S. B. S.

The Influence of Temperature on the Co-aggregation of Colloids. BERTRAM H. BUXTON and ALFRED H. RAHE (*Beitr. chem. Physiol. Path.*, 1908, 11, 479—501).—The different colloids were mixed with dye solutions, chiefly night-blue and Janus-green, and the concentration was noted at which co-aggregation of the colloids most readily took place at temperatures between 0° and 80° . In the case of negative organic colloids, it was found that the higher the temperature the greater the quantity of dye necessary to produce co-aggregation. The increased quantities necessary when the temperature is raised are much greater in the case of reversible colloids than in that of irreversible colloids. These phenomena are absent in the case of inorganic colloids.

When basic hydroxides are used to produce co-aggregation of negative organic colloids, instead of dyes, the quantity is independent of temperature. Mastic appears to be an exception to this rule.

Experiments were also made by transferring the mixtures, after the co-aggregation phenomena had been observed at a particular temperature, to higher and lower temperatures, with the object of studying reversion of the phenomena. By increasing the temperature, it was found that the type that was characteristic at the lower temperature was converted into the type characteristic for the higher. Lowering the temperature did not, however, alter the type. S. B. S.

Changes in the Physical State of Colloids. VI. Compounds of Salt Ions with Amphoteric Protein. WOLFGANG PAULI and HANS HANDOVSKY (*Beitr. chem. Physiol. Path.*, 1908, 11, 415—448).—By amphoteric protein is meant protein which has been subjected to so long a period of dialysis that the product is no longer a salt of either acid or base. For the purposes of the investigation, ox-serum was employed, which had been dialysed against repeatedly-changed carbon dioxide-free water for at least six weeks. To determine the influence of salts on such a protein, the coagulation-tempera-

ture was ascertained in the presence of varying quantities. It was found that both the ions and anions had influence on the coagulation-temperature. The chlorides of potassium, sodium, ammonium, and magnesium give curves of similar form (when the concentrations are plotted as abscissæ, and the coagulation-temperatures as ordinates), which rise at first rapidly and then slowly. The curves given by the alkaline-earth chlorides show a maximum coagulation-temperature when the concentration of the salt reaches $N/2$; after this point there is a fall. The curve for lithium chloride lies between those of the two groups, showing a maximum coagulation point only when the concentration reaches $1N$. The influence of the different anions is very varied. The potassium salts were used in the experiments. Cl , Br , SO_4 , and NO_3 form a group in which additions of salt up to concentrations of 0.5 to $1N$ cause a rise of coagulation-temperature; additions beyond this point up to 1 to $3N$ cause but slight variations. SCN and I act in a similar way up to 0.5 to $1N$; above this point they cause marked inhibition, and potassium thiocyanate in $1N$ solution and potassium iodide in $2N$ solution cause total inhibition.

The inhibition of coagulation can be due to two causes; either a change in the protein, such as the formation of an acid or alkali albumin, or an inhibition of the aggregation of charged particles. To test this point, a protein solution containing potassium thiocyanate in concentration $2N$ was boiled for some minutes, and then divided into two portions; one was kept under toluene, and the other was dialysed; the former remained clear, and the latter gradually deposited coagulated protein. The experiment indicates that the coagulation is inhibited by the salt preventing the aggregation of particles.

It was assumed that proteins in salt solutions form adsorption compounds with salts, and that the formation of such compounds exerts a marked influence on the coagulation-temperature. If this is the case, then $t - t_0 = Kc^m$, where K and m are constants, c the concentration of the salt, and t and t_0 the coagulation-temperatures of protein salt mixture and pure protein solutions respectively. If $\log(t - t_0)$ be plotted as ordinates and $\log c$ as abscissæ, the curve representing the relations between the temperature of coagulation and concentration of the salt should be a straight line. This was the case with several of the salts investigated (up to concentrations of $0.1N$). At higher concentrations, other more complex factors come into play.

The theory of surface adsorption of salt ions by proteins was further tested by the measurement of viscosities. Protein, even in small concentration, considerably increases the internal friction of water, whereas inorganic salts up to concentrations of $0.05N$ have but little influence. If the theory of surface adsorption is correct, the salt ions on the surface of the colloidal protein molecules should mask the influence of the latter on the internal friction. It was found that neutral salts, which by themselves increase the viscosity of pure water, without exception lower the internal friction of amphoteric protein; in fact, in presence of sodium chloride, thiocyanate, and sulphate, calcium chloride, and potassium thiocyanate in concentrations of 0.01 to $0.05N$ (in which concentrations of the salts alone

the viscosity of water is increased), the viscosity of the protein is lower than that of pure protein solution.

Non-electrolytes, such as sucrose, have but little influence on the coagulation-temperature; they have but little influence also on the internal friction of protein solutions. The case of urea is somewhat exceptional. This substance appears to act chemically on the proteins. The general parallelism between the influence of substances on heat coagulation and internal friction of protein supports generally a conception of adsorption compounds.

The action of alkalis and readily hydrolysed salts, such as aluminium chloride, was investigated. In these cases the conditions are much more complex. S. B. S.

The Formation of Hydrogen Sulphide from Protein and Sulphur. HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1908, 11, 409—410).—Experiments made by precipitating proteins with tannic acid and with mercuric chloride show that the substances which cause precipitation do not always prevent the reducing action of proteins on sulphur. A protein which has been precipitated with tannic acid can cause the reduction of sulphur, whereas one which has been precipitated with mercuric chloride has lost this property. S. B. S.

Complete Hydrolytic Decomposition of Egg-albumin at 180°. P. W. LATHAM (*Biochem. J.*, 1908, 3, 207—240). **The Synthesis of Living Albumin.** P. W. LATHAM (*Biochem. J.*, 1908, 3, 241—257).—Two theoretical papers, consisting of speculations based on the old results of Schützenberger, but without any new experimental facts. It is pointed out how the leucéines and a number of other substances obtained by Schützenberger might be synthesised (in the laboratory) from pyruvic acid. In accordance with Pflüger's view, the death of protoplasm is regarded as consisting in the change $R \cdot CH(OH) \cdot CN \rightarrow R \cdot CH \begin{smallmatrix} \text{NH} \\ \diagup \\ \text{CO} \end{smallmatrix}$. G. B.

A Modification of the Properties of Gluten produced by Sulphurous Acid. J. DUGAST (*Compt. rend.*, 1908, 146, 1287—1288).—Gluten undergoes a considerable change in its physical properties when treated with sulphurous acid; flour which has been submitted to the fumes of the acid, on this account, loses its value for bread-making. S. B. S.

Action of Reducing Agents on Compounds of Hæmoglobin. BEINTKER (*Chem. Zentr.*, 1908, i, 1630; from *Vrtljschr. ger. Med. öffentl. Sanitätswesen.*, 1908, 35, 262—265).—Experiments have been made with ammonium sulphide, sodium hypophosphite, sodium hydrogen sulphite, hydroxylamine hydrochloride, hydrogen sulphide, ferrous tartrate in ammoniacal solution, and stannous chloride. It is found that sodium hydrogen sulphite is as good a reducing agent for blood as hydrogen sulphide or ferrous tartrate, and has the advantage that it does not greatly increase the quantity of blood and gives a clear, colourless solution. J. V. E.

Hæmopyrrole. LEON MARCHLEWSKI and J. RETINGER (*Biochem. Zeitsch.*, 1908, 10, 437—453).—The hæmopyrrole obtained by the reduction of hæmatoporphyrin appears, according to the later researches of Küster, to be a mixture of substances. He succeeded in obtaining by oxidation an imide which was not that of methylpropylmaleic acid, but corresponded more with that of methylmaleic acid. The analyses of the product obtained by the action of diazobenzene chloride on hæmopyrrole (Marchlewski, Goldmann, and Hetper) indicated that hæmopyrrole is a methylpropyl rather than a methyl-ethyl derivative of pyrrole. Further investigations of the action of diazobenzene chloride on hæmopyrrole have revealed the fact that the product just discussed, with the formula $C_{20}H_{22}N_5Cl$, is accompanied by another crystalline product of ruby red colour, a substance crystallising in green needles, and a third product crystallising in reddish-violet needles. S. B. S.

The Carbohydrate Group in Nucleic Acid. II. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1908, 56, 212—219. Compare this vol., i, 487).—The proofs that nucleic acid yields a pentose are regarded as insufficient; on theoretical grounds, the carbohydrate is more probably a hexose, and this is supported by experiment. W. D. H.

State of Combination of Sulphur in the Keratin Molecule. OSKAR BAUDISCH (*Chem. Zeit.*, 1908, 32, 620).—With the object of obtaining evidence that the sulphur is in combination with oxygen in the keratin molecule, the author has repeated the experiments of Raikow (*Abstr.*, 1905, i, 725), using wool, and substantiated his results that syrupy phosphoric acid at the ordinary temperature oxidises the sulphur contained to sulphur dioxide. Further, the oxidation of the sulphur of the wool to sulphur trioxide has been effected at the ordinary temperature by means of hydrogen peroxide. When, however, the wool is first chlorinated, no trace of sulphur dioxide is observed when treated with phosphoric acid. J. V. E.

Phenomena of the "Precipitation" and "Insolubilisation" of Gelatin. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1908, [iv], 3, 743—750. Compare *Abstr.*, 1907, i, 573).—The action of a large number of organic and inorganic substances on gelatin solutions has been examined with a view to ascertaining (1) whether those substances which "precipitate" gelatin or render it "insoluble" have any characters in common, and (2) the nature of the "precipitated" and "insolubilised" gelatins formed.

It is found that in the "precipitation" reactions, two types of products are formed: (a) substances soluble in warm water, which have the properties and composition of the original gelatin; (b) substances insoluble in warm water, in which the properties of the original gelatin have been considerably modified. The first type of product is obtained when (1) concentrated solutions of alkali salts, (2) dilute solutions of phosphotungstic or phosphomolybdic acid, and (3) phenols or substitution products of phenols are added to solutions of gelatin. The second type of product is obtained when substances

capable of furnishing oxygen, directly or indirectly, are added to gelatin solutions, for example, the halogens, ferric salts, uranates, manganates, permanganates, &c. Among organic substances, tannin is the only substance which gives with gelatin a precipitate insoluble in warm water.

Gelatin is "rendered insoluble" but not "precipitated" by chromium salts, and by formaldehyde, quinone, and oxidation products of various polyhydric phenols (compare Abstr., 1906, i, 614, 915, 999; 1907, i, 573). T. A. H.

Gelatoses. ZDENKO H. SKRAUP and F. HUMMELBERGER (*Monatsh.*, 1908, 29, 451—469).—The hydrolysis of proteins with the object of obtaining albumoses and peptones is usually carried out by means of enzymes or very dilute acids. The authors have now studied the hydrolysis by means of relatively concentrated acid, and have endeavoured to improve the ammonium sulphate method of separating the products. Gelatin was chosen for study in consequence of its solubility in water and acids. The fractions precipitated from the product of hydrolysis by concentrated acid by means of various concentrations of ammonium sulphate were isolated and hydrolysed. Glycine, glutamic acid, arginine, and lysine, which occur in gelatin in large amounts, and histidine were estimated in the product of the hydrolysis of each fraction; other amino-acids, which occur only in small amounts, were not estimated. On complete hydrolysis, gelatin yields the following percentages of cleavage products: glutamic acid, 13.9, estimated by Horbaczewski's method, or 10.1, estimated by Fischer's esterification method; glycine, 9.6, 9.7; histidine, 0.4; arginine, 6.2; lysine, 4.4. Fischer found only 0.9% of glutamic acid, but 16.5% of glycine, and Levene (Abstr., 1907, i, 168), 16.38% of glycine from gelatin.

Whilst gelatin is hydrolysed completely to simple amino-acids by boiling 25% sulphuric acid (Levene, *loc. cit.*), products of partial hydrolysis are obtained with the same acid at 50°. The albumoses, precipitated on partial and on complete saturation of the hydrolysis product with ammonium sulphate, and the peptone fraction, which is soluble in ammonium sulphate and was purified by dialysis, were hydrolysed by boiling concentrated hydrochloric acid, or by boiling dilute hydrochloric acid and stannous chloride. The albumoses precipitated by one-third or by one-half saturation gave the following percentages, *A*, of cleavage products; those precipitated by complete saturation gave the percentages *B*; the peptone solution gave the percentages *C*; and the first solution from the dialysator, the percentages *D*.

	Glutamic acid.				Histi-	Argi-	
	Fischer's	Horbaczewski's	Glycine.		dine.	nine.	Lysine.
	method.	method.					
<i>A</i>	2.5	5.8	10.2	10.3	5.8		1.8
<i>B</i>	15	11	6.6	10.5	5.4		2.3
<i>C</i>	20.8		7.2		0.4	6.3	3.8
<i>D</i>	16		4.1		0.3	4.0	4.8

The more soluble the albumose in ammonium sulphate solution the greater its percentage of glutamic acid and histidine, but the smaller

the percentage of glycine. The peptone is distinguished from the albumoses by a high percentage of glutamic acid and small percentage of glycine. G. Y.

Preparation of Stable Soluble Compounds of Hexamethylenetetramine Silver Nitrate with Albumoses. ALBERT BUSCH (D.R.-P. 193740).—Hexamethylenetetramine silver nitrate combines with albumoses in aqueous solution to form a soluble additive compound containing 8 per cent. of silver, which is obtained as a yellowish-brown powder either on concentrating the solution under reduced pressure or by precipitation with alcohol.

The dry components may also be mixed, and an extract made with 50% alcohol; the product is then obtained by evaporating down this solution. G. T. M.

Studies on Enzyme Action. XI. Hydrolysis of Raffinose by Acids and Enzymes. HENRY E. ARMSTRONG and WILLIAM H. GLOVER (*Proc. Roy. Soc.*, 1908, 80, B, 312—321).—The rate of hydrolysis of raffinose into melibiose and lævulose, both by invertase and by acids, was investigated, and compared with the rate of action of the same reagents on sucrose. The rate of hydrolysis of raffinose is considerably smaller than that of sucrose. The influence of the stereochemical configuration on the rate of hydrolysis is discussed. S. B. S.

Physico-chemical Investigation of Amylase and Maltase. Mlle. CH. PHILOCHE (*J. Chim. Phys.*, 1908, 6, 355—423. Compare this vol., ii, 470).—*Action of Amylase on Starch and Glycogen* (continued).—In a solution containing 0.004% of amylase of malt and 2% of starch, hydrolysis is practically complete in eight to nine hours, and even for smaller enzyme concentrations there does not appear to be any interruption of the reaction. On the other hand, a 2% solution of glycogen is completely hydrolysed by a 2% solution of amylase of malt only after twenty-six hours, and in solutions containing less than 1% of the enzyme hydrolysis is incomplete. For solutions containing 0.01 to 0.125% of the enzyme, the proportion of maltose formed is approximately proportional to the enzyme concentration. The stoppage of the reaction is not due to the destruction or weakening of the enzyme, and in such partly hydrolysed solutions the glycogen is no longer present in its original form.

Glycogen is hydrolysed somewhat less rapidly than starch by pancreatic juice, but, as shown above, amylase acts much less rapidly on glycogen than on starch. The rate of reaction between amylase and starch is somewhat complicated; it diminishes fairly rapidly until about 30% of the starch is decomposed, and then proceeds as a unimolecular reaction until hydrolysis is almost complete.

The last part of the paper contains a general discussion of the mechanism of enzyme reactions in the light of all the available accurate data. The reactions take place in heterogeneous systems, and the purely chemical actions are therefore complicated by diffusion and adsorption phenomena (compare Nernst, *Abstr.*, 1904, ii, 315; Henri, *Abstr.*, 1906, ii, 13). G. S.

Organic Chemistry.

Action of Metallic Oxides on the Primary Alcohols (Irreducible Oxides). PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, 147, 106—110. Compare this vol., i, 594).—Many metallic oxides, which are not reduced by alcohol vapour, decompose primary alcohols catalytically. The decomposition may be into hydrogen and an aldehyde, as with manganous oxide (and also with stannous and cadmium oxides; these two are, however, slowly reduced); secondly, the decomposition may be a dehydration, alumina, thoria, and blue oxide of tungsten with ethyl alcohol yielding ethylene and water; with a third group of oxides (Cr_2O_3 , SiO_2 , TiO_2 , GlO , ZrO_2 , UO_2 , Mo_2O_5 , V_2O_5 , ZnO), the two reactions first mentioned proceed simultaneously, ethylene and hydrogen appearing together. With certain higher alcohols, complications may arise; thus *isobutyl* alcohol yields a little *diisobutylene*, and *benzyl* alcohol gives a resinous deposit of the composition $(\text{C}_7\text{H}_6)_n$.

The reaction is greatly accelerated by a rise of temperature, in one case being fifteen times as rapid at 350° as at 260° . G. B.

Formation of Compounds in Solutions of Tartaric Acid and Sodium Molybdate. P. QUINET (*Compt. rend.*, 1908, 147, 203—206).—The author has studied certain physical properties of solutions containing a fixed weight of *d*-tartaric acid and varying weights of sodium molybdate. The specific gravity, specific rotatory power, electrical conductivity, and freezing point of each solution have been examined and the results plotted on curves, the abscissæ of which are the weights of sodium molybdate. It is found that the curves exhibit sharply-defined maxima, which correspond in each case with a compound of one molecule of tartaric acid with two molecules of sodium molybdate. The existence of this combination was indicated by Gernez from polarimetric observations (*Abstr.*, 1887, 540). The cryoscopic curve shows a minimum corresponding with a compound containing one molecule of each substance, but the existence of this is not confirmed by the other curves. W. O. W.

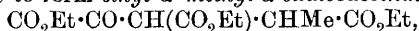
Methyl Hydrogen *d*-Tartrate. F. TANNHÄUSER (*Zeitsch. Kryst. Min.*, 1908, 45, 183—184).—The crystals are rhombic
[$a:b:c = 0.8887:1:0.557$].

L. J. S.

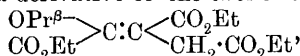
Ketonic Dibasic Acids. EDMOND E. BLAISE and H. GAULT (*Compt. rend.*, 1908, 147, 198—200).—This paper contains a preliminary account of a general method for the preparation of certain new α -monoketonic and $\alpha\alpha'$ -diketonic dibasic acids. When ethyl oxalosuccinate is treated with hydrogen chloride in the cold and the solution boiled, hydrolysis takes place and *α -ketoglutaric acid*,

$\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed. This very reactive substance has m. p. $112-113^\circ$.

Ethyl oxalate and ethyl methylsuccinate condense in presence of sodium ethoxide to form *ethyl α' -methyl- α -oxalosuccinate*,



which decomposes on distillation. An attempt to prepare the same substance by the action of propyl iodide on ethyl oxalosuccinate led to the formation of a derivative of the enolic form of this ester,



b. p. $202-203^\circ/20$ mm. When treated with hydrogen bromide, this substance yields ethyl bromide, propyl bromide, and α -ketoglutaric acid.

An attempt to prepare *aa'*-diketoglutaric acid by the hydrolysis of ethyl dioxalosuccinate resulted in the formation of *3-hydroxy-2-pyrone-6-carboxylic acid*, $\text{C}_6\text{H}_4\text{O}_5$. This, when heated at 200° , loses carbon dioxide and yields a substance identical with Limpricht's *isopyromucic acid*; thus confirming the constitution ascribed to this compound by Chavanne (Abstr., 1904, i, 77).

W. O. W.

Optically Active Thiolactic Acids and Thiodilactylic Acids.

JOHAN M. LOVÉN (*J. pr. Chem.*, 1908, [ii], 78, 63—73).—Although two inactive thiodilactylic acids were described previously (Abstr., 1896, i, 412) as the racemic and the *meso*-acid respectively, attempts to resolve either into the optically active components by means of the alkaloid salts have been unsuccessful, as was also the employment of the active forms of α -phenylethylamine. Dithiodilactylic acid readily undergoes resolution into its optically active components; these on reduction yield the corresponding optically active thiolactic acids, which on treatment with α -bromopropionic acid in alkaline solution yield the optically active thiodilactylic acids.

i-Thiolactic acid (Abstr., 1884, 1298) is best prepared by reduction of trithiodilactylic acid with sodium amalgam in dilute sulphuric acid solution. On treatment with a ferric salt in acid solution, addition of an excess of potassium carbonate, and exposure to air, it yields a mixture of *r*- and *i*-dithiodilactylic acids. The *r*-acid separates in slender needles on addition of hydrochloric acid to the concentrated aqueous solution of the potassium salts. On treatment of the *r*-acid with *d*- or *l*- α -phenylethylamine in aqueous solution, the *d*-base *d*-acid salt, or the *l*-base *l*-acid salt, $\text{S}_2(\text{CHMe}\cdot\text{CO}_2\text{H})_2\cdot\text{CHPhMe}\cdot\text{NH}_2$, separates in long, glistening needles, the isomeric salt remaining in solution. *d*-Thiodilactylic acid crystallises in rhombic plates, m. p. 116.5° , $[\alpha]_D + 429^\circ$.

The optically active thiolactic acids are prepared by reduction of *d*- and *l*-dithiodilactylic acids, or their α -phenylethylamine salts, by means of sodium amalgam. *l*-Thiolactic acid, b. p. about $99-101^\circ/15$ mm., $D^{19.2} 1.193$, $[\alpha]_D^{15} - 45.47^\circ$, closely resembles the *r*-acid. The *mercuric* derivative, $\text{Hg}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$, was analysed.

The optically active thiodilactylic acids crystallise in large, rhombic prisms, m. p. 117° ; the *l*-acid has $[\alpha]_D - 190.0^\circ$. A solution of the two isomerides deposits the inactive acid, m. p. 125° , crystallising in monoclinic prisms, which is therefore the racemic form (*loc. cit.*). *l*-Thiodi-

lactylic acid is formed also by the action of sodium sulphide on *d*-α-bromopropionic acid, the rotatory power being reversed by the substitution of sulphur for bromine. G. Y.

The Fission of Sugars [Sucroclasm]. I. Action of Zinc Carbonate on Formaldehyde Solutions. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, 12, 78—96).—In addition to a number of theoretical arguments, the following experiments are adduced in support of the author's view that alcoholic fermentation does not take place through the intermediate formation of lactic acid, but that it consists in a breaking-down of the sugar to $\text{H}\cdot\text{C}\cdot\text{OH}$ groups, with subsequent synthesis to alcohol and carbon dioxide. By boiling 40% formaldehyde solution with two volumes of 30% potassium hydroxide, there are not only formed methyl alcohol and formic acid, as found by Nef (*Abstr.*, 1905, i, 3), but also non-volatile hydroxy-acids (probably di- and tri-hydroxybutyric acids). By boiling 200 c.c. of 20% formaldehyde solution with 20 grams of zinc carbonate for several days, there are formed, in addition to the above products, acetol, $\text{COMe}\cdot\text{CH}_2\cdot\text{OH}$, and methylketol, $\text{COMe}\cdot\text{HCOMe}\cdot\text{OH}$, which are isolated after distillation with steam as osazones. The zinc carbonate does not act as an oxidising agent, since zinc dust has the same qualitative effect. G. B.

Perseulose, a New Crystalline Sugar with Seven Carbon Atoms. GABRIEL BERTRAND (*Compt. rend.*, 1908, 147, 201—203. Compare *Abstr.*, 1898, i, 550).—The best bacterial culture for the oxidation of perseitol is that obtained by the spontaneous seeding of the juice of mountain ash berries. A 45% yield of *perseulose* is obtained. The new sugar has a sweet taste; the crystals resemble those of dextrose, but are better defined. The crystals are anhydrous, and have the composition $\text{C}_7\text{H}_{14}\text{O}_7$. They decompose on heating, and have no definite m. p.; on the Maquenne block they melt at about 110—115°. A freshly-prepared 10% aqueous solution has α_D^{25} not less than -90° ; this falls rapidly, however, and after several hours becomes constant at -81° . The cupric reducing power of perseulose is less than that of dextrose, but considerably greater than that of sorbose.

The *osazone*, $\text{C}_{19}\text{H}_{24}\text{O}_5\text{N}_4$, crystallises from alcohol in silky needles, m. p. about 233° . W. O. W.

Products of the Reaction between Lactose and Calcium Hydroxide. HEINRICH KILIANI (*Ber.*, 1908, 41, 2650—2658).—Some of the products of the reaction between lactose and calcium hydroxide have been examined, but the investigation of the "residue" presented considerable difficulty (this vol., i, 128). The present communication deals with this difficulty. The reaction mixture is freed from the calcium salts of *isosaccharin* and *meta-saccharin*, and the resulting mother liquor, after removal of all the calcium by oxalic acid, is evaporated to a syrup, which is divided into four parts by extraction with (I) absolute ether (five times); (II) one part of absolute alcohol and two parts of ether, dried by calcium chloride (four times); (III) a mixture of equal parts of the preceding solvents (twice), and (IV)

absolute alcohol (twice). Each extraction, after removal of the solvents, is oxidised by nitric acid, D 1.4 (in the case of IV, D 1.2), whereby the most labile constituents are decomposed completely, whilst the saccharine substances are oxidised to di- and tri-basic acids, which can be more easily separated and characterised than the constituents of the original "residue." The author claims that the method must give some information as to the presence of compounds containing more or less than six atoms of carbon, and also as to the nature of the carbon chains in the products of the reaction between lactose and calcium hydroxide.

The paper contains a mass of detail unsuitable for abstraction. The main result is the detection of *l*-tartaric acid and of a tribasic acid, $C_6H_8O_8$ (probably identical with the α - γ -dihydroxypropane- α : α : γ -tricarboxylic acid obtained from *isosaccharin*), among the oxidation products of extracts II and III, and of a new dibasic acid, $C_6H_{10}O_7$, m. p. 159–160°, among the oxidation products of extract IV. Of this acid, which is feebly dextrorotatory, the *zinc*, *calcium*, *copper*, and *cadmium* salts are mentioned.

C. S.

Synthesis of Glucosides: Derivatives of Xylose. HUGH RYAN and GEORGE EBRILL (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 247–252. Compare Abstr., 1904, i, 223; Ryan, *Trans.*, 1899, 75, 1054; Ryan and Mills, *Trans.*, 1901, 79, 704).—A résumé is given of the work of various authors on the synthesis of acetylchloro-pentoses and -hexoses and of the corresponding glucosides. The preparation of a crystalline acetylchloroxylose and its conversion into a tetra-acetylxylose and into α -naphthyl- and carvacryl-xylosides are now described. Although the constitution of the acetylchloropentoses is uncertain, unless it is assumed that acetylchloroarabinose is the α -compound because Purdie and Rose obtained from it a product which they consider to be α -methylarabinoside (*Trans.*, 1906, 89, 1204), the phenol derivatives must be β -pentosides, since Fischer and Armstrong have shown that only β -hexosides are formed from both α - and β -acetylchlorohexoses in alkaline solution (Abstr., 1901, i, 671).

Acetylchloroxylose, $C_{11}H_{15}O_7Cl$, prepared by digesting xylose with acetyl chloride in a sealed tube in ice-water, separates from alcohol-chloroform in crystals, m. p. 101°, and on prolonged boiling with alcohol is converted into a non-reducing substance.

β - *α -Naphthylxyloside*, $C_{15}H_{16}O_5$, obtained by shaking acetylchloroxylose with α -naphthol and potassium hydroxide in alcoholic solution, crystallises from dilute alcohol in long needles, m. p. 192–193°, reduces Fehling's solution only after hydrolysis with dilute sulphuric acid, and is not hydrolysed by emulsin.

Carvacrylxyloside, $C_{15}H_{22}O_5$, prepared from carvacrol and acetylchloroxylose, crystallises from boiling water in long needles, m. p. 105°, and resembles β - α -naphthylxyloside in its behaviour towards Fehling's solution, but is more soluble in aqueous potassium hydroxide than in water.

When treated with silver acetate and glacial acetic acid, acetylchloroxylose is converted into tetra-acetylxylose, m. p. 119° (124°: Store, Abstr., 1894, i, 104).

G. Y.

Theoretical Investigations on the Charring of Wood. I. Dry Distillation of Cellulose. PETER KLASON, GUST. VON HEIDENSTAM, and EVERT NORLIN (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 1, 1—34).—The authors have investigated the products obtained by the dry distillation of cellulose derived from various sources. The results show that the charring of cellulose proceeds mainly according to the equation: $8C_6H_{10}O_5 = C_{30}H_{18}O_4$ (cellulose charcoal) + $23H_2O$ + $4CO_2$ + $2CO$ + $C_{12}H_{16}O_3$ (remaining products). The velocity of this reaction begins to become considerable at about 270° . At this temperature the dry distillation of cellulose is an exothermic process, the heat of the reaction being about 6% of the heat of combustion of cellulose. The gases evolved during the distillation have a heating value of about 3.5% of the heat of combustion of the cellulose, and include hydrogen and aromatic hydrocarbons. Methyl alcohol is not formed during the dry distillation of cellulose, and must hence be derived from the lignin of the wood. Acetic acid is formed during the dry distillation of cellulose, beech and birch cellulose yielding more of this acid than cotton, or fir or pine cellulose.

T. H. P.

Chemical Composition of Pine-wood. I. PETER KLASON (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 5, 1—20).—From the liquid obtained by boiling pine-wood with calcium hydrogen sulphite, the author has prepared *barium lignosulphonate*, $C_{40}H_{44}O_{17}S_2Ba$, which in medium concentrations exhibits cryoscopic behaviour corresponding with a molecular weight of 4378—4675. It is assumed that lignin itself has the composition $C_{40}H_{44}O_{17}S_2Ba - BaH_2S_2O_6 = (C_{40}H_{42}H_{11})_n$. Both barium lignosulphonate and lignin give many colour reactions almost identical with those exhibited by coniferyl alcohol, and the latter, when treated with calcium hydrogen sulphite, yields a salt closely resembling calcium lignosulphonate. It is probable that lignin is formed by the condensation of coniferyl or hydroxyconiferyl alcohol. Both coniferyl alcohol and lignin are readily resinified by acids. Lignin contains 40Me and 40H per 40 carbon atoms, but lignosulphonic acid contains less than 40Me. The author suggests the name "insoluble tannin" for lignin, owing to the great resemblance between the two substances; the side groups are probably in the same positions in lignin as in gallic acid. In lignosulphonic acid, part of the sulphurous acid is tightly and part loosely bound.

T. H. P.

Chemical Composition of Pine-wood. II. PETER KLASON and OSCAR FAGERLIND (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 6, 1—10).—In order to ascertain whether lignin occurs in wood combined with sugars or other carbohydrates to form glucosidic compounds, the authors have investigated the matters extracted from pine-wood by boiling water, and by the latter and alcohol used alternately.

It is found that boiling water dissolves about 12% of the dry matter of the wood, about 10% consisting of wood-gum and 2% of substances resembling true lignin. The wood-gum obtained is only sparingly soluble in alkali solution, and contains 25% of xylose, 6% of mannose, and traces of galactose, the remainder apparently consisting of unknown sugars. The other substances, resembling lignin, extracted by water

consist partly of coniferyl alcohol and of a substance which is apparently a dimeric form of hydroxyconiferyl alcohol or similarly-constituted compound. Lignin does not occur in wood in combination with carbohydrates.

T. H. P.

Constitution of Certain Cyanogen Compounds. F. CARLO PALAZZO and GIUSEPPE SCELSI (*Gazzetta*, 1908, 38, i, 659—681. Compare Palazzo and Carapelle, *Abstr.*, 1907, i, 195).—The authors have applied the action of diazomethane to thiocyanic acid, cyanamide, and cyanuric and thiocyanuric acids with the object of determining the structure of these compounds. In each case, only one of the two possible isomeric esters was obtained, the yield being quantitative.

Cyanuric acid and diazomethane yield only trimethyl *isocyanurate*, a result which confirms Hantzsch's conclusion (*Abstr.*, 1906, i, 146) that solid cyanuric acid is a complete pseudo-acid containing three $\text{CO}\cdot\text{NH}$ groups, and is, hence, tricarbimide.

On the other hand, thiocyanic acid yields methyl thiocyanate free from any trace of compound capable of combining with ammonia, so that the acid has the normal structure $\text{N}:\text{C}\cdot\text{SH}$.

Thiocyanuric acid and diazomethane give a mixed trimethyl derivative, in which part of the methyl is combined with sulphur and part with nitrogen. This acid is, hence, a partial pseudo-acid, since it forms a completely normal trisodium salt, whilst in the free state a part (one-third or two-thirds) of the HCNS groups is not directly halogenic or salt-forming.

With cyanamide, diazomethane or diazoethane yields a trisubstituted *isomelamine*, which can only be formed by the polymerisation of the compound $\text{NH}:\text{C}:\text{NMe}$ (or Et), so that cyanamide must be regarded as carbodi-imide, $\text{NH}:\text{C}:\text{NH}$.

T. H. P.

Tautomerism of the Cyanogen Compounds. H. GUILLEMARD (*Ann. Chim. Phys.*, 1908, [viii], 14, 311—432).—The paper commences with an historical résumé of the controversy concerning the isomerism of the nitriles and the carbylamines. This is followed by a detailed description of the analytical methods previously devised (*Abstr.*, 1907, i, 141) for the estimation of the nitriles and the carbylamines when alone, when mixed together, and when present in the mixture resulting from the action of an alkylating agent on a metallic cyanide. A complete account of experiments on the polymerisation and isomeric change of the carbylamines, the results of which have been previously published (*Abstr.*, 1907, i, 197), is given. When the mixture of phenylcarbylamine, aniline, and diphenylformamidine resulting from the action of alcoholic potash on a solution of aniline in chloroform is treated with silver cyanide, and the phenyl argenticyanide produced treated with potassium cyanide, after washing with ether, the product consists, not of phenylcarbylamine, but of a reddish-brown *substance*, crystallising in long, silky needles, m. p. 113° , which, when heated above its melting point, regenerates the carbylamine.

The author discusses the stereochemistry of nitrogen in the nitriles and carbylamines, and points out that the nitrogen only becomes

quinguevalent after the saturation of the carbon. Thus when ethylcarbylamine dibromide is treated with hydrogen sulphide in carbon disulphide solution, ethylthiocarbimide and ethyl dibromocarbimide hydrobromide are formed: $\text{NEt:CBBr}_2 + \text{H}_2\text{S} = \text{NEt:CS} + 2\text{HBr}$; $\text{NEt:CBBr}_2 + \text{HBr} = \text{NHEtBr:CBBr}_2$, whilst hydrogen chloride and ethyl iodide give analogous compounds. Ethyl alcohol reacts very violently with ethylcarbylamine dibromide, giving hydrogen and ethyl bromides and Gal's ethylcarbimide hydrobromide, NHBrEt:CO .

The third part of the paper is devoted to a detailed account of the experiments (Abstr., 1907, i, 300) on the action of alkylating agents (alkyl iodides and alkali alkyl sulphates) on many simple and complex metallic cyanides.

Finally, the author has determined the heats of combustion of some carbylamines and alkyl argenticyanides. The carbylamines, in order to secure complete combustion, were weighed in small glass vessels, covered with a weighed film of collodion, and, to the same end, a small quantity of water was introduced into the calorimetric bomb to avoid the deposition of carbon beneath the glass vessel. The following are the results obtained:

	Molecular heat of combustion.	Molecular heat of formation.
Methylcarbylamine	+ 320.1 Cal.	- 28.0 Cal.
Ethylcarbylamine	480.1 "	- 24.7 "
<i>n</i> -Propylcarbylamine	638.9 "	- 20.2 "
<i>iso</i> Butylcarbylamine	795.0 "	- 13.0 "
<i>iso</i> Amylcarbylamine	948.15 "	- 2.85 "
Allylcarbylamine	608.8 "	- 59.1 "
Benzylcarbylamine	1045.35 "	- 49.45 "

By extrapolation from these figures, the values + 159.1 Cal. and - 31.0 Cal. are obtained for the heats of combustion and formation of the lowest member of the homologous series, namely, carbylamine itself, HNC , whilst the values + 136 Cal. and - 7.8 Cal. are similarly deduced for hydrogen cyanide, HCN , from the numbers observed by Berthelot for acetonitrile and propionitrile. Since the values experimentally observed by Berthelot for hydrocyanic acid are + 159.3 Cal. and - 30.5 Cal. respectively, the thermochemical evidence indicates that this acid is a carbylamine and not a nitrile.

Propylcarbylamine, $\text{NPr}^a\text{:C}$, prepared by the action of propyl iodide on silver cyanide and subsequent decomposition of the propyl argenticyanide with potassium cyanide, is a liquid, b. p. 99.5° . *iso*Butylcarbylamine, prepared similarly, has b. p. $110\text{--}111^\circ$.

The alkyl argenticyanides are prepared either by melting together molecular quantities of potassium argenticyanide and the alkali alkyl sulphate, or by the addition of silver cyanide to the carbylamine dissolved in ethyl alcohol. They are well-crystallised, colourless compounds, which decompose at the ordinary temperature, evolving the carbylamine, and are decomposed by boiling aqueous alkali hydroxides, by strong acids, and by halogens, but not by hydrogen sulphide. Owing to their instability, their heats of combustion could only be determined accurately in the presence of excess of the carbylamines.

The following are the results obtained :

	Molecular heat of combustion.	Molecular heat of formation.	Heat of combination (AgNC + RNC).
Methyl argenticyanide ...	+ 440.4 Cal.	- 54.0 Cal.	+ 7.0 Cal.
Ethyl argenticyanide.....	600.5 „	- 50.8 „	+ 6.9 „
<i>n</i> -Propyl argenticyanide..	759.5 „	- 46.5 „	+ 6.7 „
<i>iso</i> Butyl argenticyanide...	916.4 „	- 40.1 „	+ 5.9 „
<i>iso</i> Amyl argenticyanide...	1071.0 „	- 31.4 „	+ 4.45 „

These figures show that the argenticyanides as well as the carbylamines are strongly endothermic compounds, whilst the combination of silver cyanide with the carbylamine is exothermic. The gradual decrease of the values in the last column explains the increase in the tension of dissociation with increasing carbon-content.

Ethyl cuprocyanide, large, colourless prisms, *propyl cuprocyanide*, rhombic tablets, and *isobutyl cuprocyanide*, rhombic prisms of the general formula CuN:C:C:NR , have similar properties to the silver compounds, and are prepared in a similar manner.

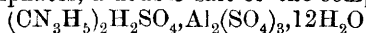
The conclusions drawn are that hydrocyanic acid and its metallic salts must be formulated as *isocyanides*, giving carbylamines with alkylating agents, that the organometallic compounds of the carbylamines decompose into nitriles and carbylamines, the proportion of each depending on the temperature and nature of the alkyl group present, and that the cyanides do not exhibit any phenomena of tautomerism.

E. H.

Preparation of Halogen-substituted Acetonitriles. WILHELM STEINKOPF (*Ber.*, 1908, 41, 2540—2542. Compare Braun, this vol., i, 627, 675).—Chloroacetonitrile is readily prepared in a 70% yield by distillation of a mixture of chloroacetamide and phosphoric oxide from a glass flask (compare Scholl, *Abstr.*, 1897, i, 9) under 200 mm. and, finally, under 11 mm. pressure (*Abstr.*, 1907, i, 490). Bromoacetonitrile is obtained in the same manner from bromoacetamide in a 60% yield (*Abstr.*, 1905, i, 756). Trichloro- and tribromo-acetonitriles are best prepared by distillation of the amides with phosphoric oxide under the ordinary pressure. Iodoacetonitrile is obtained in good yields by the action of potassium iodide on crude chloroacetonitrile.

G. Y.

Double Sulphate of Guanidine and Aluminium. F. FERRABOSCHI (*Proc. Camb. Phil. Soc.*, 1908, 14, 471—474).—From a solution containing approximately equivalent quantities of guanidine and aluminium sulphates, a double salt of the composition



crystallises in large, well-developed, hexagonal prisms terminated by basal planes. The crystals exhibit a perfect basal cleavage, and probably belong to the scalenohedral class of the rhombohedral system; $D^{13.5}$ 1.806.

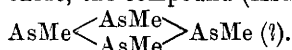
H. M. D.

Reactions of the Arsines. WILLIAM M. DEHN (*Amer. Chem. J.*, 1908, 40, 88—127. Compare *Abstr.*, 1905, i, 184; 1906, i, 150, 341).—The reactions of arsenic compounds cannot always be explained on the basis either of ionic or of kineto-molecular mechanics. Most of

the arsenic reactions are non-electrolytic, and between the initial compounds and the most easily separable end-product other compounds, usually crystalline, are formed and can often be separated. The present paper describes a systematic study of the reactions of the arsines, evidence being obtained showing that intermediate products are often formed and that arsenic compounds react largely by initial coalescence with the reagent. In most of the reducing actions effected by the arsines, there is evidence of an initial amalgamation of the oxidising agent and the arsine. Also, in the interaction of sodium arsenite with alkyl iodides, according to the equation $\text{Na}_3\text{AsO}_3 + \text{RI} = \text{Na}_2\text{RAsO}_3 + \text{NaI}$, the additive compound $\text{AsIR}(\text{ONa})_3$ is formed as an intermediate product.

In the electrolytic reduction of cacodyl chloride to dimethylarsine, cacodyl is first formed, the successive reactions being $2\text{AsMe}_2\text{Cl} + 2\text{H} = \text{AsMe}_2 \cdot \text{AsMe}_2 + 2\text{HCl}$ and $\text{AsMe}_2 \cdot \text{AsMe}_2 + 2\text{H} = 2\text{AsHMe}_2$.

[With ELRICK WILLIAMS.]—A large number of reactions of methylarsine were studied, and equations are given for the changes taking place. The reactions represented by the equations: $\text{AsMeH}_2 + \text{HI} \rightleftharpoons \text{AsMeH}_3\text{I} \rightarrow \text{AsMeHI} + \text{H}_2$ and $\text{AsMeHI} + \text{HI} \rightleftharpoons \text{AsMeH}_2\text{I}_2 \rightarrow \text{AsMeI}_2 + \text{H}_2$ are slow or readily reversible. Methylarsine gives (1) with propyl iodide, AsH_2MePrI , the reaction being reversible; (2) with silver nitrate, a mixture of silver methylarsinate and silver; (3) with methylarsine oxide, the compound $(\text{AsMe})_4$ or

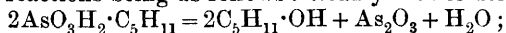


Ethylarsine reacts with (1) iodine, $\text{AsH}_2\text{Et} + \text{I}_2 = \text{AsI}_2\text{Et} + \text{H}_2$; (2) bromine, $\text{AsH}_2\text{Et} + \text{Br}_2 = \text{AsBr}_2\text{Et} + \text{H}_2$, intermediate products being formed; (3) sulphur, $\text{AsH}_2\text{Et} + \text{S}_2 = \text{AsEtS} + \text{H}_2\text{S}$; (4) mercuric chloride, $\text{AsH}_2\text{Et} + 2\text{HgCl}_2 = \text{AsCl}_2\text{Et} + 2\text{Hg} + 2\text{HCl}$; (5) mercuric iodide, $\text{AsH}_2\text{Et} + 2\text{HgI}_2 = \text{AsI}_2\text{Et} + 2\text{HgI} + \text{H}_2$; (6) stannic chloride, $\text{AsH}_2\text{Et} + 2\text{SnCl}_4 = \text{AsCl}_2\text{Et} + 2\text{SnCl}_2 + 2\text{HCl}$; (7) arsenic trichloride, $8\text{AsH}_2\text{Et} + 8\text{AsCl}_3 = (\text{AsEt})_4 + 4\text{AsCl}_2\text{Et} + 16\text{HCl} + 8\text{As}$; (8) propyl iodide, giving *ethyltripropylarsonium iodide*, AsEtPr_3I , m. p. 237° (decomp.); (9) isopropyl iodide, giving *ethyltriisopropylarsonium iodide*, which decomposes at its melting point according to the equations: $\text{AsEtPr}^\beta_3\text{I} = \text{AsPr}^\beta_3 + \text{EtI}$ and $2\text{AsEtPr}^\beta_3\text{I} = \text{AsPr}^\beta_3\text{I}_2 + \text{C}_4\text{H}_{10} + \text{AsPr}^\beta_3$.

Benzylarsine, $\text{AsH}_2 \cdot \text{CH}_2\text{Ph}$, prepared by reducing benzylarsinic acid by means of amalgamated zinc dust and hydrochloric acid, is a faintly yellow liquid, b. p. $140^\circ/262$ mm., oxidises in the air to benzylarsinic acid, and forms a *platinichloride*, $\text{C}_7\text{H}_7\text{AsH}_2 \cdot \text{PtCl}_4$.

Tripopylarsine, AsPr^α_3 , prepared by the interaction of propyl chloride, arsenic trichloride, and sodium, has b. p. $167^\circ/90$ mm. and $158^\circ/73$ mm.

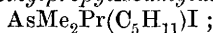
The decomposition of various arsenic derivatives by heat has been studied, the reactions being as follows: *isoamylarsinic acid*,



phenylarsinic acid, $2\text{AsO}_3\text{H}_2\text{Ph} = \text{Ph}_2\text{O} + \text{As}_2\text{O}_3 + 2\text{H}_2\text{O}$; phenylarsine, $3\text{AsH}_2\text{Ph} = \text{Ph}_3\text{As} + 2\text{As} + 3\text{H}_2$; methylarsine, $2\text{AsH}_2\text{Me} = 2\text{CH}_4 + 2\text{As} + \text{H}_2$; ethylarsine, $2\text{AsH}_2\text{Et} = 2\text{C}_2\text{H}_6 + 2\text{As} + \text{H}_2$ and $3\text{AsH}_2\text{Et} = \text{Et}_3\text{As} + 2\text{As} + 3\text{H}_2$; diisoamylarsine, $6\text{AsH}(\text{C}_5\text{H}_{11})_2 = 4\text{As}(\text{C}_5\text{H}_{11})_3 + 2\text{As} + 3\text{H}_2$ and $2\text{AsH}(\text{C}_5\text{H}_{11})_2 = \text{C}_5\text{H}_{10} + \text{C}_5\text{H}_{12} +$

$C_{10}H_{22} + 2As$; diphenylarsine, $6AsHPh_2 = 4AsPh_3 + 2As + 3H_2$ and $2AsPh_3 = 3C_{12}H_{10} + 2As$; tripropylarsine, $4AsPr^a_3 = (AsPr^a)_4 + 4C_6H_{14}$; triethylarsine, $4AsEt_3 = (AsEt)_4 + 4C_4H_{10}$; benzylarsine, $4AsH_2 \cdot CH_2Ph \rightarrow (As \cdot CH_2Ph)_4 + 4H_2$; cacodyl, $4AsMe_2 \cdot AsMe_2 \rightarrow 4AsMe_3 + (AsMe)_4$.

[With BURTON B. WILLCOX.]—Dimethylarsine gives the following reactions: (1) With phenylarsine dichloride it yields dimethylarsine-phenylarsine dichloride, $AsCl_2Ph \cdot AsHMe_2$, which decomposes rapidly in the air; (2) with diisoamylarsine chloride, dimethyldiisoamylcacodyl, $AsMe_2 \cdot As(C_5H_{11})_2$, is obtained; (3) with propyl iodide it yields *dimethylpropylarsonium iodide*, $AsHMe_2Pr^aI$, which, with *isoamyl iodide*, gives *dimethylpropylisoamylarsonium iodide*,



(4) with acetyl iodide it forms $AsHMe_2AcI$ which decomposes, giving $AsMe_2I + CH_3 \cdot CHO$; (5) with ethyl chlorocarbonate, dimethylarsine reacts thus: $AsHMe_2 + Cl \cdot CO_2Et \rightarrow AsMe_2Cl + H \cdot CO_2Et$; (6) with sulphur dichloride, $2AsHMe_2 + SCl_2 \rightarrow 2AsMe_2Cl + S$; (7) with arsenic trioxide, $2AsHMe_2 + As_2O_3 = (AsMe)_4 + H_2O + O_2$; (8) with arsenic trichloride, $4AsHMe_2 + 2AsCl_3 = (AsMe)_4 + 2AsMe_2Cl + 4HCl$.

Diisoamylarsine and propyl iodide yield dipropyldiisoamylarsonium iodide, $AsPr^a_2(C_5H_{11})_2I$, and cacodyl and propyl iodide, *dimethyl-dipropylarsonium iodide*, $AsMe_2Pr_2I$, which, with mercuric chloride, gives a white precipitate, $AsMe_2Pr_2I, HgCl_2$. T. H. P.

cycloHexadienes. II. NICOLAI D. ZELINSKY and A. GORSKY (*Ber.*, 1908, 41, 2630—2634. Compare this vol., i, 619).—A pronounced exaltation of the molecular refraction is not shown by the following hydrocarbons containing conjugate double linkings. 1-Methyl- Δ^1 -cyclohexene yields a *dibromide*, b. p. 100—102°/12 mm., from which by means of quinoline, 1-methyl- $\Delta^{2:6}$ -cyclohexadiene is obtained, which has b. p. 110°(corr.)/741 mm., D_4^{20} 0.8292, n_D^{20} 1.4710, and gives a blood-red coloration with alcoholic sulphuric acid and a bluish-violet with nitric acid (D 1.40). 1:3-Dimethylcyclohexene yields a *dibromide*, b. p. 130—135°/35 mm., which by distillation with quinoline yields 1:3-dimethyl- $\Delta^{2:4}$ -cyclohexadiene, b. p. 129—130°/745 mm., D_4^{20} 0.8225, n_D^{20} 1.4675, $[\alpha]_D$ 27.38°. 1:4-Dimethylcyclohexan-4-ol and aqueous oxalic acid yield 1:4-dimethyl- Δ^3 -cyclohexene, b. p. 128.5°(corr.), D_4^{20} 0.8005, n_D^{20} 1.4457, the *dibromide* of which, by repeated distillation with quinoline, yields 1:4-dimethyl- $\Delta^{2:4}$ -cyclohexadiene, b. p. 132.5—133.5°(corr.)/740 mm., D_4^{20} 0.8223, n_D^{20} 1.4675. 1:2-Dimethylcyclohexan-2-ol and aqueous oxalic acid yield 1:2-dimethylcyclohexene, b. p. 135.5—136.5°(corr.), D_4^{20} 0.8226, $n_D^{21.5}$ 1.4580, the derivatives of which will be considered later. C. S.

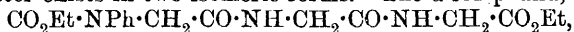
Mechanism of the Autoracemisation of Optically Active Ammonium Salts and the State of Quaternary Ammonium Salts in Solution. EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1908, 41, 2659—2665).—von Halban's measurements with inactive ammonium salts (*Abstr.*, 1907, ii, 246) do not decide whether the racemisation of

the active salts is due solely to decomposition into a tertiary base and an alkyl haloid, or is conditioned partly by intramolecular changes. That the latter alternative may be of influence is shown by the fact that active methylallyltetrahydroquinolinium iodide in methyl alcohol racemises with extraordinary velocity, although theoretically it should be stable in this solvent. The authors have therefore examined phenylbenzylmethylallyl-(or propyl)ammonium bromide and iodide polarimetrically, cryoscopically, by a slightly modified form of von Halban's titrimetric method, and by direct weighing of the undecomposed salt precipitated by ether. In every case the velocity constant of the decomposition agrees well with that of the racemisation. Ammonium salts, therefore, in suitable solvents (see later) decompose into a tertiary base and an alkyl haloid, a phenomenon which in the case of active salts is accompanied by an equally rapid diminution of the rotation. The deduction that active and inactive salts of the same base must decompose at the same rate has been verified. Moreover, the point of equilibrium of the system $RR'R''R'''NX \rightleftharpoons R'R''R'''N + RX$ must be the same for the active and the inactive modification of the same salt (compare von Halban, *loc. cit.*). This point differs greatly in bromides and iodides; in the former it corresponds with 40–50% of unchanged salt, and in the latter to 6%, at 25°. The preceding equation does not represent truly the condition of affairs in the solution, since the partition-coefficient in chloroform and cryoscopic measurements in bromoform indicate that ammonium salts are present in the solution in the bimolecular state.

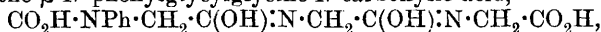
The nature of the solvent is of importance. Water and alcohol at 45° do not decompose quaternary ammonium salts appreciably, but in solvents with a small dielectric constant, such as tetrachloroethane, benzene, carbon disulphide, or ethylene tetrabromide (with the addition of alcohol to facilitate solution), the decomposition of an active ammonium salt can be followed with the polarimeter.

C. S.

Isomerism of Carbethoxydiglycylglycine Ester and the Stability of *N*-Carboxylic Acids. HERMANN LEUCHS and FREDERICK B. LA FORGE (*Ber.*, 1908, 41, 2586–2596. Compare Leuchs and Manasse, *Abstr.*, 1907, i, 770).—Carbethoxy-*N*-phenylglycylglycylglycine ester exists in two isomeric forms. The α -compound,

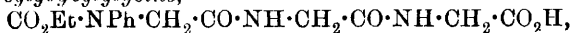


is obtained synthetically by the action of glycylglycine ester on carbethoxy-*N*-phenylglycyl chloride. When suitably hydrolysed, it yields the β -*N*-phenylglycylglycine-*N*-carboxylic acid,

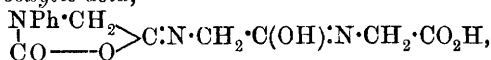


the silver salt of which reacts with ethyl iodide, yielding the isomeric β -ester.

α -Carbethoxy-*N*-phenylglycylglycylglycine ester crystallises from benzene in small, colourless needles, m. p. 135–136°. When hydrolysed with sodium hydroxide (1 mol.), it yields *α* -carbethoxy-*N*-phenylglycylglycylglycine,

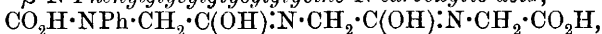


which can also be synthesised from glycyglycine and carbethoxyphenylglycyl chloride. It crystallises from ethyl acetate in needles, m. p. 145—146° after sintering at 141°, or from water in hydrated needles. When boiled with sodium hydroxide (2 mols.) and then acidified, the acid ester yields the lactone of *β*-phenylglycyglycylglycine-*N*-carboxylic acid,



which crystallises from water and has m. p. 212—213° (corr.). Alcoholic hydrochloric acid converts this lactone into the *β*-lactone

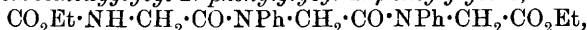
ester, $\begin{array}{c} \text{NPh} \cdot \text{CH}_2 \\ | \\ \text{CO} \text{---} \text{O} \end{array} > \text{C} : \text{N} \cdot \text{CH}_2 \cdot \text{C}(\text{OH}) : \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, m. p. 182—183° (corr.). *β*-*N*-Phenylglycyglycylglycine-*N*-carboxylic acid,



is obtained by carefully hydrolysing the *α*-ester, and when boiled with water or dilute hydrochloric acid readily yields the lactone acid, m. p. 212—213°. The *β*-ester, obtained from the silver salt of the *β*-acid, is a thick oil, and when boiled with alcoholic hydrochloric acid yields the lactone ester, m. p. 182—183°.

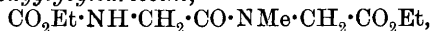
Carbethoxyglycyl-N-phenylglycine, $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$, obtained by hydrolysing the corresponding ester (Abstr., 1907, i, 770), crystallises from benzene in colourless plates, m. p. 133—134°. The corresponding chloride reacts with ethyl glycine, yielding *ethyl carbethoxyglycyl-N-phenylglycyglycine*, $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which crystallises from benzene or hot water in large prisms, m. p. 144—145° (corr.). When the ester is boiled with three equivalents of barium hydroxide, only some 30% of the theoretical amount of carbon dioxide is removed. The elimination of carbon dioxide is probably due to the fact that part of the ester is not transformed into the *β*-isomeride, but is directly hydrolysed, and the resulting *α*-acid immediately loses carbon dioxide.

Ethyl carbethoxyglycyl-N-phenylglycyl-N-phenylglycine,



obtained by condensing ethyl phenylglycine with carbethoxyglycyl-*N*-phenylglycyl chloride, has not been obtained in a crystalline form; the corresponding *acid*, $\text{C}_{21}\text{H}_{23}\text{O}_6\text{N}_3$, crystallises from ethyl acetate in nodules and contains $1\text{H}_2\text{O}$. When rapidly heated, it melts and decomposes at 128—130°. When boiled with excess of sodium hydroxide, the elimination of carbon dioxide is almost theoretical.

Ethyl carbethoxyglycylsarcosine,



crystallises from ether in long prisms, m. p. 54—55°, and, when hydrolysed with sodium hydroxide, loses an appreciable amount of carbon dioxide.

The results support the view that it is the *α*-(lactam)compounds which yield carbon dioxide, and when substituents are attached to the nitrogen atom so that molecular rearrangement into the isomeric *β*-(lactim)compound cannot take place, carbon dioxide is always eliminated during hydrolysis.

J. J. S.

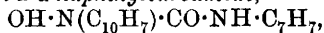
N- α -Naphthylhydroxylamine. II. JOHANNES SCHEIBER [and, in part, ERNST BECKMANN] (*J. pr. Chem.*, 1908, [ii], 78, 74—80. Compare Abstr., 1904, i, 867).—Two of the most characteristic reactions of the β -substituted hydroxylamines are the formation of *N*-aldoxime ethers, $\text{CHR} \lt \text{N}^{\text{R}}_{\text{O}}$, by condensation with aldehydes, and of disubstituted hydroxycarbamides, $\text{OH} \cdot \text{NR} \cdot \text{CO} \cdot \text{NHPh}$, by addition of phenylcarbimide (Beckmann, Abstr., 1898, i, 22). Although containing the elements of a mol. of water more than other *N*-arylhydroxylamines, *N*- α -naphthylhydroxylamine is found also to undergo these typical reactions.

The following *N*- α -naphthylaldoximes, $\text{CHR} \lt \text{N} \cdot \text{C}_{10}\text{H}_7_{\text{O}}$, are described :

$\text{R} = \text{Ph}$: yellow crystals, m. p. 106.5° , decomposes, becoming red on exposure to light. $\text{R} = \text{C}_6\text{H}_4 \cdot \text{OMe}(p)$: yellow crystals, m. p. 159° . $\text{R} = \text{C}_6\text{H}_4 \cdot \text{OH}(o)$: yellow crystals, m. p. 153° . $\text{R} = \text{C}_6\text{H}_4 \cdot \text{NO}_2(m)$: m. p. 147° .

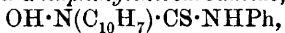
a-Hydroxy-*b*-phenyl- α -*a*-naphthylcarbamide, $\text{OH} \cdot \text{N}(\text{C}_{10}\text{H}_7) \cdot \text{CO} \cdot \text{NHPh}$, formed from *N*- α -naphthylhydroxylamine and phenylcarbimide, is obtained in white crystals, m. p. 126° , and gives an intense blue coloration with ferric chloride in alcoholic solution.

a-Hydroxy-*b*-*p*-tolyl- α -*a*-naphthylcarbamide,



formed from *N*- α -naphthylhydroxylamine and *p*-tolylcarbimide, separates from alcohol in crystals, m. p. 147° , and gives a blue coloration with ferric chloride.

a-Hydroxy-*b*-phenyl- α -*a*-naphthylthiocarbamide,



prepared from *N*- α -naphthylhydroxylamine and phenylthiocarbimide, forms nodular crystals, m. p. 119° , and gives a black solution with alcoholic ferric chloride. G. Y.

N- α -Naphthylhydroxylamines. III. JOHANNES SCHEIBER and PAUL BRANDT (*J. pr. Chem.*, 1908, [ii], 78, 80—92. Compare preceding abstract).—The *N*-aldoxime ethers derived from *N*- α -naphthylhydroxylamine behave towards mineral acids and alkalis in the same manner as other *N*-aryldoximes, yielding the aldehyde and transformation products of the *N*- α -naphthylhydroxylamine, chiefly azoxy-naphthalene. On the other hand, the isolation of an additive compound of *N*- α -naphthylhydroxylamine and phenylcarbimide has not been achieved. *N*-Aldoxime ethers, in general, are transformed by acid chlorides or anhydrides into the isomeric amides. The transformation takes place readily and at low temperatures with benzoyl or acetyl chloride, benzoylated and acetylated amides being formed with an excess of the acid chloride at high temperatures, but only at high temperatures with benzoic anhydride, when the benzoylated amide is formed. As, however, Wortmann (*Diss.*, Leipzig, 1903) found that the action of benzoic anhydride on *N*- α -naphthylbenzaloxime leads to the formation of *N*-benzoyl-1-amino- β -naphthol, it was of interest to study the mechanism of this reaction.

It is found now that *N*-benzoyl-1-amino- β -naphthol is formed by the action of benzoic anhydride, not only on *N*- α -naphthylbenzaldoxime, but also on *N*- α -naphthylanisaldoxime or on *N*- α -naphthylhydroxylamine, in the last case being accompanied by small amounts of dibenzoyl-1-amino- β -naphthol, which is formed also by the action of an excess of benzoic anhydride on *N*- α -naphthylanisaldoxime. On the other hand, the action of benzoic anhydride on *N*-anisoyl-1-amino- β -naphthol leads to the formation of *O*-benzoyl-*N*-anisoyl-1-amino- β -naphthol, together with small amounts of *N*-benzoyl- and unchanged *N*-anisoyl-1-amino- β -naphthol. It is argued that the action of benzoic anhydride on *N*- α -naphthylaldoximes must, therefore, consist in the first place of a fission of the aldoxime with formation of *N*- α -naphthylhydroxylamine, and not of an addition of the anhydride to the *N*-aldoxime ether.

When gently heated with acetic anhydride, *N*- α -naphthylanisaldoxime yields *N*-acetyl-1-amino- β -naphthol (Michel and Grandmougin, Abstr., 1893, i, 171).

[For the benzoyl and anisoyl derivatives of 1-amino- β -naphthol, see abstract below.] G. Y.

Transformation of Benzhydroxamic Acid into Anilides. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1908, 38, i, 655—657).—When benzhydroxamic acid is treated in alkaline solution with an aryl diazo-chloride, it is converted into its corresponding unstable diazo-salt, and this, when heated with alcohol, is converted into an anilide of benzhydroxamic acid.

Thus, with diazobenzene chloride, benzanilide is obtained; with *o*-diazotoluene chloride, benzo-*o*-toluidide; with *p*-diazotoluene chloride, benzo-*p*-toluidide; with *p*-diazoisole chloride, benzo-*p*-anisidide, and with *as*-*m*-diazoxylene chloride, benzo-*m*-xylidide. T. H. P.

***syn*- and *anti*-Stereoisomerism of Nitrogen Compounds.** JULIUS STIEGLITZ (*Amer. Chem. J.*, 1908, 40, 36—46).—The author gives a résumé of the various pairs of stereoisomeric chloroimino-esters prepared by him in conjunction with Earle (Abstr., 1904, i, 39) and others, and discusses them in relation to Hantzsch and Werner's hypothesis of *syn*- and *anti*-stereoisomerism. T. H. P.

Derivatives of 1-Amino- β -naphthol. JOHANNES SCHEIBER and PAUL BRANDT (*J. pr. Chem.*, 1908, [ii], 78, 92—95. Compare this vol., i, 725).—*N*-Benzoyl-1-amino- β -naphthol, m. p. 248° (245°: Böttcher, Abstr., 1883, 1113), is prepared by heating 1-amino- β -naphthol hydrochloride and sodium acetate with benzoic anhydride in glacial acetic acid solution.

Dianisoyl-1-amino- β -naphthol, $C_{26}H_{21}O_5N$, formed by shaking 1-amino- β -naphthol with anisoyl chloride and aqueous sodium hydroxide, separates from methyl alcohol in crystals, m. p. 215°, and, when treated successively with alcoholic sodium ethoxide and hydrochloric acid, yields *N*-anisoyl-1-amino- β -naphthol, $C_{18}H_{15}O_3N$, crystallising in golden leaflets, m. p. 241—243°.

N-Benzoyl-O-anisoyl-1-amino-β-naphthol, $C_{25}H_{19}O_4N$, m. p. 181° , is obtained by the action of anisoyl chloride and sodium hydroxide on *N*-benzoyl-1-amino-β-naphthol, and yields *N*-benzoyl-1-amino-β-naphthol when treated with alcoholic sodium hydroxide.

O-Benzoyl-N-anisoyl-1-amino-β-naphthol, m. p. 189° , is formed by benzylation of *N*-anisoyl-1-amino-β-naphthol, and yields this when hydrolysed with alcoholic sodium hydroxide. G. Y.

Oxidation of Eugenol by the Oxidising Ferment of Mushrooms. Formation of Dehydrodieugenol. H. COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1908, 146, 1413—1415. Compare this vol., i, 84).—Oxidation with ferric chloride or with air in presence of the oxydase from *Russula delica*, forms in very dilute eugenol solutions a precipitate of *dehydrodieugenol*, $C_{20}H_{22}O_4$, leaflets, m. p. 105 — 106° , giving a blue coloration with ferric chloride, and still having a double linking. *Diacetyldehydrodieugenol*, $C_{24}H_{26}O_6$, melts at 91 — 92° , and *dibenzoyldehydrodieugenol*, $C_{34}H_{30}O_6$, melts at 170 — 171° . G. B.

cycloHexanylethyl Alcohol and cycloPentanylcarbinol. NICOLAI D. ZELINSKY (*Ber.*, 1908, 41, 2628—2629).—The reaction between magnesium *cyclohexanyl* iodide and trioxymethylene in dry ether leads to the formation of *cyclohexanylethyl alcohol*, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 206 — $207^\circ/745$ mm. and 97 — $100^\circ/12$ mm., D_4^{20} 0.9153, n_D^{20} 1.4647. *cycloPentanylcarbinol*, $C_5H_9 \cdot CH_2 \cdot OH$, obtained from magnesium *cyclopentanyl* chloride and trioxymethylene, has b. p. 162.5 — 163.5° (corr.), D_4^{20} 0.9260, n_D^{20} 1.4555, forms a *phenylcarbamate*, m. p. 110° (corr.), and is oxidised to the corresponding *aldehyde* by 10% chromic acid in dilute acetic acid. C. S.

New Synthesis of Derivatives of Anthracene. HANS VON LIEBIG (*J. pr. Chem.*, 1908, [ii], 78, 95—96).—When fused with mandelic acid at 200 — 300° , the three dihydroxybenzenes form the corresponding dihydroxydiphenylmethanecarboxylic acids, but catechol and quinol yield also crystalline dyes, which in their behaviour resemble the dihydroxyanthraquinones, but are meso-ethers and are insoluble in aqueous sodium carbonate. These dyes are considered to

have the constitution $C_6H_2(OH)_2 \begin{array}{c} \diagup \text{C} \text{---} \text{O} \text{---} \text{C} \diagdown \\ | \quad \quad | \\ \text{C} \text{---} \text{C}_6H_4 \text{---} \text{C}_6H_4 \text{---} \text{C} \\ | \quad \quad | \\ \text{C} \text{---} \text{O} \text{---} \text{C} \diagup \end{array} C_6H_2(OH)_2$.

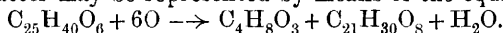
2 : 2' : 3 : 3'-*Tetrahydroxydianthranol meso-ether*, $C_{28}H_{16}O_5$, prepared from catechol and mandelic acid, crystallises in glistening, bronze-coloured leaflets, m. p. 264° , and dissolves in benzene or alcohol to a red, or in aqueous alkalis to a blue, solution.

1 : 1' : 4 : 4'-*Tetrahydroxydianthranol meso-ether*, formed from quinol and mandelic acid, crystallises in violet-red needles, m. p. 298° , and dissolves in benzene or alcohol to a red, or in aqueous alkalis to a violet, solution.

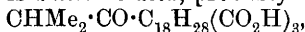
2 : 5-Dihydroxydiphenylmethanecarboxylic acid lactone, m. p. 157° (153 — 154° : Bistrzycki and Flatau, *Abstr.*, 1895, i, 419), obtained

from quinol and mandelic acid, 2:4-dihydroxydiphenylmethanecarboxylic acid lactone, m. p. 183°, from resorcinol and mandelic acid, and 2-hydroxy-4-methyldiphenylmethanecarboxylic acid lactone, m. p. 124°, from *m*-cresol and mandelic acid, give colorations with concentrated sulphuric acid. G. Y.

Cholesterol. XI. ADOLF WINDAUS (*Ber.*, 1908, 41, 2558—2568).—When the tribasic acid, $C_{25}H_{40}O_6$ (this vol., i, 265), is heated for eight hours at 75° with a mixture of equal volumes of fuming nitric and glacial acetic acids, the products are a trinitro-acid, $C_{25}H_{37}O_{12}N_3$, a tetrabasic acid, $C_{21}H_{30}O_8$, and α -hydroxyisobutyric acid; the formation of the two latter may be represented by means of the equation



The *trinitro*-acid is precipitated on the addition of water, and may be purified by washing with ethyl acetate and subsequent recrystallisation from glacial acetic acid. It forms colourless, glistening, rhombic plates, m. p. 234—235° (decomp.). It is a tribasic acid, and yields a *monorubidium* salt, $C_{25}H_{36}O_{12}N_3Rb$, which crystallises readily from 50% alcohol, and also an *acid potassium* salt, $C_{25}H_{34}O_{12}N_3K_3$, $C_{25}H_{37}O_{12}N_3$. When reduced with zinc dust and acetic acid, the trinitro-acid yields acetone and a nitrile, $C_{22}H_{31}O_6N$. The formation of acetone is in harmony with the view that the nitro-acid contains the grouping $NO_2 \cdot CMe_2 \cdot C(NO_2)_2$, and hence the original tribasic acid may be represented by the formula $CHMe_2 \cdot CH_2 \cdot C_{18}H_{28}(CO_2H)_3$. Among the products of reduction is a *ketonic acid*, probably



which yields a crystalline *oxime*, $C_{25}H_{39}O_7N$, m. p. 230—231° (decomp.). The *nitrile*, $C_{22}H_{31}O_6N$, crystallises from dilute acetic acid in needles and prisms, m. p. 137—138° after sintering at 127°. It is a tribasic acid, and, when boiled with potassium hydroxide solution, yields a *tetrabasic acid*, $C_{22}H_{32}O_8$, which crystallises from dilute acetic acid in prisms, m. p. 189°. The *caesium trihydrogen* salt, $C_{22}H_{31}O_8Cs$, crystallises from alcohol in long needles.

The *tetrabasic acid*, $C_{21}H_{30}O_8 = C_{17}H_{26}(CO_2H)_4$, crystallises from hot water in anhydrous, compact prisms or quadratic plates, m. p. 234° (decomp.), or from cold solution in hydrated needles. The needles when dehydrated in a vacuum over sulphuric acid sinter to a transparent mass at about 135°, and this, when further heated, sets to a mass of quadratic plates, m. p. 234° (decomp.). It yields a *mono-caesium* salt, $C_{21}H_{29}O_8Cs$, and is stable towards sodium hydroxide, nitric, sulphuric, and chromic acids, and bromine. The tetrabasic acid is also obtained when the ketonic acid, $CHMe_2 \cdot CO \cdot C_{18}H_{28}(CO_2H)_3$, is oxidised with an acetic acid solution of nitric acid. J. J. S.

Cholesterol. VII. OTTO DIELS (*Ber.*, 1908, 41, 2596—2600. Compare Dorée and Gardner, *Proc.*, 1908, 24, 173).—The crude ozonide of cholesterol contains more oxygen than as stated by Dorée and Gardner. After purification by digestion with cold alcohol, it has the composition $C_{27}H_{46}O_5$, and may be crystallised from hot acetone. It is

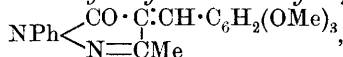
stable and does not explode when heated. The purified ozonide is somewhat more stable towards water than the crude, but when heated in sealed tubes at 140—150° it yields a yellow resin and an aqueous solution with a pleasant odour. The close relationship between cholesterol and cholestenone has been already established by Diels and Linn (this vol., i, 164) and Willstätter and Mayer (this vol., i, 636).
J. J. S.

*cyclo*Pen tanecarboxylic Acid and Chlorocyclopentane. NICOLAI D. ZELINSKY (*Ber.*, 1908, 41, 2627—2628).—*Chlorocyclopentane*, C_5H_9Cl , obtained from *cyclopentanol* and concentrated hydrochloric acid at 110°, has b. p. 114·5—115° (corr.), D_4^{20} 1·0051, n_D^{20} 1·4510, and reacts in ethereal solution with magnesium and carbon dioxide to form *cyclopentanecarboxylic acid*, b. p. 215·5—216° (corr.) and 104°/11 mm., D_4^{20} 1·0510, n_D^{18} 1·4534, the *amide* of which has m. p. 179° (corr.).
C. S.

Trimethylgallaldehyde [3 : 4 : 5-Trimethoxybenzaldehyde]. **Synthesis of Methylsinapic Acid.** FERDINAND MAUTHNER (*Ber.*, 1908, 41, 2530—2533. Compare this vol., i, 348).—When heated with aqueous hydrazine hydrate in a sealed tube at 100°, 3 : 4 : 5-trimethoxybenzaldehyde forms the *azine*, $N_2[CH \cdot C_6H_2(OMe)_3]_2$, which crystallises in yellow needles, m. p. 195—196°, and gives a red coloration with concentrated sulphuric acid. The oxime of 3 : 4 : 5-trimethoxybenzaldehyde has m. p. 83—84° (Semmler, this vol., i, 558). The *benzidine* derivative, $[C_6H_4 \cdot N : CH \cdot C_6H_2(OMe)_3]_2$, crystallises in yellow needles, m. p. 210—211°.

Methylsinapic acid (Gadamer, *Abstr.*, 1898, i, 38) is formed by heating 3 : 4 : 5-trimethoxybenzaldehyde with acetic anhydride and sodium acetate at 140—150°. 3 : 4 : 5-Trimethoxy- α -methylcinnamic acid, $C_6H_2(OMe)_3 \cdot CH : CMe \cdot CO_2H$, formed together with a neutral oil (trimethoxypropenylbenzene) from 3 : 4 : 5-trimethoxybenzaldehyde, propionic anhydride, and sodium propionate at 140—150°, crystallises in long needles, m. p. 157—158°.

4-Phenyl-3 : 4 : 5-trimethoxybenzylidene-1-methyl-3-pyrazolone,



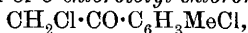
obtained by heating the aldehyde with phenylmethylpyrazolone in acetic acid solution, crystallises in red needles, m. p. 141—142°.

Trimethoxybenzylidenebisacetophenone, $C_6H_2(OMe)_3 \cdot CH(CH_2 \cdot CPh)_2$, m. p. 105—106°. α -Trimethoxyphenyl- β -naphthacinchonic acid, formed by condensation of trimethylgallaldehyde with pyruvic acid and β -naphthylamine, is obtained in yellow crystals, m. p. 262—263.

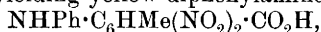
G. Y.

3-Chloro-6-chloroacetyltoiuene [5-Chloro-*o*-tolyl Chloromethyl Ketone] and **Two Chlorodinitrotoluic Acids.** FRANZ KUNCKELL (*Ber.*, 1908, 41, 2648—2650).—The reaction between aluminium
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chloride, *m*-chlorotoluene, and chloroacetyl chloride in carbon disulphide results in the formation of 5-chlorotolyl chloromethyl ketone,



m. p. 90° , from which by means of nitric acid two chlorodinitrotoluic acids, m. p. 223° and $187-191^\circ$ respectively, are obtained, the orientations of which are being investigated. The halogen is easily replaced by aniline, yielding yellow diphenylamine derivatives,



m. p. 174° and 216° respectively.

C. S.

Keto-chlorides of 1-Methyl- β -naphthol and their Relation to β -Naphthaquinols. KARL FRIES and E. HEMPELMANN (*Ber.*, 1908, 41, 2614—2626).—When chlorine is passed into a solution of 1-methyl- β -naphthol in slightly diluted acetic acid at 0° , 1-chloro-2-

keto-1-methyldihydronaphthalene, $\text{C}_6\text{H}_4\left\langle\begin{array}{l} \text{CMeCl}\cdot\text{CO} \\ \text{CH}=\text{CH} \end{array}\right.$, is ultimately ob-

tained as a colourless oil, which cannot be distilled without decomposition, is reduced again to 1-methyl- β -naphthol by stannous chloride, and dissolves in concentrated sulphuric acid with a yellow colour quickly becoming brown. By the use, alternately, of chlorine and of sodium acetate and acetic acid, the following compounds have been obtained in succession: 1:3:4-trichloro-2-keto-1-methyltetrahydronaphthalene, m. p. 78° ; 1:3-dichloro-2-keto-1-methyldihydronaphthalene; 1:3:3:4-tetrachloro-2-keto-1-methyltetrahydronaphthalene, m. p. $124-125^\circ$; 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene, m. p. 85° , and 1:3:3:4:4-pentachloro-2-keto-1-methyltetrahydronaphthalene, m. p. 105° . Of these compounds, the second and fourth resemble 1-chloro-2-keto-1-methyldihydronaphthalene in their behaviour with concentrated sulphuric acid, and all three dihydronaphthalene compounds may be regarded as the hydrochloric acid esters of 1-methyl-2-naphthaquinol, which shows similar colour reactions. The tetrahydronaphthalene derivatives are stable towards sulphuric acid.

The relation of the preceding derivatives of dihydronaphthalene to the 1-methyl-2-naphthaquinols has been further shown by taking advantage of the reactivity of the chlorine atom in position 1. All three derivatives react with silver acetate to form the corresponding methylnaphthaquinyl acetates, whilst, in addition, 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene yields 3:4-dichloro-1-methyl-2-

naphthaquinol, $\text{C}_6\text{H}_4\left\langle\begin{array}{l} \text{C}(\text{Me}\cdot\text{OH})\cdot\text{CO} \\ \text{CCl}=\text{CCl} \end{array}\right.$, when warmed in benzene

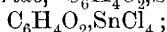
solution with silver nitrite, and the methoxy-derivative, m. p. 90° , by treatment with sodium methoxide.

3-Chloro-1-methyl- β -naphthol, $\text{C}_{10}\text{H}_5\text{MeCl}\cdot\text{OH}$, m. p. 60° , obtained by the reduction of 1:3-dichloro-2-keto-1-methyldihydronaphthalene by stannous chloride, forms an acetate, m. p. 86° , and regenerates the dichloroketo-chloride by treatment with the calculated amount of chlorine in glacial acetic acid. 3:4-Dichloro-1-methyl- β -naphthol, m. p. 132° , obtained by the reduction of 1:3:4-trichloro-2-keto-1-methyldihydronaphthalene, forms an acetate, m. p. 96° .

3-Chloro-1:2-methylnaphthaquinonitrole, $C_6H_4 \begin{matrix} \text{CMe(NO}_2\text{)} \cdot \text{CO} \\ \text{CH} = \text{CCl} \end{matrix}$, m. p.

85—86° (decomp. just above m. p.), is obtained by passing nitrous fumes into ethereal 3-chloro-1-methyl- β -naphthol at 0°. 3:4-Dichloro-1:2-methylnaphthaquinonitrole, m. p. 103—104° (decomp.), is obtained in a similar manner. The two compounds are remarkably stable towards dilute sodium carbonate or alcohol, but by prolonged heating in benzene or glacial acetic acid are converted into 3-chloro-1:2-methylnaphthaquinol, m. p. 70° (acetate, m. p. 133°), and 3:4-dichloro-1:2-methylnaphthaquinol, m. p. 114° (acetate, m. p. 149°), respectively.
C. S.

Halochromism of Quinones. KURT H. MEYER (*Ber.*, 1908, 41, 2568—2576).—Quinones combine with acids and also with certain metallic halides, forming additive compounds which have a much deeper colour than the original ketones (compare Kehrman and Mattisson, *Abstr.*, 1902, i, 229; Vorländer, *Abstr.*, 1905, i, 792). The compounds are unstable, and are decomposed by water, yielding the original quinones. The following compounds are all red in colour: *p*-benzoquinone stannic chloride, $C_6H_4O_2 \cdot SnCl_4 \cdot C_6H_6$ and



α -naphthaquinone antimony pentachloride, $C_{10}H_6O_2 \cdot 2SbCl_5$; anthraquinone antimony pentachloride, $C_{14}H_8O_2 \cdot 2SbCl_5$; phenanthraquinone mercuric chloride, $2C_{14}H_8O_2 \cdot HgCl_2$; phenanthraquinone zinc chloride, $C_{14}H_8O_2 \cdot ZnCl_2$; phenanthraquinone ferric chloride, $3C_{14}H_8O_2 \cdot FeCl_3$. Phenanthraquinone also forms a red additive compound with sulphur dioxide at about -50°.

The following compounds have a green colour: phenanthraquinone stannic chloride, $C_{14}H_8O_2 \cdot SnCl_4$, which turns red on exposure to the air; phenanthraquinone aluminium chloride, $C_{14}H_8O_2 \cdot AlCl_3$. The absorption curves for chloroform solutions of the additive compounds of a quinone with an acid and with a metallic halide are very similar.

Ketones also form coloured additive compounds with metallic chlorides. Benzophenone antimony pentachloride, $COPh_2 \cdot 2SbCl_5$, crystallises in yellow needles, and benzil stannic chloride, $C_{14}H_{10}O_2 \cdot SnCl_4$, in yellow plates.

Triphenylchloromethane absorbs hydrogen chloride at -60°, yielding a yellow additive compound, $CPh_3Cl \cdot 6HCl$; the bromo-derivative yields a similar compound with hydrogen bromide.

The introduction of halogen into the quinone molecule, as, for example, in tetrachloro-*o*- and -*p*-benzoquinone, inhibits the formation of additive compounds with metallic salts.
J. J. S.

Quinonoid Compounds. XVI. Two Forms of *o*-Quinones. RICHARD WILLSTÄTTER and FRITZ MÜLLER (*Ber.*, 1908, 41, 2580—2586. Compare *Abstr.*, 1905, i, 144; this vol., i, 475).—A colourless modification of *o*-benzoquinone is obtained when the oxidation of catechol is carried out rapidly (fifteen seconds) at low temperatures.

It is necessary to wash the silver oxide well and to dry it by means of acetone and ether. The colourless crystals are obtained when the

filtered ethereal solution is mixed with light petroleum, or cooled to -15° to -20° . The ethereal solutions are green, but the crystals are colourless. The compound has quinonoid properties, but is extremely unstable, and is either transformed into the red modification or decomposes.

When the pure red compound is dissolved in ether and the solution cooled, a mixture of the colourless and red crystals is obtained, so that in the solution the two compounds are present in a state of equilibrium.

The ketonic formula $\text{O}:\text{C}_6\text{H}_4:\text{O}$ is assigned to the red compound, and the formula $\text{C}_6\text{H}_4\begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix}$ to the colourless.

J. J. S.

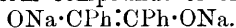
The Claisen Condensation. II. Mechanism of the Reaction. J. BISHOP TINGLE and ERNEST E. GORSLINE (*Amer. Chem. J.*, 1908, **40**, 46—88. Compare Abstr., 1907, i, 498).—The authors have carried out a number of experiments with the object of ascertaining the influence of change of conditions on the Claisen condensation between certain ketones and esters, and, hence, on the yield of diketone. The principal results obtained are as follows.

With camphor as the ketone, calcium or sodamide is practically useless as a condensing agent unless alcohol is added, and, even then, a relatively high temperature is required (compare Claisen, Abstr., 1905, i, 286).

The nature of the "solvent product," or the residue left after the distillation of the solvent, varies in different cases. With condensations between camphor and ethyl oxalate in presence of sodium or sodamide, considerable quantities of camphoroxalic acid can be extracted from the solvent product, and the same holds when camphor and ethyl cinnamate are condensed by means of either of these agents. When, however, calcium is used, no trace of the condensation product is found in the solvent product.

The reaction is markedly influenced by the nature of the ketone or aldehyde employed, and also by that of the ester, and this influence is probably not confined to the velocity, but, in some cases, extends to the actual mechanism of the reaction. The readiness with which the reaction takes place is increased by the proximity of two carbethoxyl groups, and there are indications that the mechanism of the reactions resulting in the formation of diketones varies in the two cases of aliphatic and aromatic esters.

Experiments on the acetoacetic ester condensation, in which small quantities of ether, light petroleum, or pyridine were used as solvents, show that the catalytic influence of ether and pyridine on the velocity of the reaction is appreciable. No evidence could be obtained to show that ether or a tertiary base has any catalytic action when sodium reacts with esters to form compounds of the class



It seems probable that the two reactions take place simultaneously, and that in the presence of solvents the reaction $2\text{CH}_3\cdot\text{CO}_2\text{Et} + 4\text{Na} = \text{ONa}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{ONa} + 2\text{NaOEt}$ preponderates considerably.

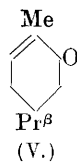
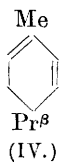
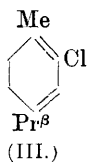
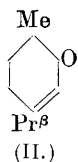
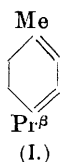
If the explanation of the Claisen condensation given by its discoverer (Abstr., 1895, i, 62) is correct, sodium ethoxide should be an excellent accelerator, and this is found to be the case, the addition of a little alcoholic sodium ethoxide accelerating to a marked degree the reactions between camphor and the esters of various acids in presence of light petroleum as solvent. Absolute alcohol is a still more effective accelerating agent, but sodium ethoxide free from alcohol affects the speed of the reaction very little, if at all. A striking fact is the very great reduction in the yield of diketone occurring when alcohol or alcoholic sodium ethoxide is added.

When the esters of the aliphatic series are condensed with camphor, the use of more than one atomic proportion of sodium does not increase the yield of the diketone. The catalytic agent does not accelerate the reaction between sodium and the ester, or that between sodium and camphor. Sodium camphor acts as a feeble condensing agent.

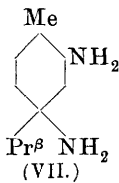
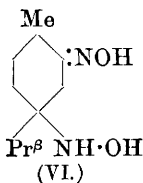
The authors' results indicate that, taken in connexion with the action of sodium on esters and with the catalytic influence of ether and the tertiary bases, Michael's explanation of the Claisen condensation (Abstr., 1901, i, 123; 1905, i, 506) is the most satisfactory.

T. H. P.

Constitution of Terpinene. CARL D. HARRIES and RIKO MAJIMA (*Ber.*, 1908, 41, 2516—2529).—Amenomija (Abstr., 1905, i, 803) suggested that carvenene (I) might be identical with terpinene, and attempted to prepare it from carvenone (II) in the same manner as Harries and Johnson obtained α -phellandrene (IV) from Δ^6 -menthene-2-one (V), but was unable to reduce the intermediate chloro-compound (III).



It is now found that when carvenone is converted by way of its oxime into 2-amino- Δ^3 -menthene, and the phosphate of this base is distilled, a single hydrocarbon, which must be carvenene, is obtained, but if the ketone is converted into its hydroxylamino-oxime (VI), and this into 2:4-diaminomenthane (VII), distillation of the phosphate leads to the formation of a mixture of hydrocarbons.

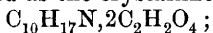


its oxime into 2-amino- Δ^3 -menthene, and the phosphate of this base is distilled, a single hydrocarbon, which must be carvenene, is obtained, but if the ketone is converted into its hydroxylamino-oxime (VI), and this into 2:4-diaminomenthane (VII), distillation of the phosphate leads to the formation

The relation of carvenone to terpinene is discussed (compare Wallach, Abstr., 1907, i, 64; Semmler, Abstr., 1907, i, 714).

Carvenone forms two oximes, one of which, m. p. 90—92° (Wallach, Abstr., 1894, i, 44; 1895, i, 672), forms a hydrochloride, m. p. 113—114°, crystallising from ether-alcohol. The other oxime is an

oil, and forms a *hydrochloride*, m. p. 105—113°, which remains dissolved in the ether-alcoholic mother liquor. Reduction of carvenone-oxime with zinc dust in acetic acid solution leads to the formation of the *imine*, which is isolated as the crystalline *oxalate*,



this is readily hydrolysed by water, forming ammonium oxalate and carvenone. The free imine, b. p. 105°/12 mm., decomposes at the ordinary temperature, and yields benzamide when benzoylated by the Schotten-Baumann method. Contrary to Wallach and Boedecker's statement (Abstr., 1907, i, 943), carvenoneoxime cannot be formed intermediately in the reduction of terpinene nitrosite, as, although hydrolysed by sulphuric acid, it is stable towards boiling glacial acetic acid.

2-Amino- Δ^3 -menthene (*carvenylamine*), $\text{C}_{10}\text{H}_{19}\text{N}$, prepared by reduction of carvenoneoxime by means of aluminium amalgam in ethereal solution, is separated from the imine formed simultaneously by hydrolysis of the latter with hydrochloric acid. It has b. p. 86—89°/10 mm., D_4^{20} 0.8762, and n_D^{20} 1.46966. When boiled with acetic anhydride, it forms a *syrup*, which decolorises bromine. The *benzoyl* and *phenylcarbamide* derivatives are syrups. The *hydrochloride*, *nitrate*, and *acid oxalate*, m. p. about 120°, are described.

Carvenene ($\Delta^{1,3}$ -menthadiene), $\text{C}_{10}\text{H}_{16}$, b. p. 68—70°/15 mm., D_4^{18} 0.8453, n_D^{18} 1.48579, prepared by distillation of carvenylamine phosphate, has a faint odour of lemons, and forms terpinene nitrosite, m. p. 155—156°.

Carvenone hydroxylamino-oxime, prepared from dihydrocarvone or from terpinene nitrosite, has m. p. 162—162.5° (167—168°: Tiemann and Semmler, Abstr., 1899, i, 224), and when treated with mercuric oxide forms the *nitroso-oxime*, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$, blue crystals, m. p. 113—115°, together with a white, sparingly soluble, crystalline *substance*.

2:4-Diaminomenthane, $\text{C}_{10}\text{H}_{22}\text{N}_2$, prepared by reduction of the hydroxylamino-oxime with sodium and alcohol, is an oil, b. p. 121.5°/12 mm., D_4^{20} 0.9192, n_D^{20} 1.4848. The *hydrochloride*, *sulphate*, *nitrate*, *platinichloride*, *oxalate*, *benzoyl* derivative, and *phenylcarbamide* derivative, m. p. 220—222°, are described. On distillation, the phosphate of the diamine yields a mixture of hydrocarbons, b. p. 62—65°/11 mm., D_4^{17} 0.8611, n_D^{17} 1.48802, which gradually forms a *syrup*. The fresh mixture yields small amounts of terpinene nitrosite. The action of sodium nitrite on the diamine hydrochloride leads to the formation of an *oil*, b. p. 65—100°/12 mm., which does not yield terpinene nitrosite.

G. Y.

Components of Ethereal Oils. Elimination of Methoxy-groups in the para-Position with Respect to Allyl or Propenyl Radicles. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 2556—2557. Compare this vol., i, 557, 558, 664).—The product obtained by reducing elemicin or, even better, *isoelemicin* with sodium and alcohol is shown to have the composition $\text{C}_{11}\text{H}_{16}\text{O}_2$, and is 3:5-dimethoxy-1-n-propylbenzene, since it yields 3:5-dimethoxybenzoic acid when oxidised. The reduction thus consists in the conversion of the propenyl to a

propyl group, and the elimination of the methoxy-radicle which was in the para-position with respect to the propenyl group. The propenyl group thus behaves in much the same manner as the keto-group (compare Kostanecki, this vol., i, 359). J. J. S.

Position of Bromine Atoms in Derivatives of Methronic Acid. HYPOLYT TREPHILIEFF (*Ber.*, 1908, 41, 2543—2544).—The tetrabromo-derivative of methronic acid described recently (Abstr., 1907, i, 1063) may have the constitution (I)
$$\text{O} \begin{array}{l} \text{C}(\text{CHBr}_2) = \text{C} \cdot \text{CO}_2\text{H} \\ \text{C}(\text{CBr}_2 \cdot \text{CO}_2\text{H}) : \text{CH} \end{array}$$

or (II)
$$\text{O} \begin{array}{l} \text{C}(\text{CBr}_2) = \text{C} \cdot \text{CO}_2\text{H} \\ \text{C}(\text{CHBr} : \text{CO}_2\text{H}) : \text{CH} \end{array}$$
. It is now found that the action of bromine on ethyl phenithronate leads to the formation of a *dibromo*-derivative, $\text{C}_{15}\text{H}_{12}\text{O}_3\text{Br}_2$, which is obtained in yellow crystals, and

on 3-carboxy-2-methylfuran-4-acetic acid,
$$\text{O} \begin{array}{l} \text{CH} = \text{CMe} \\ \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) : \text{C} \cdot \text{CO}_2\text{H} \end{array}$$
 (Feist, Abstr., 1899, i, 675), to that of a *tribromo*-derivative, $\text{C}_8\text{H}_5\text{O}_5\text{Br}_3$, which crystallises from acetic acid. Both these derivatives decompose without melting when heated. Bromine does not react, on the other hand, with the methyl groups of 3:4-dimethylfurandicarboxylic acid; hence it is considered that the tetrabromo-derivative of methronic acid has the constitution (I). G. Y.

Constitution of Methronic Acid. HYPOLYT TREPHILIEFF (*Ber.*, 1908, 41, 2545—2546. Compare Abstr., 1906, i, 528).—The fraction, b. p. 300—305°, obtained from the product of the action of sodium succinate on ethyl acetoacetate (Fittig and Hantzsch, Abstr., 1889, 126), contains ethyl methronate, which on hydrolysis yields methronic acid. This, when treated with aqueous ammonia at 320°, forms dimethylpyrrole, b. p. 165°.

When exposed to bromine vapour for two to three months, 2:5-dimethylfuran-3-carboxylic acid forms a *tetrabromo*-derivative, $\text{C}_7\text{H}_4\text{O}_3\text{Br}_4$, which is obtained as a crystalline mass. G. Y.

Crystallography of the Fulgides. ZOLTÁN TOBORFFY (*Zeitsch. Kryst. Min.*, 1908, 45, 155—181).—Crystallographic details are given concerning thirty-nine fulgide compounds recently prepared by Stobbe (Abstr., 1905, i, 857; 1906, i, 960). L. J. S.

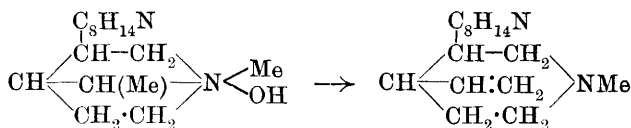
Reactions of Hordenine Based on the Constitution of this Substance. GEORGES DENIGES (*Bull. Soc. chim.*, 1908, [iv], 3, 786—792).—The constitution assigned by Léger to this alkaloid (Abstr., 1906, i, 204, 761; 1907, i, 151, 234, 337) indicates that it contains residues of *p*-cresol and of trimethylene, and the following reactions characteristic of substances containing these residues confirm Léger's formula.

When a drop of a solution of hordenine sulphate is placed on a glass slip and a drop of iodine solution is added, characteristic crystals of a brown iodo-compound separate, which are visible under the microscope. Trimethylamine yields a crystalline derivative under the same conditions, as does also choline.

Hordenine (0.02—0.03 gram) dissolved in 4 c.c. of acetic acid gives, on boiling with four drops of formaldehyde solution and the subsequent addition of 3 c.c. of sulphuric acid, a green coloration, which rapidly deepens. Tyrosine, under the same conditions, gives a red coloration, which, on gently warming, passes into green. Under somewhat similar conditions, *p*-cresol also gives a green coloration. Similar green colorations are obtained with tyrosine or hordenine when formaldehyde solution is replaced by paraldehyde. Precise instructions for the application of these tests under various conditions are given in the original. It is suggested that Aloy and Rabaut's tyrosine colour reaction with bromine and ammonia solution (this vol., i, 341) is probably due to the presence of the *p*-cresol residue. *p*-Cresol gives with bromine water, followed by ammonia, a yellow coloration, passing into orange, and hordenine an intense yellow.

T. A. H.

Sparteine. Transformation of *iso*Sparteine into α -Methylsparteine. AMAND VALEUR (*Compt. rend.*, 1908, 147, 127—129. Compare this vol., i, 43, 44, 103, 206).—When the solution of α -methylsparteine, after isomerisation by boiling with dilute sulphuric acid, is evaporated in a vacuum, crystals of *isosparteine methosulphate*, $C_{15}H_{26}N_2Me.HSO_4.9H_2O$, are formed, having $[\alpha]_D - 13.65^\circ$. This salt is decomposed by baryta with the formation of α -methyl*isosparteinium hydroxide*, which yields a precipitate of *isosparteine methiodide* with potassium iodide, and is quantitatively transformed into α -methylsparteine by heating in a vacuum below 100° . Adopting the author and Moureu's constitutional formula for sparteine, the last change may be represented thus :



G. B.

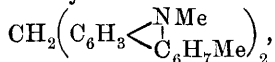
Organic and Fused Salts (Conductivity). CARL SCHALL (*Zeitsch. Elektrochem.*, 1908, 14, 397—405).—*Quinoline n*-butiodide, m. p. $175.5-176.1^\circ$, and *isobutiodide*, m. p. $159-159.5^\circ$, were prepared. The following salts were also prepared in a very pure state: Pyridine methiodide dibromide, m. p. $68-69^\circ$; quinoline hydriodide di-iodide, m. p. 67° ; quinoline methiodide di-iodide, m. p. $108.6-109.6^\circ$; quinoline methiodide tetra-iodide, m. p. $72-73^\circ$; quinoline ethiodide di-iodide, m. p. $43-45^\circ$; quinoline propiodide di-iodide, m. p. 60° ; quinoline *n*-butiodide di-iodide, m. p. 60.7° , and quinoline *isobutiodide* di-iodide, m. p. 85.6° . The *isopropyl* salt could not be obtained pure. The di-iodides of the hydriodides and methiodides show slight dissociation at their melting points; the other salts evolve mere traces of iodine or none. The electrical conductivity of the *n*-propyl, *n*-butyl, and *isobutyl* compounds was measured for the fused anhydrous substances at several temperatures.

T. E.

Dihydrazines. II. Diphenylmethanedimethylhydrazine and Cyclic Ketones. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2604—2607. Compare this vol., i, 700).—*cyclo*Hexanone (2 mols.) reacts with an acetic acid solution of diphenylmethanedimethyldihydrazine (1 mol.) in the presence of a little sulphuric acid, yielding the *bistetrahydrodicarbazole* of the diphenylmethane series, $\text{CH}_2(\text{C}_6\text{H}_5 \angle \text{C}_6\text{H}_5 \begin{smallmatrix} \text{NMe} \\ | \\ \text{C}_6\text{H}_5 \end{smallmatrix})_2$

It is best purified by solution in pyridine and precipitation with alcohol, has m. p. 175° , and dissolves in concentrated acids.

1-Methyl*cyclo*hexan-4-one yields a similar derivative,



m. p. 143° , and the corresponding *m*-compound, an isomeride, m. p. 200° .

1-Methyl*cyclo*hexan-2-one, menthone, 1 : 3-dimethyl*cyclo*hexen-5-one, and sabinaketone do not react with diphenylmethanedimethyldihydrazine. It thus appears that only those cyclic ketones which contain the grouping $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$ are capable of reacting with the dihydrazine.

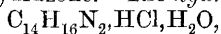
*cyclo*Pentanone does not react so readily as *cyclo*hexanone, and does not yield a pure product. J. J. S.

Reduction of Phenylhydrazones in Alkaline Solution. OSKAR SCHLENK (*J. pr. Chem.*, 1908, [ii], 78, 49—63).—Whilst the action of sodium amalgam on phenylhydrazones in acid solution leads to the formation of amines, $\text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh} \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{NH}_2 + \text{NH}_2\text{Ph}$ (Tafel, *Abstr.*, 1887, 975), the reduction in alkaline solution allows, in the case of phenylhydrazones of aromatic aldehydes, of the isolation of the intermediate hydrazine, $\text{R}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NHPh}$. In the following alkaline reductions, part of the excess of sodium hydroxide was neutralised by a current of carbon dioxide.

β -Phenylbenzylhydrazine, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NHPh}$, formed by the action of sodium amalgam on phenylbenzylidenehydrazine in boiling alcoholic solution, crystallises in colourless rhombohedra, m. p. 35° , b. p. 290° (decomp.) (m. p. $155\cdot5^\circ$: Schlömann, *Abstr.*, 1893, i, 452), reduces Fehling's solution when heated and silver solutions at the ordinary temperature, and, on exposure to air, changes into a yellow mass, from which phenylbenzylidenehydrazine gradually crystallises. The *hydrochloride*, $\text{C}_{13}\text{H}_{14}\text{N}_2\cdot\text{HCl}$, forms white leaflets, m. p. 205° ; the *hydrogen oxalate*, $\text{C}_{15}\text{H}_{16}\text{O}_4\text{N}_2$, m. p. 190° . The action of oxidising agents on β -phenylbenzylhydrazine leads to the formation of phenylbenzylidenehydrazine, and the prolonged action of mercuric oxide to that of the yellow tetrazone. On reduction with sodium amalgam and acetic acid, β -phenylbenzylhydrazine yields aniline and benzylamine. The *acetyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{Ac}\cdot\text{NHPh}$, prepared by adding the hydrazine to a cooled solution of zinc chloride in acetic anhydride, crystallises in prisms, m. p. 91° , reduces Fehling's solution only on prolonged boiling, and forms a *nitroso*-derivative, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{Ac}\cdot\text{NPh}\cdot\text{NO}$, crystallising in yellow rhombohedra, m. p. 84° . This gives Liebermann's reaction, and on reduction with zinc dust and acetic acid yields phenylhydrazine and

acetylbenzylamine. The *benzoyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{NBz}\cdot\text{NHPh}$, formed by the action of benzoyl chloride on the hydrazine in cooled ethereal solution, crystallises in colourless needles, m. p. 121—122°, and yields a *nitroso*-derivative, $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_3$, crystallising in yellow needles, m. p. 102°. The *dibenzoyl* derivative, $\text{CH}_2\text{Ph}\cdot\text{NBz}\cdot\text{NPhBz}$, formed by the Schotten-Baumann method, crystallises in hexagonal prisms, m. p. 131°.

p-Tolylbenzylidenehydrazine, $\text{C}_{14}\text{H}_{14}\text{N}_2$, crystallises from alcohol in colourless needles, m. p. 125°, becomes intensely red on exposure to air, and on reduction with sodium amalgam in boiling alcoholic solution yields β -*p-tolylbenzylhydrazine*, $\text{C}_{14}\text{H}_{16}\text{N}_2$, which is obtained as a viscid, yellow oil, b. p. 212°/17 mm., reduces Fehling's solution when heated, and on exposure to air or when treated with oxidising agents again forms the hydrazone. The *hydrochloride*,



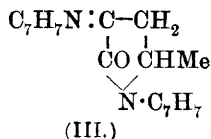
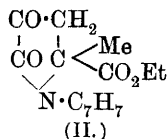
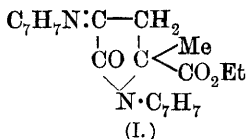
long, thin needles, m. p. 185° (decomp.), loses H_2O slowly in a vacuum. The *benzoyl* derivative, $\text{C}_{21}\text{H}_{20}\text{ON}_2$, crystallises in white needles, m. p. 159°.

Reduction of the phenylhydrazone of benzylideneacetone by means of sodium amalgam and acetic acid in alcoholic solution leads to the formation of γ -*amino- α -phenylbutane*, $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NH}_2$, which is obtained as a colourless oil, b. p. 222°/716 mm., D_4^{15} 0.9289, has a slight ammoniacal odour and a strong alkaline reaction, is only sparingly soluble in water, and absorbs carbon dioxide from the air, forming a crystalline *carbonate*. The *hydrochloride*, needles, m. p. 144°; the *platinichloride*, $(\text{C}_{10}\text{H}_{15}\text{N})_2\text{H}_2\text{PtCl}_6$, yellow leaflets, decomp. 220°; the *sulphate*, m. p. 255° (decomp.); the *hydrogen oxalate*, m. p. 110°; the *oxalate*, m. p. 232°; the *benzoyl* derivative, needles, m. p. 107°. The action of sodium nitrite on the base in hot hydrochloric acid solution leads to the formation of α -phenyl- β -butylene and a product of high boiling point, which may be the corresponding alcohol or a polymeride of the butylene. When heated with sodium amalgam in alcoholic solution at 55°, the phenylhydrazone of benzylideneacetone yields the *phenylhydrazone* of benzylacetone, $\text{C}_{16}\text{H}_{18}\text{N}_2$, which crystallises in colourless leaflets, m. p. 59°, is unstable, changing to a reddish-yellow oil, and has slight basic properties.

The alkaline reduction of benzilosazone leads to the formation of diphenylhydroxyethylamine, diphenylethylenediamine, m. p. 107—110° (90—92°: Feist, Abstr., 1894, i, 196; 120°: Grossmann, Abstr., 1889, 1191), and tetraphenylpyrazine, m. p. 244°. G. Y.

Mechanism of the Synthesis of Cyclic Nitrogen Compounds.

Action of Ethyl Pyruvate on *p*-Toluidine. LOUIS J. SIMON (*Compt. rend.*, 1908, 147, 125—127. Compare this vol., i, 296, 687).—The ester, $\text{C}_{22}\text{H}_{24}\text{O}_3\text{N}_2$ (I), previously obtained by the interaction of *p*-toluidine and ethyl pyruvate, is hydrolysed by cold concentrated sulphuric acid to a *substance*, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}$ (II), m. p. 152°, and is transformed by alcoholic potassium hydroxide into a *substance*, $\text{C}_{19}\text{H}_{20}\text{ON}_2$, m. p. 190°. The three substances may be represented thus:



Simultaneously with the substance (I), there is also formed a more soluble *substance*, $\text{C}_{24}\text{H}_{30}\text{O}_4\text{N}_2$, m. p. 142° , which may be represented thus: $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CMe}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{C}_7\text{H}_7$, and is transformed by alcoholic potassium hydroxide into an *acid*, m. p. 265° (decomp.), in all probability 4 : 6-*dimethylquinoline-2-carboxylic acid*.

G. B.

Action of Nitric Acid on 2:6-Dioxypyrimidines. Nitrohydroxyhydrothymine. XXX. TREAT B. JOHNSON (*Amer. Chem. J.*, 1908, 40, 19—36. Compare this vol., i, 692).—The author has not been able to obtain Steudel's nitrothymine (*Abstr.*, 1901, i, 434), which he regards as a secondary decomposition product, and not as a simple thymine derivative.

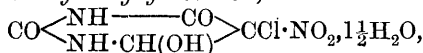
With fuming nitric acid (D 1.5) at the ordinary temperature, uracil gives 5-nitouracil; 5-bromouracil, 5-bromo-5-nitro-4-hydroxyhydrouracil (compare Behrend, *Abstr.*, 1887, i, 919); 5-chlorouracil, 5-chloro-5-nitro-4-hydroxyhydrouracil, and thymine, 5-nitro-4-hydroxyhydrothymine. The formation of these hydropyrimidines involves a direct addition of nitric acid to the double linking between the 4- and 5-positions of the pyrimidine ring (compare Behrend, *Annalen*, 1885, 229, 1—44).

The reduction of 5-bromo-5-nitro-4-hydroxyhydrouracil by means of tin and hydrochloric acid yields Behrend's hydroxyxanthine (*loc. cit.*).

5 : 5-Dichloro-4-hydroxyhydrouracil, $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \diagdown \quad \diagup \\ \text{NH}\cdot\text{CH}(\text{OH}) \end{array} \text{CCl}_2, \text{H}_2\text{O}$, prepared by the action either of chlorine water or of potassium chlorate and hydrochloric acid on uracil, crystallises from water in large prisms, m. p. $212\text{--}215^\circ$ (decomp.).

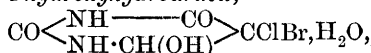
5-Chlorouracil, $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{NH}\cdot\text{CH} \end{array} \text{CCl}$, prepared by the action of chlorine water on uracil or by reducing the preceding compound by means of tin and hydrochloric acid, crystallises from water in prisms, m. p. $300\text{--}305^\circ$.

5-Chloro-5-nitro-4-hydroxyhydrouracil,



obtained by the action of fuming nitric acid (D 1.5) on 5-chlorouracil, separates in hard, prismatic crystals, which decompose with effervescence at $150\text{--}160^\circ$.

5-Chloro-5-bromo-4-hydroxyhydrouracil,

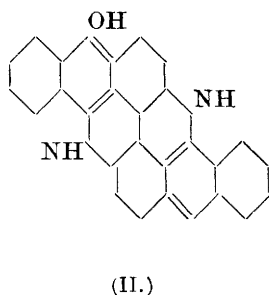
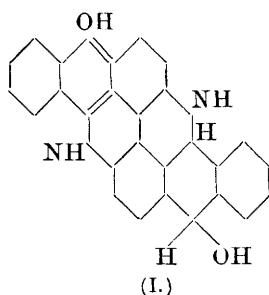


prepared from 5-bromouracil or 5-chlorouracil by the action of chlorine or bromine water respectively, crystallises from bromine water in prisms, decomposing with effervescence at $195\text{--}200^\circ$, and yields 5-chlorouracil when boiled with alcohol.

The action of bromine water on 5-iodouracil yields 5:5-dibromo-4-hydroxyhydrouracil (compare Wheeler and Johnson, *Abstr.*, 1907, ii, 826).

5-Nitro-4-hydroxyhydrothymine, $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{CH}(\text{OH}) \end{array} \text{CMe} \cdot \text{NO}_2$, exists in the following two modifications: (1) the α -form, obtained by dissolving thymine in fuming nitric acid, separates in triclinic prisms or blocks [W. E. FORD: $a:b:c=0.578:1:0.420$; $\alpha=107^\circ 35'$, $\beta=100^\circ 25'$, $\gamma=80^\circ 59'$], m. p. 183° (decomp.), and dissolves in water, giving an acid solution, or in alcohol. (2) The β - or unstable modification, obtained under certain conditions when thymine is dissolved in fuming nitric acid, crystallises from water or alcohol in prisms, m. p. $230\text{--}235^\circ$, and gradually changes into the β -form when kept at the ordinary temperature. Both modifications yield thymine when reduced with tin and hydrochloric acid. T. H. P.

Indanthren and Flavanthren. XI. Reduction Products of Flavanthren. ROLAND SCHOLL and W. NEOVIUS (*Ber.*, 1908, 41, 2534—2540. Compare this vol., i, 696).—Energetic reduction of flavanthren with zinc dust and sodium hydroxide leads to the formation of α -hexahydroflavanthren (I) and flavanthrinol (II):

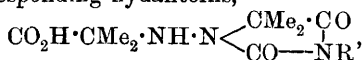


α -Hexahydroflavanthren hydrate is obtained as a stable, blackish-blue powder, $\text{C}_{28}\text{H}_{18}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$, which loses H_2O at 160° , dissolves in alcohol to a bluish-red, or if highly dilute to a violet, solution with brilliant, scarlet fluorescence, but in nitrobenzene to a non-fluorescent solution, forms fluorescent solutions in alcoholic alkalis or concentrated acids, and dyes unmordanted wool in an alkaline bath red, becoming greenish-blue on treatment with acids, and violet with water. On prolonged heating with zinc dust in alkaline solution, α -hexahydroflavanthren hydrate is converted into flavanthrinol hydrate, whilst the anhydrous hexahydro-compound forms anhydrous flavanthrinol when heated at 300° in a current of carbon dioxide. On treatment with a current of air in alkaline solution, the hexahydro-compound is oxidised to flavanthren.

Flavanthrinol hydrate, $\text{C}_{28}\text{H}_{16}\text{ON}_2 \cdot \text{H}_2\text{O}$, forms a blue, voluminous precipitate, becoming blackish-blue when dried, loses H_2O at 160° , is less soluble than α -hexahydroflavanthren hydrate, forms red solutions with olive-green fluorescence in organic solvents, except nitrobenzene,

in which it is not fluorescent, gives coloured solutions with reddish-brown fluorescence in concentrated acids, and dyes unmordanted wool violet-red, becoming green with acids, and blue with water. Flavanthrinol is not oxidised by air at the ordinary temperature, but, on treatment with ferricyanide or when heated in air, yields flavanthren. G. Y.

Desulphurisation of Thiohydantoins. JAMES R. BAILEY and C. P. RANDOLPH (*Ber.*, 1908, 41, 2494—2505).—Bailey observed (Abstr., 1904, i, 826) that 1-carboxyisopropylamino-5:5-dimethyl-2-thiohydantoins, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{N}<\begin{smallmatrix} \text{CMe}_2\cdot\text{CO} \\ \text{CS—NR} \end{smallmatrix}$, having R = an aliphyl or aryl group in position 3, are readily converted by means of mercuric oxide into the corresponding hydantoins,



which on treatment with bromine water are oxidised, forming the azo-compounds, $\begin{smallmatrix} \text{CO}\cdot\text{CMe}_2 \\ \text{NR—CO} \end{smallmatrix}>\text{N}\cdot\text{N}:\text{N}\cdot\text{N}<\begin{smallmatrix} \text{CMe}_2\cdot\text{CO} \\ \text{CO—NR} \end{smallmatrix}$, containing the tetrazone grouping $\cdot\text{N}\cdot\text{N}:\text{N}\cdot\text{N}\cdot$. It is found now that the desulphurisation and the oxidation to the tetrazone take place in one operation when the thiohydantoin is treated with bromine water. These observations led to the study of the desulphurisation of thiohydantoins in general. Although the statements of Aschan (Abstr., 1884, 907) and of Marckwald, Neumark, and Stelzner (Abstr., 1892, 149) suggest that this desulphurisation takes place with ease, it is found that the thiohydantoins studied other than those already mentioned are not converted into hydantoins by the action of mercuric oxide. On the other hand, the desulphurisation does take place readily when the alkali salts of the thiohydantoic acids are treated with mercuric oxide, the resulting hydantoates being readily converted into the hydantoins. Thus 3-methylhydantoin and 3-ethylhydantoin are formed by heating potassium methylthiohydantoate and ethylthiohydantoate respectively with mercuric oxide in aqueous solution.

Whilst 1-carboxyisopropylamino-3-phenyl-5:5-dimethyl-2-thiohydantoin is readily desulphurised by mercuric oxide, 3-phenyl-5:5-dimethylhydantoin is not obtained by the action of mercuric oxide on the thiohydantoin, $\text{NH}<\begin{smallmatrix} \text{CMe}_2\cdot\text{CO} \\ \text{CS—NPh} \end{smallmatrix}$, but, on the other hand, all thiohydantoins derived from α -aminoisobutyric acid are desulphurised normally by bromine water. Thiohydantoins derived from glycine or alanine, that is, containing one or two hydrogen atoms in position 5, when treated with bromine water, yield sulphuric acid and halogen-substitution products of the hydantoins (compare Andreasch, Abstr., 1902, i, 157).

Ethylhydantoic acid, $\text{C}_5\text{H}_{10}\text{O}_3\text{N}_2$, prepared from the hydantoin, has m. p. 132° (decomp.).

3-Allylhydantoin, $\text{C}_6\text{H}_8\text{O}_2\text{N}_2$, crystallises in thin needles, m. p. 78° .

3-p-Tolylhydantoic acid, $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$, separates from alcohol in crystals, m. p. 203° (decomp.); the *ethyl* ester, m. p. 166° . *3-p-Tolyl-*

hydantoin crystallises in needles, m. p. 211° (205° : Quenda, Abstr., 1892, 828).

Phenylmethylhydantoic acid, prepared by the action of mercuric oxide on the corresponding potassium thiohydantoate, has m. p. 170° (decomp.), and on treatment with acids is converted into 3-phenyl-5-methylhydantoin.

The following hydantoins were prepared by the action of bromine water on the corresponding thiohydantoins, sulphuric acid being formed to the extent of about 66% of the theoretical amount. The thiohydantoins were formed from α -aminoisobutyronitrile by Marckwald, Neumark, and Stelzner's method (*loc. cit.*). The data in brackets after the m. p.'s are those given by Marckwald, Neumark, and Stelzner.

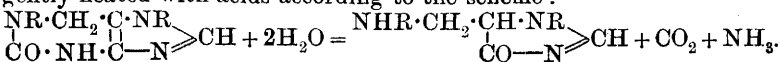
3-Phenyl-5:5-dimethylthiohydantoin crystallises in prisms, m. p. 174° (67°); the methyl ether, $C_{11}H_{11}ON_2 \cdot SMe$, m. p. 96° (viscid liquid), forms a platinichloride, $(C_{12}H_{14}ON_2S)_2H_2PtCl_6$, decomp. about 240° (132°), and a picrate, $C_{12}H_{14}ON_2S \cdot C_6H_3O_7N_3$, m. p. 194° (174°). 3-Phenyl-5:5-dimethylhydantoin, $C_{11}H_{12}O_2N_2$, crystallises in broad prisms, m. p. 171° , and is obtained also from α -aminoisobutyronitrile and phenylcarbimide.

3:5:5-Trimethylthiohydantoin, $C_6H_{10}ON_2S$, crystallises in microscopic prisms, m. p. 145° (53°), and appears to form a sparingly soluble compound with mercuric oxide, blackening not taking place. 3:5:5-Trimethylhydantoin, $C_6H_{10}O_2N_2$, crystallises in long prisms, m. p. 149° .

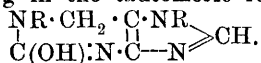
3-p-Tolyl-5:5-dimethylthiohydantoin, $C_{12}H_{14}ON_2S$, forms needles, m. p. 223° (85°). 5-p-Tolyl-5:5-dimethylhydantoin, $C_{12}H_{14}O_2N_2$, m. p. 175° . G. Y.

Thiohydantoins and Bases derived from These. JAMES R. BAILEY and C. P. RANDOLPH (*Ber.*, 1908, 41, 2505—2508).—The authors draw attention to, and discuss some possible explanations of, the differences in the properties of the thiohydantoins described by Marckwald, Neumark, and Stelzner (Abstr., 1892, 149), and of those prepared by the same methods by themselves (preceding abstract). The constitution of the thiohydantoins now obtained is confirmed by the conversion of 3-phenyl-5:5-dimethyl-2-thiohydantoin into 3-phenyl-5:5-dimethylhydantoin, which is formed also by condensation of α -aminoisobutyronitrile with phenylcarbimide, and by the action of sulphuric acid on 1-azo-3-phenyl-5:5-dimethylhydantoin, $N_2 \left[N \begin{smallmatrix} \text{CMe}_2 \cdot \text{CO} \\ \text{CO} - \text{NPh} \end{smallmatrix} \right]_2$. G. Y.

Hydrolysis of Xanthines and Deoxyxanthines. JULIUS TAFEL and RUDOLF MAYER (*Ber.*, 1908, 41, 2546—2556. Compare Abstr., 1907, i, 984).—It has been observed that, whilst some deoxyxanthines decompose readily with evolution of carbon dioxide when heated with dilute acids, others exhibit much greater stability. A systematic study has now shown that xanthine itself and all methylated xanthines which are not methylated in position 3 are readily hydrolysed when gently heated with acids according to the scheme:



Thus, under the same conditions, deoxyxanthine, deoxyheteroxanthine, and deoxyparaxanthine form 5-aminomethyl-4-iminazolones and evolve carbon dioxide, with similar velocities. On the other hand, 3-methylxanthine, theobromine, theophylline, and caffeine are much more stable towards acids, and when hydrolysed undergo more complicated reactions, which do not yield definite products. It is suggested that the ready and simple hydrolysis depends on the possibility of the deoxyxanthine reacting in the tautomeric form



Tables are given showing the results of determinations of the rate of hydrolysis of deoxyxanthine, deoxyheteroxanthine, and deoxyparaxanthine, as measured by the carbon dioxide evolved and by the ammonia formed. The 5-aminomethyl-4-iminazolones, formed by the acid hydrolysis of the deoxyxanthines, are strongly basic, amorphous substances, readily soluble in water, and are unstable, but form stable, crystalline salts.

5-Aminomethyl-1-methyl-4-iminazolone, from deoxyheteroxanthine, is isolated as the *hydrochloride*, $\text{C}_5\text{H}_9\text{ON}_3 \cdot \text{HCl}$, which crystallises in needles, decolorises bromine water, and gives an odour of *isonitrile* when heated with chloroform and alcoholic potassium hydroxide. The *platinichloride*, $(\text{C}_5\text{H}_8\text{ON}_3)_2\text{H}_2\text{PtCl}_6$, yellowish-red needles; the *picrate*, $\text{C}_{11}\text{H}_{12}\text{O}_8\text{N}_6$, yellow needles. *5-Aminomethyl-4-iminazolone hydrochloride*, $\text{C}_4\text{H}_7\text{ON}_3 \cdot \text{HCl}$, from deoxyxanthine, and *5-methylaminomethyl-1-methyl-4-iminazolone hydrochloride*, $\text{C}_6\text{H}_{11}\text{ON}_3 \cdot \text{HCl}$, from deoxyparaxanthine, were analysed.

The hydrolysis of the deoxyxanthines by baryta also has been studied and compared with that of the xanthines. From Fischer's results (Abstr., 1899, i, 262), it was to be expected that the rate of hydrolysis would be related directly to the acidity of the xanthine (Wood, Trans., 1906, 89, 1839). The results now obtained with xanthine, 3-methylxanthine, heteroxanthine, theophylline, paraxanthine, theobromine, and caffeine, and with the corresponding deoxy-compounds, show that this is not the case with either class of substance. Moreover, the rule that the ease of hydrolysis increases with the number of methyl groups, to which the behaviour of the xanthines approximates, does not hold good for the deoxyxanthines.

G. Y.

Brominations by means of Diazobenzene Perbromides. CARL BÜLOW and HERMANN SCHMACHTENBERG (*Ber.*, 1908, 41, 2607—2614). —When diazobenzene perbromide is dissolved in well-cooled acetone or acetophenone and the temperature allowed to rise, a vigorous reaction begins at 14.9°, hydrogen bromide is evolved, crystals of diazobenzene bromide separate, and a monobromo-derivative of the ketone is formed. When the perbromide is kept for some four to five days, decomposition occurs, phenol and tribromophenol being formed according to the equation: $3\text{PhN}_2\text{Br}_3 + 3\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_2\text{Br}_3\text{OH} + 2\text{PhOH} + 6\text{HBr} + 3\text{N}_2$. Unsaturated compounds can also be converted into dibromides by the action of an acetic acid solution of the per-

bromide. Cinnamic acid, ethyl cinnamate, and phenylpropionic acid have been brominated in this manner.

Acetyl-*p*-aminodiazobenzene perbromide (Silberrad and Smart, *Trans.*, 1906, 89, 170) is much more stable than diazobenzene perbromide, and gives up bromine only when kept for several weeks in a moist atmosphere. The corresponding *acetyl-p-aminodiazobenzene bromide*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Br}$, is also stable, m. p. 116° . It may be kept in a desiccator over calcium chloride; it is readily soluble in water, and is very slowly decomposed by water at the ordinary temperature. The perbromide of the acetyl derivative also acts as a brominating agent. J. J. S.

Hydrolysis of Vignin. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 22, 362—372).—Vignin is the name given to the principal protein of the seeds of the cow-pea (*Vigna sinensis*); it is a globulin freely soluble in a 5% solution of sodium chloride, and nearly insoluble in a 1% solution of the same salt. The yield of cleavage products brought about by acid hydrolysis was: glycine, 0; alanine, 0.97; valine, 0.34; leucine, 7.82; proline, 5.25; phenylalanine, 5.27; aspartic acid, 3.97; glutamic acid, 16.89; serine, 0; oxypoline, 0; tyrosine, 2.26; cystine, not determined; arginine, 7.2; histidine, 3.08; lysine, 4.28; ammonia, 2.32; tryptophan, present; total, 59.65%. W. D. H.

Constitution of Nucleo-proteins. The Constituents of Pepsin. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1908, 147, 212—214).—Crude pepsin extracted from the gastric mucous membrane of the pig by 4 parts of 0.2% hydrochloric acid at 50° yielded on hydrolysis by concentrated acids: tyrosine, 1.7%; alanine, 3.2%; valine, 7.5%; leucine, 11.4%; phenylalanine, 2.2%; lysine, 6.5%; arginine, 2.0%; adenine, 0.5%; xanthine, less than 0.01%; guanine, 0.2%; glucosamine, 1.4%; ψ -histidine, 0.4%, and ψ -lysines, 0.5%. The last-named substances are new; ψ -histidine, $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$, is a diamino-acid, precipitable by silver nitrate, which was analysed as such and as the benzoyl derivative; the ψ -lysines are two substances yielding picrates which remain dissolved in the mother liquor of lysine picrate. One of the new picrates melts at 216° , and belongs to a substance, $\text{C}_{11}\text{H}_{24}\text{O}_5\text{N}_3$, which appears to be a dipeptide derived from lysine and glutamic acid. G. B.

Identity of Nucleic Acids of Thymus, Spleen, and Pancreas. WALTER JONES (*J. Biol. Chem.*, 1908, 5, 1—26).—It is pointed out that many of the differences which have been described in various nucleic acids are due to the difficulties in estimating their cleavage products, to different methods employed, and to admixture with guanylic acids. The three nucleic acids investigated in this research appear to be identical, the special points worked out being specific rotation under varying conditions, and the degree of viscosity of the sodium salts. The so-called gelatinous sodium salt and the non-gelatinous salt are readily convertible one into the other, and this

offers a simple explanation of the physiological localisation and migration of nucleic acid.

W. D. H.

Adsorption of Ferments. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1908, 12, 26—27. Compare this vol., i, 587).—By using more dilute solutions of pepsin, it is found that it is adsorbed by kaolin in acid or alkaline media. It is uncertain how much of this may not be due to mechanical adsorption.

W. D. H.

Enzyme Action. XII. The Enzymes of Emulsin. HENRY E. ARMSTRONG, E. FRANKLAND ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1908, 80, B, 321—331).—The enzyme solutions were prepared for the purposes of the experiments directly from almonds. The extract at 15° exerted but little action on lactose, whereas β -methylglucoside underwent hydrolysis to a considerable extent; at 36° both substances were hydrolysed rapidly. On heating the extract at 45° for three hours, it lost its power of hydrolysing milk-sugar; it retained its activity as a hydrolyst of β -methylglucoside, amygdalin, and salicin, not only after twenty hours' heating at 45°, but also when heated for several hours at 55°. The enzyme was destroyed at about 59°. Other experiments were carried out with the object of effecting a separation of different enzymes by macerating almonds at different temperatures; by macerating with water at 0°, for example, and then macerating the extracted paste with a further quantity of water at 45°, two preparations of emulsins were obtained; both hydrolysed lactose at 38°; only that made at the lower temperature, however, produced any perceptible hydrolysis at 15°, indicating that the gluco-lactase had been preferentially extracted at 15°. The rate of hydrolysis of milk-sugar by extracts of almonds was investigated both without addition of, and in the presence of, added dextrose and galactose. The former alone caused considerable inhibition. The evidence obtained indicates the existence of a lactase in almonds, distinct from emulsin proper (β -glucase). Investigations were also made on the rate of hydrolysis of amygdalin, both the hydrocyanic acid and dextrose being estimated during the course of hydrolysis by special methods, which are described. The amount of Fischer's glucoside separated from partly hydrolysed material was always small; apparently there is no great difference in the rate at which this glucoside and amygdalin are hydrolysed by the β -glucase.

S. B. S.

Action of Acids on the Coagulation of Milk by Vegetable Rennets. C. GERBER (*Compt. rend.*, 1908, 146, 1111—1114).—It is shown that with vegetable ferments which coagulate boiled milk more readily than fresh milk, the addition of small quantities of citric, succinic, butyric, phosphoric, or hydrochloric acids retards the action of the rennet, whilst larger quantities accelerate it. In the case of rennets which curdle fresh milk more quickly than boiled milk, all the above acids, with the exception of citric acid, have an accelerating action; citric acid has a retarding effect, except when present in small quantity (compare Abstr., 1907, i, 1100).

W. P. S.

Influence of Certain Iron Compounds and of Peroxydases on the Catalysis of Hydriodic Acid by Hydrogen Peroxide. JULES WOLFF and E. DE STOEKLIN (*Compt. rend.*, 1908, 146, 1415—1417. Compare this vol., i, 490; ii, 573).—Colloidal ferrous ferrocyanide behaves as a peroxydase in most cases, but does not activate the decomposition of hydriodic acid by hydrogen peroxide. The latter activation is, however, brought about by ferric thiocyanate and by most peroxydases, but in the case of the ferments it appears to be due to the admixture of a specific enzyme, since particularly pure and potent peroxydases have been prepared which had but a feeble effect on the reaction between hydriodic acid and hydrogen peroxide.

G. B.

A Graphic Method for Registering Certain Fermentation Processes. CARLO FOÀ (*Biochem. Zeitsch.*, 1908, 11, 382—399).—An apparatus is described for graphically registering oxidative processes taking place in the presence of oxydases. The substances under investigation are placed in one vessel, which is connected with a second vessel containing water, with a layer of oil on the surface to prevent oxidation. The two vessels are immersed in a constant-temperature bath, and can be filled with either air or oxygen. The second flask is connected with a Mosso plethysmograph. The apparatus is so arranged that, as the oxygen is used up in the process, water flows back from the plethysmograph into the second vessel; the amount which flows back can be automatically registered by means of a feather pointer on a blackened surface. A special thermo-regulator was constructed for maintaining constant temperatures, as the Ostwald thermostat was not sufficiently sensitive. The carbon dioxide evolved during the oxidative processes was also investigated.

S. B. S.

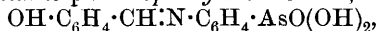
Purification of Peroxydase. ALEXIS BACH and JACOB TSCHERNIACK (*Ber.*, 1908, 41, 2345—2349).—Peroxydase, prepared by the Bach-Chodat method (*Abstr.*, 1903, i, 377), always contains large amounts of carbohydrates and gum-like substances, and activates comparatively small amounts of hydrogen peroxide. Attempts to purify the peroxydase by alternate solution in water and precipitation by means of alcohol have been unsuccessful (this vol., i, 238). A more active peroxydase has now been obtained by treating the expressed juice of turnips with basic lead acetate, removing the excess of lead by means of sodium carbonate, dialysing the solution through a parchment membrane, and finally precipitating the peroxydase by means of alcohol. The peroxydase thus obtained forms a greyish-white powder, contains 7.87% of water, 81.66% of organic matter, 1.47% of ash, and 3.44% of nitrogen calculated for the ash-free substance, and has the activation coefficient, 22.7. As Stocklin's purified peroxydase, containing 11.41% water, 65.88% organic matter, 22.71% ash, and 3.43% nitrogen, had the activation coefficient 2, the activity of the peroxydase is evidently not related to its percentage of nitrogen or of ash. The new peroxydase gives the biuret and xanthoprotein reactions, but not Millon's reaction, and when heated evolves pyrrole and a strongly alkaline base. It renders hydrogen peroxide active towards the oxida-

tion of phenols and aromatic bases, as also towards that of hydrogen iodide. These observations are in agreement with Bach's view (Abstr., 1907, i, 268, 810) that peroxydase is a single enzyme. Whilst when heated in the water-bath the purified peroxydase is destroyed completely only in eighteen minutes, if diluted with 20 vols. of water, it is destroyed under the same conditions in three minutes. G. Y.

Occurrence of Formaldehyde in Cell-free Fermentation. ALEXANDER LEBEDEF (Biochem. Zeitsch., 1908, 10, 454—457).—In cases of fermentation by yeast juice in Walton's shaking apparatus, after the fermentation was over, and shaking was continued day and night, a reverse action occurred, and some of the carbon dioxide was absorbed. No proof, however, could be obtained that sugar was formed anew, but formaldehyde was found. W. D. H.

Preparation of Derivatives of *p*-Aminophenylarsinic Acid. KURATORIUM DER GEORG AND FRANJISKA SPEYER'SCHEN STUDIENSTIFTUNG (D.R.-P. 193542).—*p*-Aminophenylarsinic acid condenses readily with aldehydes to furnish azomethine derivatives.

p-Hydroxybenzylidene-*p*-aminophenylarsinic acid,



obtained by melting its components together at 140—150° and crystallising the product from alcohol, is a sparingly soluble, yellow powder, which is hydrolysed by boiling water, the components again condensing as the aqueous solution is cooled. Similar products are described from *p*-dimethylaminobenzaldehyde and resorcyaldehyde. G. T. M.

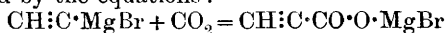
Secondary Aromatic Arsinic Acids. LOUIS BENDA (Ber., 1908, 41, 2367—2373).—Michaelis prepared dinitrodiphenylarsinic acid (Abstr., 1902, i, 515) from diphenylchloroarsine, but was unable to obtain the corresponding diamino-acid by reduction. Such diamino-diarylsaric acids, $\text{As}(\text{R} \cdot \text{NH}_2)_2 \cdot \text{O} \cdot \text{OH}$, have now been prepared by heating aromatic amines with arsenic acid at 170—180° (compare Bechamp, Compt. rend., 1863, 56, 1172). These diamino-acids resemble aminophenylarsinic acid in their general behaviour, having both acid and basic properties, but do not form precipitates with magnesia mixture, are soluble in alcoholic sodium hydroxide, and, when diazotised and coupled with β -naphthylamine, form dyes which are insoluble in alkalis. Unmordanted vegetable fibres have only a small affinity for the dye formed by coupling diazotised di-*p*-aminodiphenylarsinic acid with 6-amino-1-naphthol-3-sulphonic acid. When diazotised and boiled, the diamino-diarylsaric acids yield the corresponding dihydroxy-acids, $\text{As}(\text{R} \cdot \text{OH})_2 \cdot \text{O} \cdot \text{OH}$.

Di-p-aminodiphenylarsinic acid, $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_2\text{As}$, formed together with *p*-aminophenylarsinic acid by heating arsenic acid with aniline at 180—200°, crystallises in needles, m. p. 232°, and forms a white precipitate with silver nitrate in neutral solution. The *diacetyl* derivative, $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_2\text{As}$, forms amber-coloured prisms, m. p. 263°. *Di-p-hydroxydiphenylarsinic acid*, $\text{C}_{12}\text{H}_{11}\text{O}_4\text{As}$, crystallises in plates, m. p. 239°.

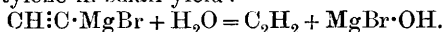
Di-p-aminodi-o-tolylarsinic acid, $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_2\text{As}$, crystallises in

prisms, m. p. 243° . The *diacetyl* derivative, $C_{18}H_{21}O_4N_2As$, forms glistening prisms, m. p. 237° , decomp. 255° . *Di-p-hydroxy-o-tolyl-arsinic acid*, $C_{14}H_{15}O_4As$, has m. p. 247° . G. Y.

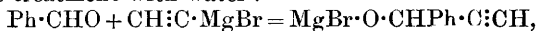
Magnesio-acetylene Bromide. II. BERNARDO ODDO (*Gazzetta*, 1908, **38**, i, 625—635. Compare Abstr., 1904, i, 862).—When magnesio-acetylene bromide is treated successively with carbon dioxide and dilute sulphuric acid, a small amount of propiolic acid is formed, the reactions being expressed by the equations:



and $2CH:C \cdot CO \cdot O \cdot MgBr + H_2O + H_2SO_4 = MgSO_4 + MgBr_2 + H_2O + 2CH:C \cdot CO_2H$. The interaction of magnesio-acetylene bromide and water gives acetylene in small yield:



The hydrocarbon, m. p. 213 — 214° , which is obtained by the action of benzaldehyde on magnesio-acetylene bromide, to which the formula $C_{18}H_{14}$ was ascribed (*loc. cit.*), is shown to be *s*-tetraphenylethane, m. p. 209° . The formation of this compound and of the others mentioned (*loc. cit.*) is due to the interaction of benzaldehyde and magnesium phenyl bromide which has remained unchanged during the action of the acetylene. Phenylacetylenecarbinol is formed in small quantity by the action of benzaldehyde on magnesio-acetylene bromide and subsequent treatment with water:



which with H_2O gives $OH \cdot CHPh \cdot C:CH$.

T. H. P.

Organic Chemistry.

Formal Types of Structural Isomerides. CONRAD LAAR (*J. pr. Chem.*, 1908, [ii], 78, 165—200).—An attempt to classify the different types of structural isomerides.

The main groupings are :

(I). Didesmic forms or isomerides with two changes of linking, for instance, $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_3$ and $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$.

(II). Tridesmic forms or isomerides with three changes of linking, such as *o*-nitrophenol and *o*-quinoneoxime.

(III). Tetradesmic forms or isomerides with four changes of linking, for instance, *p*-nitrosophenol and *p*-quinoneoxime.

Each of these main groups is divided into sub-groups : (a) Isomerism without change of valency ; (b) isomerism with change of valency, and each sub-group is split up into a number of smaller divisions.

J. J. S.

Some Physical Properties of Butane and *iso*Butane. PAUL LEBEAU (*Bull. Acad. roy. Belg.*, 1908, 300—304).—The author has re-determined the boiling points and some other physical constants of butane and *isobutane* on specimens of the pure hydrocarbons obtained by the action of metalammonium compounds on the corresponding alkyl halide (Abstr., 1905, i, 401).

n-Butane, prepared by the action of sodammonium on *n*- or *sec.*-butyl iodide, solidifies in liquid air, has b. p. $0.5^\circ/755$ mm., and a critical temperature $151\text{--}152^\circ$; *isobutane*, obtained by the action of sodammonium or calcium-ammonium on *isobutyl* chloride, is also solid in liquid air, has b. p. $-10.5^\circ/757$ mm. [Noyes, this vol., i, 305, finds b. p. $-11.5^\circ/760$ mm.], and a critical temperature $134\text{--}135^\circ$. The solubilities of the two hydrocarbons in various solvents have also been determined, and the results are comprised in the following table :

	Pressure in millimetres of mercury.	Temperature.	Volume of gas dissolved in one volume of solvent.	
			Butane.	<i>iso</i> Butane.
Water	772	17°	0.15	0.13
Alcohol	775	17	18.83	13.2
Ether	773	18	29.8	27.9
Chloroform .. .	768	17	32.5	39.5

M. A. W.

Molecular Weight of Hexacontane. KARL STRUVE (*Annalen*, 1908, 362, 123—124).—Hexacontane was prepared by Hell and Hägele (Abstr., 1889, 575) by acting on myricyl iodide with potassium. These authors did not, however, determine the mol. wt. of the compound, and, since it might possibly be an unsaturated hydrocarbon,

$C_{80}H_{60}$, the mol. wt. has been determined by Landsberger's boiling-point method. The values obtained agree with the formula $C_{60}H_{122}$.
W. H. G.

Reciprocal Transformation of Isomerides under the Influence of Chemical Induction. SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 806—810).—It was discovered by Skraup (Abstr., 1891, 1338) that one exothermic reaction may induce another reaction, also exothermic, a phenomenon to which this author gave the name consonance. Thus, when hydrogen sulphide and sulphur dioxide react together in a medium containing maleic acid, the latter is transformed into fumaric acid.

The author gives further instances of this phenomenon. The transformation of cyclopropane into propylene is induced by the reaction $2NO + O_2 = N_2O_4$ at the ordinary temperature, but the interaction of hydrogen sulphide and sulphur dioxide has no such effect; so that not all exothermic reactions are able to induce isomeric change, the conditions necessary in any particular case being unknown.

T. H. P.

Action of Sulphur on Acetylene. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1908, 305).—Two years ago the author observed that thiophen is not formed by the action of acetylene on fused sulphur in the absence of air, and he is therefore able to confirm the results obtained by Capelle (this vol., i, 201).

M. A. W.

Preparation of Acetylene Di- and Tetra-chlorides from Acetylene and Antimony Pentachloride. HARRY K. TOMPKINS (D.R.P. 196324).—Acetylene di- and tetra-chlorides (*s*-dichloroethylene and *s*-tetrachloroethane) may be prepared by passing the required amounts of acetylene into antimony pentachloride, or a mixture of this chloride with antimony trichloride, and then distilling the product, which contains probably an additive compound of acetylene and the pentachloride.

G. T. M.

Decomposition of Chloroform by Alcoholic Alkali Hydroxides. GUSTAV MOSSLER (*Monatsh.*, 1908, 29, 573—581).—The decomposition of chloroform by alcoholic potassium hydroxide yields carbon monoxide, formic acid, and ethylene, the latter hitherto undetected. Contrary to the general belief, carbon monoxide is the main product; only in favourable circumstances is as much as half of the chloroform converted into formic acid. In the first two series of experiments, 20%, 5%, and 1% solutions of potassium hydroxide in absolute or in 50% alcohol are added to known amounts of chloroform. In all cases a constant volume ratio, 75:25, exists between the amounts of carbon monoxide and ethylene. The same ratio is attained in the third series of experiments, in which an alcohol-chloroform mixture is dropped on to powdered potassium hydroxide, provided that the molecular proportion of alcohol to chloroform exceeds 5:1.

The decomposition of chloral by alcoholic potassium hydroxide also

leads to the formation of carbon monoxide and ethylene in the ratio 3 : 1 by volume.

The formation of these two gases is explained by the decomposition of the chloroform into hydrogen chloride and carbon dichloride, CCl_2 , the transitory existence of which is indicated by the formation of carbonyl chloride in an experiment in which air and chloroform vapour are passed over a layer of potassium hydroxide. The production of formic acid is due to direct hydrolysis of the chloroform.

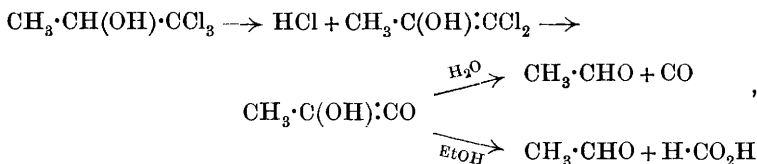
The decomposition of bromoform by alcoholic potassium hydroxide, in which, apart from potassium bromide, only carbon monoxide and ethylene in the ratio 3 : 1 are produced, is similarly explained by the total conversion of the bromoform into hydrogen bromide and carbon dibromide. The constant ratio of carbon monoxide to ethylene is explained by the action of the carbon dichloride on the alcohol, whereby the esters $\text{CCl}(\text{OEt})$ and $\text{C}(\text{OEt})_2$ are formed in the proportion of 1 : 2; the latter is directly hydrolysed, and the former decomposes into carbon monoxide and ethyl chloride, which is then converted by the alkali into ethylene. C. S.

Decomposition of Trichloroisopropyl Alcohol by Aqueous or Alcoholic Alkali Hydroxides. GUSTAV MOSSLER (*Monatsh.*, 1908, 29, 583—590. Compare preceding abstract).—The organic products of the decomposition of *aaa*-trichloroisopropyl alcohol by 5—20% aqueous potassium hydroxide are mainly carbon monoxide and acetaldehyde, together with small amounts of formic and lactic acids.

When 5% alcoholic potassium hydroxide (6 mols.) reacts with the alcohol (1 mol.), the chief products are acetaldehyde and formic acid, lactic acid being formed only in small amount; no gas is evolved unless the mixture is warmed, when a relatively small amount of carbon monoxide is liberated.

In no case could the intermediate formation of chloroform be detected.

The author's explanation is indicated in the scheme :



with the intermediate formation of ethyl formate.

C. S.

Composition of the Vapour from Mixtures of Ethyl Alcohol and Water. H. MASING (*Chem. Zeit.*, 1908, 32, 745).—With the object of verifying Gröhning's tables, a careful study of the composition of the alcohol vapour has been made, and it is found that the original values given by him are all too high; those given by Sorel are too low. The influence of pressure and the presence of

impurities such as acetaldehyde, ethyl acetate, and amyl alcohol on the volatility has also been observed. J. V. E.

Preparation of Difluoroethyl Alcohol. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1908, 272—282).—In earlier papers (Abstr., 1903, i, 222, 725) the author has described the preparation of difluoroethyl alcohol by the action of metallic oxides and water on difluoroethyl bromide, and has shown that the best results are obtained with mercuric or lead oxide at 160°, but in no case is a theoretical yield obtained.

A repetition of the experiments, using large quantities (1400 grams) of difluoroethyl bromide, shows that when mercuric oxide is the hydrolytic agent, the yield of the alcohol is 93% of that required by theory, the 7% loss being due to a secondary reaction, yielding difluoroacetic acid (Abstr., 1903, i, 727) and mercurous bromide. When lead oxide replaces mercuric oxide, the yield of the alcohol amounts to 92% of that required by theory, the loss being again due to secondary reactions resulting in the formation of glycollic and oxalic acids, together with metallic lead. In this case, the lead oxide first hydrolyses the difluoroethyl alcohol to glycollaldehyde, which in its turn reduces the lead oxide, forming glycollic acid and metallic lead, and part of the glycollic acid undergoes a further oxidation, yielding oxalic acid.

M. A. W.

Methylation in the Ethylene Derivatives from the Point of View of Volatility. LOUIS HENRY (*Compt. rend.*, 1908, 147, 405—408).—The normal effect of the replacement of hydrogen combined with carbon in organic compounds by the methyl group is to raise the boiling point. This is the case even with the monatomic aliphatic alcohols. Substitution of hydrogen by methyl in the glycols, however, has the reverse effect, thus: $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ has b. p. 197—198°; $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, b. p. 188°; $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$, b. p. 184°; $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, b. p. 178°; $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{OH}$, b. p. 178°, and $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OH}$, b. p. 174°, although in the case of the corresponding hydrocarbons the b. p. rises regularly, thus: $\text{CH}_2\cdot\text{CH}_2$, b. p. -102°; $\text{CHMe}\cdot\text{CH}_2$, b. p. -50°; $\text{CMe}_2\cdot\text{CH}_2$, b. p. -6°; $\text{CHMe}\cdot\text{CHMe}$, b. p. 1—2°; $\text{CMe}_2\cdot\text{CHMe}$, b. p. 36°; $\text{CMe}_2\cdot\text{CMe}_2$, b. p. 72°. The explanation of this difference lies in the fact that the hydrocarbons are unimolecular, whilst their hydroxyl derivatives are associated in the liquid state.

The decreasing rise in boiling point as the hydrogen of methyl alcohol is replaced by methyl shows that the degree of association is thereby lowered, the elevation of the boiling point by increase in molecular weight being more and more counteracted by the decrease in molecular complexity. The progressive fall in the boiling points of the glycols indicates that here the latter effect is greater than the former.

The dichlorohydrins and the ethylene oxides derived from the above hydrocarbons correspond with the latter in volatility; thus the compounds resulting when the double linking in the above five hydrocarbons is

saturated by chlorine (2 atoms) or by oxygen (1 atom) have their boiling points in the same order as those of the parent compounds. It is deduced that the oxides, as well as the chlorohydrins, are unimolecular or very slightly associated.

E. H.

Use of Magnesium in place of Zinc in the Synthesis of Alcohols of the Allyl Series. W. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 782—787).—Several authors have attempted to replace by magnesium the zinc employed in the synthesis of alcohols of the allyl series from an allyl haloid and a carbonyl compound, but with unsatisfactory results. The author finds, however, that this synthesis takes place readily if the reacting compounds in molecular proportions are allowed to act on magnesium (1 atom) in anhydrous ether. In this way, he has obtained good yields of (1) dimethylallylcarbinol from a mixture of allyl chloride and bromide with acetone; (2) phenylmethylallylcarbinol from allyl iodide or bromide and acetophenone; (3) diphenylallylcarbinol from allyl bromide and benzophenone; (4) methylpropylallylcarbinol from allyl bromide and methyl propyl ketone.

Also, ω -bromostyrene reacts readily in ethereal solution with magnesium, yielding styrene and diphenylvinylethylene. If the magnesium compound formed is treated with carbon dioxide, cinnamic acid, as well as diphenylvinylethylene, is formed. The reaction between magnesium and ω -bromostyrene hence proceeds in two directions: (1) the removal of the halogen from 2 molecules of the bromostyrene by the magnesium; (2) normally, giving an organo-magnesium compound, which, on decomposition with water, yields styrene and with carbon dioxide gives cinnamic acid.

T. H. P.

Contact Oxidation of Ethyl Ether. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 799—800).—When oxidised by the contact process, ethyl ether yields acetaldehyde and a small proportion of formaldehyde: $\text{Et}_2\text{O} + \text{O}_2 = 2\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$; $\text{Et}_2\text{O} = 2\text{C}_2\text{H}_4 + \text{H}_2\text{O}$; $\text{C}_2\text{H}_4 + \text{O}_2 = 2\text{CH}_2\text{O}$. The gaseous products consist of carbon dioxide (7.55%), oxygen (2.11%), carbon monoxide (5.33%), hydrogen (1.86%), nitrogen (78.25%), and ethylene (2.9%).

T. H. P.

Pressure and Composition of the Vapours of Aqueous Solutions of the Ether of Ethylene Glycol. A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 752—760).—The author makes use of the following dynamical method, which allows of the simultaneous and accurate determination of the pressure and composition of the vapour from a mixture of two volatile liquids.

In a small thermostat filled with water at the room temperature is a flask containing air and provided with a manometer. By means of a known weight of water, a known volume of air, V , at pressure p mm., and saturated with water vapour having the pressure h at t° , is driven out of the flask, through a calcium chloride tube, and then through a nine-bulbed Will and Bredig apparatus placed in a thermostat and containing the solution to be investigated; in all the author's experiments, this second thermostat was maintained at $50 \pm 0.05^\circ$. The

vapour-laden air then passes through a spiral condenser immersed in solid carbon dioxide, and deposits its vapour quantitatively. The spiral is subsequently dipped into alcohol and into ether to remove traces of oil and water, and is then weighed, the increase in weight giving the amount of vapour in the volume V of air.

For determining the proportions of the ether of ethylene glycol and water in the condensed liquid, the author made use of the refractive index, which had been previously measured for a number of aqueous solutions of the ether.

Knowing the composition of the vapour, the number of milligram-mols. of each of the components in a weighed quantity of the condensed liquid can be calculated, and from the sum, a , of the numbers of milligram-mols. for the two components, the vapour pressure of the solution in mm. of mercury can be found by means of the equation: $H = B/[V(B + p - h)/22.4.a.760(1 + \alpha t) + 1]$, where B is the atmospheric pressure, t the temperature of the thermostat containing the flask filled with air, and H the sum of the partial pressures of the two components of the vapour.

A solution containing 56.5 mols. % of the ether of ethylene glycol has the maximum vapour pressure, and boils unchanged. The specific heat and D of this solution are considerably higher than the calculated values.

For the pure ether, the mean specific heat at 16—100° is 0.4365—0.4377, and the heat of evaporation at atmospheric pressure, 89.95—90.08 Cals. per gram. Trouton's constant is hence 21.2, which shows that in the liquid condition the ether is not associated, although the lowering of the partial pressure of water by the vapour is twice as small as it should be according to Raoult's law. T. H. P.

Studies in Steam Distillation. Formic and Acetic Acids.

H. DROOP RICHMOND (*Analyst*, 1908, 33, 305—312).—The results of experiments on the rate of distillation of aqueous solutions of formic and acetic acids are given, the apparatus employed being specially designed to prevent condensation in the head of the retort. The rate of distillation of the acids relatively to that of water is given, together with the results calculated from the formulæ given previously (this vol., i, 495). W. P. S.

Spectroscopic Reaction for Oleic Acid. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1908, 56, 446—452).—The characteristic reaction given by oleic acid (this vol., i, 263) is best shown when an acetic acid solution of chromic acid is used as the oxidising agent. To a mixture of 1 drop of oleic acid in 3—4 c.c. of glacial acetic acid and 1 drop of a 10% solution of chromic acid, also in glacial acetic acid, 10 drops of concentrated sulphuric acid are added. After a short time, a violet to cherry-red coloration develops, and ultimately becomes so deep that dilution with acetic acid is necessary before the characteristic absorption bands can be observed. Oleoglycerides give the same reaction, but the addition of chloroform is advisable.

The sensitiveness is 1 in 10,000 to 1 in 15,000.

Trichloroacetic acid produces the same coloration as the acetic

and sulphuric acids. These reactions for oleic acid and cholesterol are thus practically identical.

J. J. S.

Formation of γ -Lactones. ALEXIS A. SHUKOFF and PETER J. SCHESTAKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 830—839).—The authors have investigated the conditions of transformation of oleic acid into lactone, and also the extent to which other unsaturated ethylenic acids with the double linking not in the γ -position are able to undergo this transformation. It has been found that saturated alcohol-acids also yield lactones, the hydroxyl group wandering to the γ -position, giving a γ -hydroxy-acid and subsequently a γ -lactone. The best method of converting the acids into lactones is to heat them with anhydrous zinc chloride or concentrated sulphuric acid. When treated in this way, oleic, elaidic, *isoleic*, *th*-hydroxystearic, and *l*-hydroxystearic acids all yield γ -stearolactone, erucic acid yields γ -behenolactone, and $\kappa\lambda$ -undecylic acid, γ -undecolactone. Crotonic and α -hydroxybutyric acids, however, give no lactone. Indeed, under these conditions, lactones are only given by those ethylenic acids and saturated hydroxy-acids in which the double linking or hydroxyl group is at least four carbon atoms away from the carboxyl group.

It is probable that the oleic acid separated from fats is not a chemical individual, but consists of a mixture of isomerides having double linkings, not only in the *th*-position, but also in the $\beta\gamma$ - or $\gamma\delta$ -position. To see whether it is the latter alone which yields lactone, the *th*-acid was prepared from *l*-hydroxystearic acid, and was found to give about 10% of γ -stearolactone when treated with zinc chloride. γ -Stearolactone, obtained in 35% yield by the action of concentrated sulphuric acid on commercial oleic acid (compare Abstr., 1904, i, 646), has an iodine number 16—20 and a mean molecular weight, assuming it to be a monobasic acid, 375, which, after boiling with alcoholic potassium hydroxide, falls to 291. This indicates that the lactone contains a considerable proportion of a compound with the character of an anhydride or complex ether, analogous to those formed on heating hydroxystearic acid. After distillation, the iodine number and, consequently, the proportion of unsaturated compound increase considerably, indicating the presence of hydroxystearic acids, which are converted into unsaturated acids on distillation. If the pure stearolactone is treated with sulphuric acid, it is partly converted into soluble, acid products, which contain sulphur and are probably sulphonic-acids. Conversion of part of the stearolactone into these sulpho-compounds probably determines, to some extent, the small yield of the lactone.

γ -Behenolactone, $\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{CH} < \begin{array}{c} \text{O} - \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, crystallises from light petroleum in shining plates, m. p. 63.5° , and, on oxidation with chromic acid, yields γ -ketobehenic acid, $\text{C}_{22}\text{H}_{42}\text{O}_3$, forming colourless crystals, m. p. 103° .

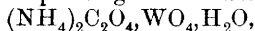
γ -Undecolactone, $\text{C}_{11}\text{H}_{20}\text{O}_2$, b. p. 286° , is converted into γ -hydroxyundecic acid, m. p. 34° , by acids or alkalis.

T. H. P.

Complex Ozo-salts of Tungsten. ARRIGO MAZZUCHELLI and GIUSEPPE INGHILLERI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 30—33. Compare Abstr., 1907, i, 748).—The tendency of tungsten to form ozo-

salts is not so marked as that exhibited by its higher analogue, uranium, or by molybdenum, and the ozo-salts are readily soluble and difficult to obtain free from the normal salts used in their preparation. On this account no lithium ozotungsten oxalate could be isolated, whilst the potassium and barium salts were only obtained in an impure condition.

Sodium ozotungsten oxalate, $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{WO}_4 \cdot 5\text{H}_2\text{O}$, obtained by the action of hydrogen peroxide on the compound $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{WO}_3$, forms white crystals. The corresponding *ammonium* salt,



forms white, sphaero-crystals; the *calcium* salt, $\text{CaC}_2\text{O}_4 \cdot \text{WO}_4 \cdot \text{H}_2\text{O}$, was also prepared.

T. H. P.

Esterification of Malonic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 243—252).—In earlier papers (Abstr., 1907, i, 823; this vol., i, 166), methods have been described for obtaining good yields of ethyl succinate and benzoate. A study has now been made of the best conditions for the esterification of malonic acid. The largest yield, 96.1%, was obtained by heating an alcoholic solution of malonic acid with sulphuric acid at 50° for eight hours, and treating the residue with a fresh quantity of alcohol for two hours.

E. G.

Purification of Esters. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], 26, 253—256).—A study has been made of the purification of ethyl succinate, malonate and benzoate, containing alcohol, water, unchanged organic acid, and small quantities of mineral acid. It has been found that these esters may be purified without much loss by heating them in suitable conditions with dry potassium carbonate under reduced pressure. A comparison of this method with that of extracting the ester with ether has shown that the loss by the former method is rather greater in the case of ethyl benzoate, but is smaller in the cases of ethyl succinate and malonate. The potassium carbonate method, however, is to be preferred even with ethyl benzoate, since it affords greater ease of manipulation and is less expensive. The smaller the quantity of free acid present, the more completely can the ester be recovered.

E. G.

Conversion of Ethyl Cyanoacetate into Ethyl Malonate. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 257—263).—The conditions under which ethyl cyanoacetate is converted into ethyl malonate have been carefully investigated. It was found that when a well-cooled mixture of 50 grams of ethyl cyanoacetate, 125 c.c. of absolute alcohol, and 4 grams of sulphuric acid was saturated with hydrogen chloride by passing in a stream of the dry gas for four hours, and the product heated for two hours at 100—110° with 200 c.c. of absolute alcohol, a yield of 96.3% of ethyl malonate was obtained.

E. G.

Influence of Catalytic Agents in Ester Formation. Esterification of Cyanoacetic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 264—266).—The effects

produced on the esterification of cyanoacetic acid by varying the proportions of the reagents, the catalysers, and the time of reaction have been studied. The results show that by the use of alcohol alone, a yield of 63% of the ester can be obtained, but that the yield is increased by the presence of a catalytic agent, and within certain limits by the amount of the catalyst employed. The esterification is rendered more complete by increasing the time of reaction. Alcoholic hydrogen chloride causes the formation of some ethyl malonate, but this change does not occur when sulphuric acid is employed. Nearly theoretical yields of ethyl cyanoacetate can be obtained by heating 50 grams of cyanoacetic acid with 2 grams of sulphuric acid and 200 c.c. of absolute alcohol for two hours at 100–110°. E. G.

Preparation of Malonic Acid or its Ester from Monochloroacetic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 267–274).—In earlier papers (preceding abstracts) an account has been given of the best conditions for the esterification of malonic acid and for the conversion of ethyl cyanoacetate into ethyl malonate. A further study has now been made with special reference to the preparation of ethyl malonate from chloroacetic acid.

It has been found that the reaction between potassium cyanide and sodium chloroacetate to form sodium cyanoacetate proceeds best in alkaline solution, and takes place vigorously at 110°, or slowly at 90–95°, without affecting the yield of ethyl malonate. The alkaline solution of sodium cyanoacetate should not be evaporated to dryness at a high temperature, or even be boiled for a long time, since these conditions favour the formation and subsequent decomposition of sodium malonate. After acidifying the solution of sodium cyanoacetate with sulphuric acid and removing the precipitated salt by filtration, the resulting solution of cyanoacetic acid is concentrated under reduced pressure at 70–80°. The precipitated salt is washed with alcohol, and the alcoholic solution is evaporated at about 60°. The residues, consisting of cyanoacetic acid and some of its ester and sodium salt, are converted into ethyl malonate by the method described previously (*loc. cit.*). By this means a yield of 92% of ethyl malonate can be obtained.

The ester can be converted into pure malonic acid by heating it with an equal quantity of water and a few drops of nitric acid at about 60° for some time after the mixture has become homogeneous, and evaporating the solution to the point of saturation. The malonic acid which separates on cooling is recrystallised from hot water. E. G.

Preparation of Cyanoacetic Acid and its Ester from Monochloroacetic Acid. ISAAC K. PHELPS and E. W. TILLOTSON, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 275–280).—Sodium chloroacetate and potassium cyanide react quantitatively in alkaline solution to form sodium cyanoacetate. A study has now been made of the formation of ethyl cyanoacetate from monochloroacetic acid, the method of esterification of cyanoacetic acid being that described previously (preceding abstract). The results show that ethyl cyanoacetate can be obtained in

good yield if precautions are taken to minimise the transformation into malonic acid. Pure cyanoacetic acid can be prepared by heating a mixture of two parts of water with one part of the ester and a few drops of nitric acid at about 60° for some time after the mixture has become homogeneous. The solution is then evaporated at $50-60^\circ$ to the point of saturation, and the cyanoacetic acid which separates on cooling is recrystallised from a mixture of ether and chloroform.

E. G.

Saponification of Fats by means of Hydroxylamine. EUGENIO MORELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 74—78).—In order to obtain derivatives of fats which crystallise well and have melting points higher than those of the acids from which they are derived, the author has studied the action of hydroxylamine on fats. The hydroxamic acids obtained are very stable, and fulfil the above conditions.

Stearohydroxamic acid, $C_{17}H_{35}\cdot C(OH)\cdot NOH$, prepared from tri-stearin and hydroxylamine, separates from alcohol in crystals, m. p. 104° , and in alcoholic solution gives a reddish-violet colour with ferric chloride.

Palmitohydroxamic acid, $C_{15}H_{31}\cdot C(OH)\cdot NOH$, which is deposited from alcohol in crystals, m. p. 99° , and *oleohydroxamic acid*, $C_{17}H_{33}\cdot C(OH)\cdot NOH$,

m. p. 61° , both give the red colour with ferric chloride in alcoholic solution. The latter is resolved into oleic acid and hydroxylamine sulphate when boiled with dilute sulphuric acid.

A mixture of stearohydroxamic and palmitohydroxamic acids has m. p. 95° ; the lowering of m. p. here observed can doubtless serve to establish the proportions of the two acids in a mixture of them.

T. H. P.

New Synthesis of Citric Acid. ENOS FERRARIO (*Gazzetta*, 1908, 38, ii, 99—100).—By the condensation of ethyl bromoacetate with diethyl oxalate in presence of magnesium according to the equation: $CO_2Et\cdot CO_2Et + 2CH_2Br\cdot CO_2Et + 2Mg =$

$Br\cdot Mg\cdot OEt + CO_2Et\cdot CH_2\cdot C(OMgBr)(CO_2Et)\cdot CH_2\cdot CO_2Et$, the author obtains a compound which, when treated with dilute sulphuric acid, yields an oil, b. p. $215^\circ/35$ mm., and appears to be triethyl citrate. The reaction is being studied further. T. H. P.

Structure of Glucinum Salts. SEBASTIAN M. TANATAR and E. K. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 787—790. Compare Abstr., 1907, i, 888; this vol., i, 166, 502).—The following salts of glucinum have been prepared:

With tricarballic acid, the salt, $Gl_3(C_6H_5O_6)_2$, obtained as a white powder insoluble in all the ordinary solvents.

With citric acid, the salt, $\left[\begin{array}{c} O-Gl-O-CO \\ | \\ Gl\cdot CO\cdot O\cdot CH_2 \end{array} \right]_2 C(OH)\cdot CH_2\cdot CO_2$, Gl , which is of a more basic type, $Gl_5O_2X_2$, than most of the glucinum salts, Gl_4OX_6 .

With salicylic acid, glucinum forms the salt, $(OH\cdot C_6H_4\cdot CO_2Gl\cdot O)_2Gl$;

with phthalic acid, the salt, $C_6H_4 \begin{smallmatrix} \diagup CO_2Gl \cdot CO_2 \cdot C_6H_4 \cdot CO_2Gl \cdot O \\ \diagdown CO_2Gl \cdot CO_2 \cdot C_6H_4 \cdot CO_2Gl \cdot O \end{smallmatrix} Gl$, and with lactic acid, the salt, $(OH \cdot CHMe \cdot CO_2Gl \cdot O)_2Gl$.

In addition to the benzoate already described (this vol., i, 166), glucinum yields a *benzoate* of the normal type, $Gl_4O(C_7H_5O_2)_6$, which is obtained on prolonged boiling of a solution of benzoic acid in a mixture of equal volumes of alcohol and benzene with glucinum carbonate; this salt has the molecular weight 710 (theor. 779) in freezing benzene.

The interaction of sodium benzoate and a glucinum salt in aqueous solution yields various salts, which are more or less basic according to the concentrations, temperatures, and acidities of the solutions, and are insoluble in organic solvents. T. H. P.

Isomerism of Ethyl Acetoacetate. R. H. McCREA (*Chem. News*, 1908, 98, 127).—The enolic form of ethyl acetoacetate may, like other unsaturated compounds, be represented as having a *trans*- (I) and a *cis*- (II) configuration:



The *cis*-configuration (II) must be unstable, as it corresponds with the hypothetical intermediate product in Bernthsen's representation of the Beckmann change:



and must therefore change at once into the ketonic form of the ester. The action of phosphorus pentachloride leads, now, to the formation of β -chlorocrotonic acid, $\begin{array}{c} Me \cdot \overset{\overset{O}{\parallel}}{C} \cdot Cl \\ | \\ H \cdot \overset{\overset{O}{\parallel}}{C} \cdot CO_2H \end{array}$ or $\begin{array}{c} Me \cdot \overset{\overset{O}{\parallel}}{C} \cdot Cl \\ | \\ CO_2H \cdot \overset{\overset{O}{\parallel}}{C} \cdot H \end{array}$. This acid should be stable, as it cannot undergo the second stage of the Beckmann change; in agreement with this view is its conversion into *isocrotonic* acid, which is considered to be the stereoisomeride of crotonic acid. It cannot be decided which of the modifications, the stable or the unstable, has the *cis*-configuration, as either configuration might be the unstable form. It is suggested that *isocrotonic* acid has the form

$\begin{array}{c} Me \cdot \overset{\overset{O}{\parallel}}{C} \cdot OH \\ | \\ CO_2H \cdot \overset{\overset{O}{\parallel}}{C} \cdot H \end{array}$, as it is formed from the chloro-acid, which also forms

tetrolic acid, $\begin{array}{c} Me \cdot \overset{\overset{O}{\parallel}}{C} \\ | \\ CO_2H \cdot \overset{\overset{O}{\parallel}}{C} \end{array} + \begin{array}{c} Cl \\ | \\ H \end{array}$, and may therefore be considered to have the hydrogen and chlorine atoms spatially near each other,

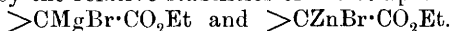
$\begin{array}{c} Me \cdot \overset{\overset{O}{\parallel}}{C} \cdot Cl \\ | \\ CO_2H \cdot \overset{\overset{O}{\parallel}}{C} \cdot H \end{array}$ G. Y.

Action of Magnesium on Esters of Brominated Fatty Acids. **New Synthesis of Ketonic Esters.** JOSEF ZELTNER (*J. pr. Chem.*, 1908, [ii], 78, 97—123. Compare this vol., i, 243).—In the ordinary Reformatzky synthesis of hydroxy-acids, the zinc cannot be replaced by magnesium. When magnesium is used, at least three reactions take place: (1) Reduction of the brominated ester to the corresponding

fatty ester; (2) formation of a β -ketonic ester; (3) production of a high boiling, crystalline compound. The yield of ketonic ester is best when an *isobromo*-ester is used, for example:

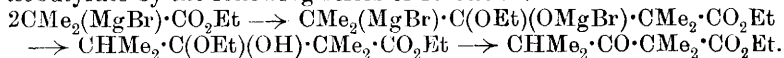
Ethyl bromopropionate	gives 35.3 per cent.	ethyl propionylpropionate.
Ethyl bromobutyrate	„ 40.5 „	ethyl butyrylbutyrate.
Ethyl bromoisobutyrate	„ 67.3 „	ethyl <i>isobutyryl</i> dimethylacetoacetate.
Ethyl bromoisovalerate	„ 60.3 „	ethyl valerylvalerate.

The difference in the reactions with zinc and magnesium is accounted for by the relative stabilities of the compounds



By the action of *p*-tolualdehyde on the product of the interaction of magnesium and ethyl α -bromoisobutyrate, a small amount of a crystalline substance, $\text{C}_{16}\text{H}_{20}\text{O}_3$, m.p. 138—139°, is obtained.

Ethyl *isobutyryl*dimethylacetate, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, has b. p. 202.5—203°/745.5 mm., and, when boiled with aqueous potassium hydroxide, yields diisopropyl ketone. It is formed from ethyl α -bromoisobutyrate by the following series of reactions:



Ethyl butyrylbutyrate has b. p. 222.8—223.4°/755 mm. (compare Hamonet, Abstr., 1890, 235).

Ethyl *isovaleryl*isovalerate, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CHMe}_2)\cdot\text{CO}_2\text{Et}$, obtained from ethyl α -bromoisovalerate, has b. p. 237.2—237.4°/768 mm. (corr.), and, on hydrolysis, yields isovalerone.

Ethyl bromoacetate does not give ethyl acetoacetate (compare Stollé, this vol., i, 310).

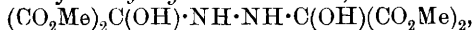
J. J. S.

Methyl Mesoxalate and Some of its Reactions. RICHARD S. CURTISS and PAUL T. TARNOWSKI (*J. Amer. Chem. Soc.*, 1908, 30, 1264—1271).—In an earlier paper (Curtiss, Abstr., 1906, i, 480), a method was described for the preparation of ethyl mesoxalate by the action of nitrogen trioxide on ethyl malonate by which a yield of 90—95% could be obtained.

It has now been found that a yield of 80—85% of methyl mesoxalate can be obtained in a similar manner. The mother liquor obtained in this reaction yields a light green mixture of unstable, oily esters, which are of an acid nature and contain nitrogen. This product decomposes suddenly at 120—130°, and yields yellow potassium, ammonium, and silver salts.

When methyl mesoxalate is distilled under reduced pressure, methyl oxomalonate, $\text{CO}(\text{CO}_2\text{Me})_2$, b. p. 100°(uncorr.)/20 mm., is obtained. Pure anhydrous methyl oxomalonate has been prepared, and its reactions are being studied.

By the action of hydrazine carbonate on methyl mesoxalate, a compound, probably *methyl hydrazotartronate*,



m. p. 154—155°, is obtained, which forms white crystals. If this substance is mixed with phosphoric oxide, it is converted into a yellow, crystalline compound, which is probably an azimethylene derivative. When the hydrazo-compound is treated with benz-

aldehyde, benzyldeneazine (Curtius and Jay, Abstr., 1889, 393) is produced.
E. G.

Conversion of Methyl Alcohol into Formaldehyde and Preparation of Formalin. IV. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 796—799. Compare this vol., i, 77).—The author gives further details for carrying out this oxidation. Platinised pumice and platinised asbestos act as good catalysts. By using these, the preliminary heating in a furnace of the tubes containing copper gauze may be dispensed with. The proportion of acetone in the methyl alcohol should not exceed 2%. When 4% of acetone is present, the contact mass does not ignite, and with 2.5%, ignition takes place when the temperature is 34—35° and the current of air amounts to 3 litres per minute; only when the greater part of the acetone has burnt away does the copper gauze begin to ignite.

T. H. P.

Condensation Products of Acetaldehyde containing Six and Ten Atoms of Carbon. SIMON ZEISEL and BÉLA VON BITTÓ (*Monatsh.*, 1908, 29, 591—605).—Ten volumes of acetaldehyde are heated for thirty-six hours at 95—97° with 1 volume of saturated sodium acetate solution, and the product distilled in steam. The distillate is fractionated, and, after removal of crotonaldehyde, the portion boiling above 120°, purified by repeated distillation in steam, shaking with calcium carbonate, and drying, is separated by fractional distillation into two substances, both having the composition C_6H_8O and exhibiting the properties of an aldehyde with two ethylenic linkings; the one has b. p. 75—80°/24—26 mm., yields an impure oxime, m. p. 155.5°, and an unstable, crystalline phenylhydrazone, whilst the other has b. p. 55—60°/24—26 mm. and 141—143° under ordinary pressure, forms an unstable oxime and phenylhydrazone, and yields, by oxidation with free oxygen, formic acid and resinous and other unexamined products.

From the residue of the original preparation non-volatile in steam, a substance, $C_{10}H_{14}O_2$, b. p. 159—163°/16.5 mm., has been isolated, which contains one CHO group (the other oxygen atom being probably in the form of a "bridge"), does not form a definite oxime or phenylhydrazone, and reacts with bromine, evolving hydrogen bromide.

C. S.

Crystalline Polymeride of *iso*Butaldol. R. MUSSELIUS (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 822—826).—The author has subjected to further investigation the crystalline substance, m. p. 90—92°, isolated by Brauchbar (Abstr., 1897, i, 137) from the condensation products of *isobutaldehyde*, and characterised by him as *isobutaldol*. By repeated fractional crystallisation from benzene, the compound is obtained in bundles of slender, white needles, m. p. 96.5—97°. In freezing benzene, the molecular weight corresponds with the formula $(C_8H_{16}O_2)_2$, a result in accordance with those of Kohn (Abstr., 1900, i, 274) for other crystalline aldols, which were all found to be bimolecular polymerides of the liquid aldols. In freezing acetic acid,

the molecular weight is 300—309·5 (theory, 288), but ebullioscopic measurements in ether gave unsatisfactory results, probably owing to decomposition of the double molecules of the aldol. T. H. P.

Preparation of Ketone ortho-Ethers. EDGAR HESS (D.R.-P. 197804).—Nitriles of the general formula $R\cdot CN$ are converted into the hydrochlorides of imino-esters by treatment with hydrogen chloride in absolute alcohol, and the product mixed with a ketone in the same medium. After eight days' shaking, the ammonium chloride produced is precipitated by ether, the filtrate poured into ice water, and the ketone ortho-ether separated from any ester by fractional distillation. The following acetals were thus produced: From methyl ethyl ketone, $CMeEt\cdot C(OEt)_2$, b. p. $68^\circ/10$ mm., $120^\circ/760$ mm.; from diethyl ketone, $CEt_2\cdot C(OEt)_2$, b. p. $71^\circ/44$ mm., $154^\circ/760$ mm., and from dipropyl ketone, $CPr_2\cdot C(OEt)_2$, b. p. $69^\circ/12$ mm. G. T. M.

Action of Ammonia on Methyl Ethyl Ketone. CARL THOMAE (*Arch. Pharm.*, 1908, 246, 373—377).—The use of alcohol as a solvent in this reaction, described by Traube (this vol., i, 362), was introduced by the author (*Abstr.*, 1905, i, 509). G. B.

Solubility and Certain Reactions of Pinacolin. LÉON DELANGE (*Bull. Soc. chim.*, 1908, [iv], 3, 910—915).—The author finds that, contrary to Denigès' statement (*Abstr.*, 1903, i, 606), pinacolin does not form an additive compound with mercuric sulphate, but that the precipitate obtained with ordinary samples of pinacolin is due to the presence of impurities which are not entirely removed by fractionation. In order to prepare pure pinacolin, the ordinary product is rectified seven times with a Le Bel column, warmed with mercuric sulphate, and the filtrate again warmed with the reagent. After decanting, the pinacolin is dried, washed, and rectified (b. p. $106\cdot2^\circ$). Pure pinacolin dissolves in water to the extent of 2·44% at 15° , and its solubility at 15° in aqueous acetone is (by volume) 1 part in 28·8 parts of 20%, 1 in 16·5 of 33%, 1 in 11·0 of 50%, and 1 in 7·0 of 60%. When 1 c.c. of pinacolin is added to a mixture of 0·45 c.c. of acetone and 1·8 c.c. of water, 0·30 c.c. of acetone is absorbed by the water and 0·15 c.c. by the pinacolin, and in a mixture of 1·65 c.c. of acetone and 0·85 c.c. of water, 0·75 c.c. of acetone is absorbed by the water and 0·60 c.c. by the pinacolin. The author shows that acetone can be estimated in presence of pinacolin by precipitation with mercuric sulphate. Pure pinacolin gives Legal's colour reaction (*Abstr.*, 1897, ii, 467), as stated by Denigès, but it does not furnish iodoform when treated with iodine and potassium hydroxide; the precipitate obtained is soluble in acetic acid, and has m. p. 68° , and at the same time there is formed a small amount of a volatile liquid of a piquant odour. J. C. C.

Action of Hydroxylamine on Ketones of the Type



ROBERTO CIUSA and A. TERNI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 724—728. Compare *Abstr.*, 1907, i, 62).—In addition to the compounds α -cinnamylideneacetophenonehydroxylamine and α -cinnamyl-

ideneacetophenoneoxime previously isolated as products of the action of hydroxylamine on cinnamylideneacetophenone, isomeric forms of these substances can also be separated in small quantities. These are denoted as β -forms, and their properties are compared with those of the α -compounds.

α -Cinnamylideneacetophenoneoxime (m. p. 135°) gives a benzoyl derivative crystallising from alcohol in white needles, m. p. 125° . β -Cinnamylideneacetophenoneoxime crystallises in white needles, m. p. 139 — 140° , and gives a benzoyl derivative, m. p. 137° . β -Cinnamylideneacetophenonehydroxylamine forms small, white spangles, m. p. 196° .

Cinnamylideneacetophenone is not toxic in its properties; the α -oxime is more poisonous, but 4—5 grams can be administered per day; so-called resinoid acids are then found in the urine, together with large quantities of urorosein. The latter fact is remarkable, as uroroseinuria has not previously been induced by artificial means. α -Cinnamylideneacetophenonehydroxylamine differs from the other substances in being highly poisonous, probably in virtue of the $\cdot\text{NH}\cdot\text{OH}$ group, as in the case of phenylhydroxylamine. W. A. D.

***N*-Alkylketoximes.** JOHANNES SCHEIBER (*Annalen*, 1908, 362, 54—63).—Previous work has shown that *N*-alkylketoximes are produced only with great difficulty by the condensation of β -substituted hydroxylamines with ketones (compare Scheiber and Wolf, *Abstr.*, 1907, i, 1028). In the case of acetone, ethyl acetoacetate, methyl ethyl ketone, and diacetyl, the additive compounds first formed by the reaction with the β -substituted hydroxylamine, namely, *N*-alkylketoxime hydrates, were isolated, but similar substances were not obtained from benzyl methyl diketone or benzil. With the object of ascertaining to what extent various ketones condense with β -benzylhydroxylamine, the following method was devised, by which the isolation of the additive product became unnecessary.

Known weights of β -hydroxylamine and of the ketone are added to a known weight of benzene, and the depression of the freezing point of the solvent noted at once and at intervals of some hours. If no interaction takes place, the depression observed is that calculated from the weights of ketone and β -benzylhydroxylamine added; should the observed depression be smaller than the calculated, then interaction must have taken place. Methyl ethyl diketone is found to react at once, whilst benzil does not react with β -benzylhydroxylamine.

The following ketones interact slowly with β -benzylhydroxylamine, the difference between the observed and calculated depression of the freezing point increasing slowly during several hours: acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl butyl ketone, benzyl methyl ketone, diethyl ketone, acetophenone, and *m*-nitroacetophenone. It is found that the homologues of acetone do not condense so readily with β -benzylhydroxylamine as acetone itself, with the one exception of benzyl methyl ketone, which apparently interacts more rapidly than acetone. The additive power of the ketone is reduced considerably by replacing a methyl group by ethyl, phenyl, or *m*-nitrophenyl.

The effect on the rate of formation of the additive compounds, produced by the addition of *p*-toluidine, diphenylamine, dimethylaniline, triethylamine, and tribenzylamine, was also investigated.

Generally speaking, the presence of a base does not bring about an acceleration in the rate of condensation; in fact, triethylamine appears to retard the reaction.

W. H. G.

***N*-Alkylketoximes.** JOHANNES SCHEIBER and PAUL BRANDT (*Annalen*, 1908, 362, 64—77).—The work described in the previous paper (compare Scheiber, preceding abstract) has been repeated, and so that the reactivities of the various ketones might be compared, equal molecular solutions have been used in each case. In all cases an experiment was performed in which the molecular proportions of ketone and β -benzylhydroxylamine were as 1:1, and sometimes as 5:1. The results obtained may be summarised as follows:

(1) In the absence of a base, the rate of formation of the additive product decreases rapidly in the following order: benzyl methyl ketone, acetone, methyl butyl ketone (methyl ethyl ketone = methyl hexyl ketone), diethyl ketone, acetophenone. Acetophenone, even in strong solutions, is almost indifferent towards β -benzylhydroxylamine.

(2) In the presence of a base, such as triethylamine, tribenzylamine, or dimethylaniline, the rate at which the additive product is formed is apparently smaller, but it is only apparent, for in some cases the difference between the calculated and observed depression of the freezing point at first increases and then decreases, undoubtedly because the second reaction, *N*-benzylketoxime hydrate \rightarrow *N*-benzylketoxime + water, is taking place. The apparent reduction in the velocity of formation of the *N*-benzylketoxime hydrate is due to the occurrence of this second reaction. In fact, the solution containing β -benzylhydroxylamine, benzyl methyl ketone, and triethylamine, or tribenzylamine, becomes turbid after some time, owing to separation of water.

It is therefore evident that the difference in the behaviour of an aldehyde and a ketone towards β -substituted hydroxylamines is merely one of degree and not of kind.

W. H. G.

The Scission of Sugars. [Sucroclasm.] II. The Action of Zinc Dust and Iron on Formaldehyde Solutions; the Action of Zinc Dust on Dextrose. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, 12, 466—472. Compare this vol., i, 715).—As products of the action of zinc dust on formaldehyde were isolated, formic acid and two other volatile products were obtained in the form of their condensation products with phenylhydrazine. The one gave an insoluble osazone, m. p. 243°, which corresponded in properties with diacetyl-osazone, and the other gave an osazone, m. p. 148°, which is methylglyoxalosazone. The other products of reaction have not yet been all identified. They appear to include β -acrose, as an osazone of m. p. 165° was obtained. Polyhydroxy-acids were also obtained. When formaldehyde solutions are treated with iron, condensation to sugars takes place to only a slight extent, and only traces of polyhydroxy-

acids are formed. Methyl alcohol and formic acid are produced, however, in larger quantities. Dextrose, on treatment with zinc, yields formic acid, diacetyl, and methylglyoxal, also polyhydroxy-acids, but no methyl alcohol. S. B. S.

The Depolymerisation of Sugars. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 12, 337—341).—Pure crystalline glycerose was prepared by the method of Fenton and Jackson, and polymerised by treating with a colloidal solution of barium carbonate in methyl alcohol. By this means a pentose was obtained, as furfuraldehyde could be obtained by distillation of the condensation product with hydrochloric acid, and was isolated in the form of its condensation product with *p*-nitrophenylhydrazine. As pure glycerose was employed, the formation of a pentose from the triose can only be explained by assuming that the latter depolymerises to formaldehyde, an assumption that is rendered probable by the work of Buchner and other investigators. S. B. S.

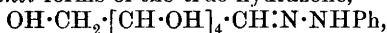
Preparation of an Anhydrous Crystalline Compound of Dextrose and Sodium Iodide. FUNIA JOHANN A. WÜLFING (D.R.-P. 196605).—The compound $2C_6H_{12}O_6 \cdot NaI$, octahedral crystals, m. p. 185—186°, is produced by boiling together anhydrous dextrose and sodium iodide in alcoholic solution; it separates on diluting the solution with about 10% of water and allowing to cool. G. T. M.

Phenylhydrazones of Dextrose. ROBERT BEHREND and FRIEDRICH LOHR (*Annalen*, 1908, 362, 78—114).—The compound, m. p. 106—107°, obtained by the action of an alcoholic solution of phenylhydrazine on dextrose, either in the solid state or in strong aqueous solution, and described previously (Abstr., 1907, i, 481) as being identical with Skraup's β -phenylhydrazone, is now shown to be a loose combination of 1 mol. of phenylhydrazine with 2 mols. of a hydrazone, which it is proposed to call dextrose- β -phenylhydrazone. Skraup's β -hydrazone is merely a mixture of this hydrazone with some α -hydrazone. Another compound, containing 1 mol. of phenylhydrazine loosely combined with 1 mol. of the β -hydrazone, has also been isolated. A solution of either of the hydrazones or phenylhydrazone additive compounds in hot pyridine deposits on cooling a pyridine additive compound of the β -hydrazone, from which the pure β -hydrazone is obtained by washing with cold alcohol. It is thus possible to pass from the α - to the β -isomeride.

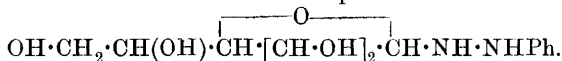
Solutions of either the α - or β -hydrazone in pyridine, having the approximate initial values $[\alpha]_D - 87^\circ$ and -10° respectively, become dextrorotatory when kept for some time. If these solutions are heated at 80—85° for about one and a-half hours and then cooled rapidly, the value observed in each case is roughly $[\alpha]_D + 18.5^\circ$; the rotation gradually decreases at the ordinary temperature, the final value being roughly $[\alpha]_D + 5^\circ$. All attempts to separate the dextrorotatory isomeride present in these solutions were unsuccessful.

The possible structural formulæ of the isomeric phenylhydrazones

are discussed. It is considered probable that the α - and β -hydrazones are the *syn*- and *anti*-forms of the true hydrazone,



or that one of them is a true hydrazone, whilst the other is one of the possible stereoisomeric forms of the compound



The velocity with which one isomeride passes into the other in solution is increased by traces of acid and diminished by alkalis. The equilibrium mixture of the two hydrazones in aqueous solution has the optical rotatory power $[\alpha]_D^{19} = 53.74^\circ$.

The substance, $(\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPH})_2\cdot\text{NHPH}\cdot\text{NH}_2$, previously described as dextrose- β -phenylhydrazone (*loc. cit.*), is best prepared by the action of phenylhydrazine on dextrose in dilute aqueous alcoholic solution; traces of ammonia retard the formation of this substance to a great extent. The same compound is also formed by the action of an alcoholic solution of phenylhydrazine on either solid α - or β -dextrose. An aqueous solution (2—4%) ten minutes after dissolving the substance gave $[\alpha]_D = 4.4^\circ$, the final value being $[\alpha]_D = 48.2^\circ$.

The substance, $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPH}\cdot\text{NHPH}\cdot\text{NH}_2$, prepared by the action of phenylhydrazine (3 parts) on dextrose (1 part), crystallises in concentric groups of large, white prisms, which sinter at about 80° , m. p. $85\text{--}87^\circ$; a 4% aqueous solution ten minutes after dissolving the substance gave $[\alpha]_D = 2.82^\circ$, the final value being $[\alpha]_D = 28.45^\circ$.

The change in the optical rotatory power of an alcoholic solution with the time is very remarkable; a solution of 0.5017 gram in 25 c.c. gave the following values: $[\alpha]_D + 3.24^\circ$, $\pm 0.00^\circ$, $- 3.49^\circ$, $- 4.99^\circ$, $\pm 0.00^\circ$, $+ 2.49^\circ$, $- 7.97^\circ$, $- 14.95^\circ$ at 20, 30, 70, 90 minutes, 4.5, 21.5, 46.5, and 94 hours respectively.

The pyridine additive compound of dextrose- β -phenylhydrazone, $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPH}\cdot\text{C}_5\text{NH}_5$, crystallises in small, colourless, trapezoid plates, m. p. $100\text{--}101^\circ$. In aqueous solution, the initial value is $[\alpha]_D = 4.08^\circ$, the value after several hours being $- 38.87^\circ$.

Dextrose β -phenylhydrazone, $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}\cdot\text{NHPH}$, is best prepared by treating the pyridine additive compound with small quantities of alcohol. It may also be obtained in the same way from the phenylhydrazine compound, m. p. 107° . It crystallises in small needles, m. p. $140\text{--}141^\circ$; the optical rotation of an aqueous solution containing a trace of pyridine twenty minutes after dissolution was $[\alpha]_D = 5.50^\circ$, the equilibrium value being $[\alpha]_D = 53.74^\circ$. The α -hydrazone crystallises from a solution of the β -hydrazone in alcohol containing a small amount of acetic acid at about 20° ; the substance, m. p. $106\text{--}107^\circ$, which separates from the same solution at 0° , and was previously thought to be the β -hydrazone, is a mixture of the two isomerides. The β -hydrazone may be obtained from the α -isomeride by boiling an alcoholic solution of the latter for some time and then rapidly cooling to 0° .

W. H. G.

The Precipitation of Sugars by Cupric Hydroxide. S. YOSHIMOTO (*Zeitsch. physiol. Chem.*, 1908, 56, 425—445. Compare Salkowski, this Journ., 1872, 25, 1122; Worm-Müller and Hagen, *Pflüger's Archiv*, 1876, 17, 568).—Experiments have been made by

precipitating cupric hydroxide (from cupric sulphate solution by the addition of sodium hydroxide) in the presence of various sugars. Even when excess of alkali is used, small amounts of sugar are found in the filtrates.

The amount of sugar, however, tends to decrease if the mixture is shaken thoroughly and kept for some little time before filtration.

In the case of all the sugars examined, the amount of sugar left in the filtrate decreases as the amount of alkali is increased, but this value reaches a minimum, and further addition of alkali tends to increase the amount of sugar in the filtrate. With lactose, xylose, and arabinose, the curves are fairly regular, but with dextrose, lævulose, galactose, maltose, sucrose, and raffinose the curves are irregular. In no case is the amount of sugar present in the filtrate directly proportional to the excess of alkali. The minimum has the smallest value in the case of dextrose, namely, 1.66%. J. J. S.

The Molecular Weight of Dextrin from Honey from Coniferous Plants. HERMANN BARSCHALL (*Chem. Zentr.*, 1908, ii, 91; from *Arbb. Kais. Gesundh.-Amt.*, 1908, 28, 405—419).—The molecular weight of this substance was determined by the cryoscopic method, although it was not found possible to obtain a honey-dextrin free from ash. After the necessary correction for ash has been made, it is found that the value obtained (473) is well above that required for a disaccharide, $(C_5H_{10}O_5)_2 = 324.16$, and falls within the limits of experimental error for a trisaccharide (486.32).

J. V. E.

Action of Nitric Acid on Starch. II. ANTONY G. DOROSCHEWSKY, ADAM W. RAKOWSKY, and A. A. BARDT (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 932—940. Compare *Abstr.*, 1907, i, 678).—In continuation of their previous work, the authors have studied the hydrolysis, by means of 0.4*N* nitric acid, (1) of starch in 8.6% and 14% concentrations, and (2) of starches derived from potatoes, maize, rice, Bermuda arrowroot, and St. Vincent arrowroot.

The results show that in reactions with intermediate stages of the first order, the velocity constant, calculated from the formula for unimolecular reactions, increases slightly as the concentration of the reacting compounds increases. Further, if in these reactions the velocity of the latter stage is much less than that of the first stage, the velocity constant given by the unimolecular formula increases for some time and then remains constant. In particular, a constant velocity-coefficient is obtained when some intermediate stage is taken as the beginning of the reaction.

The velocity constants for the final stage of the hydrolysis of the various starches are: potato, 0.0097; maize, 0.0097; rice, 0.0094; Bermuda arrowroot, 0.0100; St. Vincent arrowroot, 0.0103. The initial stages of the course of hydrolysis vary considerably with the different starches investigated, which may be divided into two groups: (1) rice and maize starches, with which the hydrolysis at first increases,

reaching a maximum in about ten minutes ; (2) potato and the two arrowroot starches, with which no such increase is observed.

T. H. P.

Action of Nitric Acid on Cellulose. CARL HAEUSSERMANN (*Chem. Zentr.*, 1908, i, 2024 ; from *Zeitsch. Schiess. Sprengstoffwesen*, 1908, 3, 121—122).—With nitric acid, cellulose yields additive as well as substitution products. Cotton immersed in cold nitric acid, D 1.1—1.45, then pressed, and allowed to dry for three or four days over lime in a vacuum, as described by Knecht (*Abstr.*, 1904, i, 293), gives additive products. This is shown by the fact that cold water removes the acid, and also the bluish-black coloration produced with iodine-potassium iodide solution. When left in the nitric acid, cotton becomes disintegrated, giving soluble substances, amongst which there is scarcely any nitrate. Left in contact with nitric acid of D above 1.45 for a sufficient length of time, cellulose is converted into the nitrate, which is stable towards water, and when free from acid gives no coloration with iodine-potassium iodide solution.

When cellulose fibre is saturated with excess of concentrated acid and the liquid removed before the action is complete, the product gives a blue coloration with iodine-potassium iodide. Cellulose also gives with stronger nitric acid an additive product, which loses water in presence of excess of acid, forming the ester.

J. V. E.

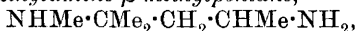
Influence of Sulphuric Acid in Nitration. Especially of Cellulose. CARL KULLGREN (*Chem. Zentr.*, 1908, i, 2024—2025 ; from *Zeitsch. Schiess. Sprengstoffwesen*, 1908, 3, 146—149. Compare this vol., i, 504).—The author concludes from the results of Schaposhnikoff, Küster and Kremann, Lunge, and others, that the nitric acid is only capable of nitrating when present as the compound HNO_3 , and not as hydrate ; the part played by the added sulphuric acid being to set free HNO_3 from the hydrate.

J. V. E.

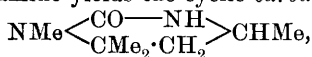
Two Methods of Preparing Methylamine. MAURICE FRANCOIS (*Compt. rend.*, 1908, 147, 428—430).—The existing methods of separating ammonia and methylamine are incomplete (compare this vol., i, 505 ; Bertheaume, this vol., ii, 742). The method of separation by means of yellow mercuric oxide (*Abstr.*, 1907, i, 391) is only applicable to a crude methylamine hydrochloride which contains no other nitrogen base besides ammonia. The crude product obtained in Brochet and Cambier's method (*Abstr.*, 1895, i, 325) of preparing methylamine contains as impurities ammonium chloride, formaldehyde, and trimethyltrimethylenetriamine hydrochloride. The author finds that moderately-concentrated solutions of the latter in hydrochloric acid decolorise a solution of iodine in potassium iodide, afterwards precipitating a brown periodide, and give a pale yellow precipitate with a solution of mercuric iodide in potassium iodide, and that trimethyltrimethylenetriamine hydrochloride is easily soluble in chloroform. By means of these reactions, it is found that Brochet and Cambier's crude hydrochloride, after once recrystallising from alcohol, still contains 3% of the triamine hydrochloride ; accordingly, the

mercuric oxide separation is inapplicable. On the other hand, the crude hydrochloride resulting from Hofmann's reaction with bromoacetamide contains nothing soluble in chloroform (which dissolves the hydrochlorides of secondary and tertiary bases), and treatment by yellow mercuric oxide gives pure methylamine hydrochloride. The conclusion is drawn that Hofmann's reaction, followed by a separation by mercuric oxide, is the more satisfactory method of preparing pure methylamine. The yield, however, is not good; the author obtained 35% of theory, and probably Hofmann's high apparent yield contained ammonium chloride. E. H.

δ -Amino- β -methylamino- β -methylpentane. MORITZ KOHN and OTTO MORGENSTERN (*Monatsh.*, 1908, 29, 519—523).—The oxime of methyl diacetoneamine, when reduced by sodium and absolute alcohol, yields δ -amino- β -methylamino- β -methylpentane,



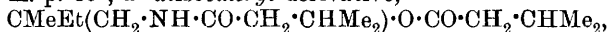
b. p. 166—167°, a mobile, fuming liquid with an intense basic odour; the *aurichloride* and *platinichloride* decompose at 215° and 220° respectively, whilst the *picrate* melts in hot water and decomposes at 199—200°. When heated with 1 mol. of ethyl carbonate for thirty hours at 200°, the diamine yields the cyclic *carbamide*,



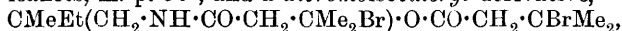
m. p. 132—133°, b. p. 292—293°/741 mm.

C. S.

Preparation of Acylated Aminoalkyl Esters. J. D. RIEDEL (D.R.-P. 194051. Compare Abstr., 1906, i, 631; 1907, i, 897).—*Aminodimethylethylcarbinol*, b. p. 75—80°/30 mm., and the secondary base, $\text{NH}(\text{CH}_2 \cdot \text{CMeEt} \cdot \text{OH})_2$, b. p. 145°/30 mm., and *hydrochloride*, m. p. 144°, are obtained by heating, at 125°, chlorodimethylethylcarbinol and aqueous ammonia; the former furnishes a *hydrochloride*, leaflets, m. p. 85°, a *diisovaleryl* derivative,



greasy leaflets, m. p. 50°, and a *dibromoisovaleryl* derivative,



needles, m. p. 74°.

Phenylaminodimethylcarbinol, $\text{CMePh}(\text{CH}_2 \cdot \text{NH}_2) \cdot \text{OH}$, b. p. 175°/40 mm., together with the secondary base,



b. p. 258°/40 mm., are obtained by heating, at 125°, phenylchlorodimethylcarbinol and aqueous ammonia; the *dibenzoyl* derivative, prisms, m. p. 110°, is obtained by treating the primary base with benzoyl chloride in pyridine solution. G. T. M.

Preparation of α -Iodoisovalerylcaramide. KNOLL & Co. (D.R.-P. 197648. Compare Abstr., 1907, i, 1017).— *α -Iodoisovalerylcaramide*, leaflets, m. p. 180°, is prepared by heating α -chloro- or α -bromo-*isovalerylcaramide* with an alkali iodide, or the iodide of an alkaline earth metal, either in alcoholic solution or in the presence of benzene. G. T. M.

Synthesis of α -Aminonitriles. NICOLAI D. ZELINSKY and GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 790—791).—In the formation of the nitriles of α -amino-acids (Abstr., 1906, i, 425) by the action of potassium cyanide (1 mol.) and ammonium chloride (1 mol.) on aldehydes or ketones, the hydrolysis of the potassium cyanide plays an important part, so that the presence of water is necessary in order that the reaction may take place. That this is the case is shown by experiments with benzaldehyde and with cyclohexanone, which yield no nitrile in the absence of water.

T. H. P.

Preparation of Barium Cyanide from Barium Cyanamides. BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 197394).—The reversible reaction $\text{Ba}(\text{CN})_2 \rightleftharpoons \text{BaCN}_2 + \text{C}$ is applied to the production of barium cyanide. The crude product, containing 60% of cyanide and 40% of barium cyanamide, is heated at 600—800° in a stream of acetylene.

A mixture of barium carbonate and wood-charcoal powder is heated in nitrogen at 1500° until no further absorption of gas is observed. The temperature is then lowered to 1100°, and the mixture treated with a current of producer gas previously freed from carbon dioxide until the product is wholly converted into barium cyanide.

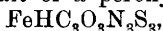
G. T. M.

Mercuric Oxycyanide. ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1908, 246, 367—373. Compare Holdermann, Abstr., 1906, i, 75, 411; Rupp, Abstr., 1906, i, 340).—Mercuric oxide takes part in the formation of the oxycyanide as hydroxide, hence the reaction is accelerated by hydroxyl ions. It is best carried out by mixing 22.2 grams of mercuric oxide in a mortar with 60 c.c. of water and 4 c.c. of 10% sodium hydroxide, adding 27 grams (a slight excess) of mercuric cyanide, and stirring until the mixture is colourless.

Details are also given for the preparation of the oxycyanide from mercuric chloride, mercuric cyanide, and sodium hydroxide, and from alkali cyanide and mercuric chloride. The fact that mercuric salts are not precipitated by sodium hydroxide in the presence of mercuric cyanide depends on the formation of mercuric oxycyanide.

G. B.

Oxidations Effected by Ferric Salts. C. BONGIOVANNI (*Gazzetta*, 1908, 38, ii, 5—9).—The author produces fresh evidence in support of his view concerning the reaction between ferric chloride and potassium thiocyanate (Abstr., 1907, i, 833). According to Tarugi (Abstr., 1905, i, 176), the red coloration produced in this reaction is due to the formation of the ferrous salt of a peroxythiocyanic acid,



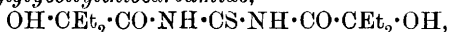
which, like the free acid, is decolorised by dilution or by solutions of oxalates, tartrates, &c., being converted thereby into normal thiocyanic acid or thiocyanate. The author, however, explains the decoloration produced by dilution as due to the hydrolysis of the non-dissociated red, $\text{Fe}(\text{CNS})_3$, into yellow, colloidal ferric hydroxide and thiocyanic acid; and the decoloration effected by oxalates, tartrates,

&c., by the formation by these substances of complex ions with the iron of the ferric thiocyanate and consequent displacement of the equilibrium $\text{Fe}^{+++} + 3\text{CNS} \rightleftharpoons \text{Fe}(\text{CNS})_3$ in such a manner that the coloured part is diminished in amount. This view is supported by the observation that the substances which decolorise ferric thiocyanate also hinder the displacement of iodine from potassium iodide by ferric salts.

The author also traverses the statement of Tarugi and Revello (*Atti Soc. Chim. Roma*, July, 1907), that ferric chloride exerts an oxidising action on potassium ferrocyanide, so that the interaction of these compounds results in the formation of ferrous oxyferrocyanide and not of ferric ferrocyanide. By means of a special apparatus, the author has carried out this reaction in an atmosphere of nitrogen, thus avoiding, as far as possible, the formation of soluble Prussian blue. By washing the precipitate, precipitating by sodium hydroxide solution, again washing, and dissolving in acid, always in an atmosphere of nitrogen, a solution is obtained which contains only traces of ferrous salt, attributable to secondary reactions. Tarugi and Revello's interpretation of the reaction is hence erroneous. T. H. P.

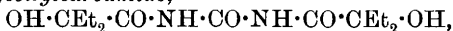
Ureides and Cyanamides of the Dialkylglycollic Acids. ERIK CLEMMENSEN and ARNOLD H. C. HEITMAN (*Amer. Chem. J.*, 1908, 40, 280—302).—The authors have prepared ureides of the dialkylglycollic acid by substituting one or more of the hydrogen atoms in carbamide by the radicle $\text{OH}\cdot\text{CR}_2\cdot\text{CO}$. By the action of carbamide and sodium ethoxide on the esters of the dialkylglycollic acids, ureides of the formula $\text{OH}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CR}_2\cdot\text{OH}$ are obtained, but when thiocarbamide or guanidine (as thiocyanate) is substituted for carbamide in this reaction, glycolcyanamides are produced, thus :
 $\text{OH}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et} + \text{CS}(\text{NH}_2)_2 + 2\text{NaOEt} =$

$\text{OH}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NNa}\cdot\text{CN} + \text{NaSH} + 3\text{EtOH}$,
 and these cyanamides are converted by boiling with acids or alkalis into the ureides just mentioned. It was found possible, however, to obtain *C-diethylglycollylthiocarbamide*,



by heating a mixture of diethylglycollic acid and thiocarbamide to 180° . At 200° , and with an excess of the latter, $\beta\beta$ -diethylthiohydantoin is formed.

C-Diethylglycollylcarbamide,



forms long, needle-shaped crystals, m. p. $30-31^\circ$. In 100 parts of water, 6.5 parts dissolve at 20° , and 14 at 100° . On dry distillation, its salts yield a mixture of diethyl ketone, diethylcarbinol, and probably triethylcarbinol. The calcium, magnesium, copper (normal and acid), zinc, silver, mercury, and double magnesium-copper salts are described.

C-Dipropylglycollylcarbamide forms a white, crystalline mass, m. p. 39° ; the magnesium and mercury salts are described. *C-Dimethylglycollylcarbamide* crystallises from light petroleum in white needles, m. p. 74° . It forms double salts of the formula $\text{C}_{18}\text{H}_{28}\text{O}_{10}\text{N}_4\text{CuR}$ ($\text{R} = \text{Ca}, \text{Ba}, \text{Sr}, \text{or Mg}$); the zinc and silver salts were analysed. *C-Diethyl*

glycollylthiocarbamide separates from water in long, slender, yellow needles or small, rhombic prisms, m. p. 117—118°. $\beta\beta$ -*Diethylthiohydantoin*, $\begin{matrix} \text{CEt}_2-\text{S} \\ \text{CO}\cdot\text{NH} \end{matrix} > \text{C}\cdot\text{NH}$, separates from water in colourless cubes or octahedrons, m. p. 224°. On boiling with barium hydroxide for an hour, it is converted into *diethylthioglycollamide*, $\text{SH}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 147°, and on prolonged boiling it yields *diethylthioglycollic acid*, $\text{SH}\cdot\text{CEt}_2\cdot\text{CO}_2\text{H}$, which is being further examined. *Diethylglycolcyanamide*, $\text{OH}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, separates from water in shining plates, m. p. 235°. *Dipropylglycolcyanamide* crystallises from water in colourless, monoclinic needles, m. p. 184°. *Dimethylglycolcyanamide* separates from water in tiny, colourless, monoclinic needles, m. p. 248—250°. J. C. C.

Resolution of α -Methylisoserine into its Optically Active Components. FRANCIS W. KAY (*Annalen*, 1908, 362, 325—332).— α -Methylisoserine is readily resolved in the form of its benzoyl derivative by means of brucine or quinine.

dl-Benzoyl- α -methylisoserine, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$, prepared by the action of benzoyl chloride and sodium hydroxide on the amino-acid, crystallises in plates, m. p. 153° (corr.). The *brucine* salt of the *d*-compound crystallises from the alcoholic solution of the *dl*-benzoylamino-acid and brucine. *d-Benzoyl- α -methylisoserine*, liberated from its brucine salt by means of sodium hydroxide, crystallises in needles, m. p. 124° (corr.), $[\alpha]_D^{20} + 9.51^\circ$, or, in more dilute solution, $[\alpha]_D^{20} + 8.40^\circ$. *l-Benzoyl- α -methylisoserine*, obtained from the mother liquor of the brucine salts, has $[\alpha]_D^{20} - 9.23^\circ$, or, in more dilute solution, $[\alpha]_D^{20} - 8.39^\circ$, and resembles its optical antipode.

The optically active α -methylisoserines are obtained by hydrolysis of their benzoyl derivatives with boiling hydrobromic acid. The *d-acid*, $\text{C}_4\text{H}_9\text{O}_3\text{N}$, when quickly heated, has m. p. about 230° (decomp.), $[\alpha]_D^{20} + 4.34^\circ$. The *l-acid* has $[\alpha]_D^{20} - 4.15^\circ$, and resembles its optical antipode. G. Y.

Resolution of α -Amino-*n*-hexoic Acid into its Optical Components. DEMETRIUS MARKO (*Annalen*, 1908, 362, 333—337).— α -Amino-*n*-hexoic acid was resolved previously in the form of its benzoyl derivative (Fischer and Hagenbach, *Abstr.*, 1902, i, 85). It is now found better to employ the formyl derivative.

*dl-Formyl- α -amino-*n*-hexoic acid*, $\text{C}_7\text{H}_{13}\text{O}_3\text{N}$, prepared by Fischer and Warburg's method (*Abstr.*, 1906, i, 72), crystallises in colourless needles, m. p. 113—115° (corr.). On treatment of the *dl*-compound with brucine in alcoholic solution, the *brucine* salt of the *l-acid* separates, and, on hydrolysis by means of hydrochloric acid, yields *l-formyl- α -amino-*n*-hexoic acid*, which crystallises in silky needles, m. p. 115—118.5° (corr.), $[\alpha]_D^{20} - 17.56^\circ$. The *d-formyl* derivative, obtained from the alcoholic mother liquor, has $[\alpha]_D^{20} + 17.63^\circ$.

The formylamino-acids are hydrolysed by boiling 10% hydrobromic acid. *l- α -Amino-*n*-hexoic acid*, $[\alpha]_D^{20} - 22.99^\circ$; the *d-acid*, $[\alpha]_D^{20} + 23.14^\circ$.

Fischer and Hagenbach (*loc. cit.*) obtained the values $[\alpha]_D^{20} - 22.4^\circ$ and $+21.3^\circ$; by a fermentation process, Schulze and Likiernik obtained an acid having $[\alpha]_D - 26.5^\circ$. G. Y.

Synthesis of Polypeptides. XXVI. 1. Derivatives of α -Aminostearic Acid. EMIL FISCHER and WALTER KROPP (*Annalen*, 1908, 362, 338—347).—In comparison with the α -amino-derivatives of the simple fatty acids, the derivatives of the high molecular acids have so far been little studied. As a contribution to the filling of this gap in our knowledge, the authors now describe the combination of glycine with α -aminostearic acid.

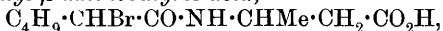
Methyl α -aminostearate hydrochloride, $C_{19}H_{40}O_3NCl$, prepared by treating α -aminostearic acid with methyl alcohol and hydrogen chloride, separates from ethyl acetate in needles, m. p. 112° (corr.). The *hydrochloride* of the ethyl ester crystallises in needles, m. p. 89° (corr.).

Methyl chloroacetylaminostearate, $C_{21}H_{40}O_3NCl$, prepared by the successive action of sodium methoxide and chloroacetyl chloride on the hydrochloride of the preceding methyl ester, crystallises from light petroleum in colourless needles, m. p. 78° (corr.). The *ethyl* ester, prepared in the same manner, crystallises in colourless needles, m. p. 68° (corr.). Hydrolysis of the methyl ester with alcoholic sodium hydroxide leads to the formation of *chloroacetylaminostearic acid*, $C_{20}H_{38}O_3NCl$, which crystallises in colourless needles, m. p. 107° (corr.), and, when heated with alcoholic ammonia at 100° , forms *glycyl- α -aminostearic acid*, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(C_{16}H_{33}) \cdot CO_2H$, crystallising in microscopic prisms, m. p. about 218° (corr.). It dissolves in hot dilute hydrochloric acid or sodium hydroxide, forming frothing solutions; concentrated sodium hydroxide precipitates the *sodium* salt.

The *anhydride*, $CH_2 \begin{smallmatrix} < NH \cdot CO \\ < CO \cdot NH \end{smallmatrix} CH \cdot C_{16}H_{33}$, formed by the action of alcoholic ammonia on ethyl chloroacetyl- α -aminostearate at 100° , separates in microscopic crystals, m. p. 219° (corr.), and is insoluble in dilute sodium hydroxide. G. Y.

Synthesis of Polypeptides. XXVI. 2. Derivatives of β -Aminobutyric Acid and of α -Methylisoserine. FRANCIS W. KAY (*Annalen*, 1908, 362, 348—360).—So far only two polypeptides derived from β -amino-acids, leucylisoserine and isoserylisoserine, have been described. As a knowledge of such substances is desirable for the discussion of certain theoretical questions, the author has studied the combinations of *r*- β -aminobutyric acid with *i*-leucine and alanine, and of *r*- α -methylisoserine with *i*-leucine. In the last case both isomeric racemic compounds have been obtained, and are distinguished, as in other similar cases, as the *A* and *B* compounds.

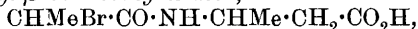
α -Bromoisohexyl- β -aminobutyric acid,



prepared by the action of *i*-bromoisohexoyl chloride and sodium hydroxide on β -aminobutyric acid, crystallises in small prisms or needles, m. p. $97-98^\circ$; attempts to resolve it into two forms were unsuccessful. The action of 25% aqueous ammonia on the bromo-compound at 25° leads to the formation of *leucyl- β -aminobutyric acid*,

$\text{NH}_2 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which is obtained as a colourless, crystalline powder, m. p. 232° (corr.). The *copper* salt, $(\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}_2)_2\text{Cu} \cdot \text{CuO}$, forms deep blue, six-sided plates. The *anhydride*, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$, formed by heating the dipeptide at 225° , is obtained as a yellow, sandy powder, m. p. $197\text{--}198^\circ$ (corr.), and is probably quadrimolecular.

Bromopropionyl-β-aminobutyric acid,



prepared from β-aminobutyric acid and bromopropionyl bromide, crystallises from water in colourless needles, m. p. 131° (corr.), and, when treated with aqueous ammonia at 25° , yields *alaninyl-β-aminobutyric acid*, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which forms an amorphous, slightly grey mass, m. p. about 250° (decomp.), when quickly heated. The *copper* salt, $(\text{C}_7\text{H}_{13}\text{O}_3\text{N}_2)_2\text{Cu} \cdot \text{CuO} \cdot 4\text{H}_2\text{O}$, forms deep blue, six-sided plates.

When coupled with *i*-α-bromoisohexoyl chloride, α-methylisoserine forms two α-bromoisohexoyl-α-methylisoserines, $\text{C}_{10}\text{H}_{18}\text{O}_4\text{NBr}$. The *A* compound crystallises from the aqueous solution in needles, m. p. 173° (corr.); the *B* compound, obtained from the aqueous mother liquor, crystallises in hexagonal plates, m. p. $125\text{--}126^\circ$ (corr.). *Leucyl-α-methylisoserine A*, $\text{NH}_2 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CO}_2\text{H}$, crystallises in microscopic prisms, m. p. about 240° (decomp.); the *phenylcarbimide* derivative, $\text{C}_{17}\text{H}_{25}\text{O}_5\text{N}_3$, crystallises in stout prisms, m. p. 180° (corr.). *Leucyl-α-methylisoserine B* crystallises in colourless plates or needles, m. p. 250° (decomp.); the *phenylcarbimide* derivative forms silky needles, m. p. 187° (corr.). G. Y.

Experiments on the Decomposition of Arginine. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1908, 56, 305—315).—The substance described as putridine (*ibid.*, 54, 24) is now shown to be δ-aminovaleric acid (Salkowski, Abstr., 1898, i, 404). It is thrown down by the reagents usually employed for precipitating alkaloids. When its hydrochloride is heated, it sublimes, and does not yield a ring compound.

Experiments made with the object of proving whether, when arginine undergoes putrefaction, δ-aminovaleric acid is formed, gave negative results. Amongst the products isolated was *r*-ornithine; thus indicating that racemisation had occurred during the reaction. The purification of this base is facilitated by precipitation with mercuric chloride and sodium acetate. Tetramethylenediamine could not be detected.

d-Lysine yields an *aurichloride*, $\text{C}_{12}\text{H}_{28}\text{O}_4\text{N}_4 \cdot \text{HCl} \cdot 3\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$, which sinters at 120° and melts at $152\text{--}155^\circ$. The *aurichloride* of the racemic base has the composition $\text{C}_{12}\text{H}_{28}\text{O}_4\text{N}_4 \cdot 4\text{HAuCl}_4 \cdot \text{H}_2\text{O}$, and decomposes at $173\text{--}176^\circ$. The corresponding *platinichloride* crystallises with 1 molecule of alcohol, $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot \text{EtOH}$, which it loses at 120° . J. J. S.

Derivatives of a Complex Chloride of Gold and Phosphorus. MARIO LEVI-MALVANO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 847—857).—The author has prepared the following complex compounds of gold and phosphorus:

Aurophosphorous chloride, $(\text{AuPCl}_2)_2\text{Cl}$ (compare Lindet, Abstr., 1887, 227). Methyl aurophosphite chloride, $[\text{AuP}(\text{OMe})_3]\text{Cl}$ (Lindet, *loc. cit.*), which has the molecular weight 384—425 (calc. 356.65) in freezing benzene, and with chloroplatinic acid solutions gives slender, yellow needles of the *platinichloride*, $[\text{AuP}(\text{OMe})_3]_2\text{PtCl}_6$.

Aurotriethylphosphine chloride, $(\text{AuPET}_3)_2\text{Cl}$, prepared by the action of triethylphosphine on auric chloride dissolved in alcohol, forms colourless needles, m. p. 80° , is stable in the air, and exhibits all the properties of a stable complex salt, since the gold is not precipitated by its ordinary reagents.

Aurotriphenylphosphine chloride, $(\text{AuPPh}_3)_2\text{Cl}$, prepared by the interaction of alcoholic solutions of triphenylphosphine and auric chloride, crystallises in colourless, truncated prisms, decomposes at $180\text{--}230^\circ$, and has the molecular weight 524—532 (calc. 494.6) in freezing benzene. It is stable in the air, and is not dissolved or decomposed by dilute nitric acid, concentrated hydrochloric acid, or potassium hydroxide solution. It forms the *platinichloride*, $(\text{AuPPh}_3)_2\text{PtCl}_6$, and the *sulphate*, $[\text{AuPPh}_3]_2\text{SO}_4$.

Methyl auroaminophosphite chloride, $[\text{AuP}(\text{OMe})_3(\text{NH}_3)_2]\text{Cl}$, forms microscopic, prismatic crystals, m. p. $75\text{--}76^\circ$.

Auroaminotriethylphosphine chloride, $[\text{AuPET}_3(\text{NH}_3)_2]\text{Cl}$, forms microscopic, colourless prisms, decomposing at $90\text{--}150^\circ$.

Aurotriphenylphosphine chloride is quite insoluble in ammonia.

T. H. P.

Certain Homologues of Naphthalene. GUIDO BARGELLINI and G. MELACINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 26—30).—The two *n*-propylnaphthalenes and the two *n*-butylnaphthalenes are obtained by treating a solution of naphthalene in carbon disulphide with *n*-propionyl chloride or *n*-butyryl chloride in presence of aluminium chloride, separating the isomeric α - and β -ketones thus obtained by means of picric acid, and reducing them with iodide, red phosphorus, and water (compare Claus, Abstr., 1892, 985; 1893, i, 162).

β -Naphthyl propyl ketone crystallises from alcohol in colourless, triclinic plates [*A. ROSATI*: $a:b:c = 0.6774:1:0.6029$; $\alpha = 94^\circ 31'$, $\beta = 140^\circ 3.5'$, $\gamma = 90^\circ 27'$].

α -*n*-Propylnaphthalene, $\text{C}_{10}\text{H}_7\text{Pr}^\alpha$, prepared by reducing α -naphthyl ethyl ketone, has b. p. $274\text{--}275^\circ$, and yields a *picrate*, m. p. $141\text{--}142^\circ$.

β -*n*-Propylnaphthalene, $\text{C}_{10}\text{H}_7\text{Pr}^\alpha$, prepared by the reduction of β -naphthyl ethyl ketone, has b. p. $277\text{--}279^\circ$, and yields a *picrate*, m. p. $90\text{--}92^\circ$.

The β -propylnaphthalene prepared by Roux (Abstr., 1888, 1305) by the interaction of *n*-propyl bromide and a carbon disulphide solution of naphthalene in presence of aluminium chloride, is probably β -*iso*-propylnaphthalene, and results in consequence of isomeric change caused by the aluminium chloride.

α -*n*-Butylnaphthalene, $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Pr}^\alpha$, obtained by reducing α -naphthyl propyl ketone, has b. p. $281\text{--}283^\circ$, and forms a *picrate*, m. p. $104\text{--}106^\circ$.

β -*n*-Butylnaphthalene, $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Pr}^\alpha$, prepared by the reduction of

β -naphthyl propyl ketone, has b. p. 283—285°, and yields a *picrate*, m. p. 71—74°.

The β -butylnaphthalene, b. p. 280°, prepared by Wegscheider (Abstr., 1884, 1185) and by Baur-Thurgau (Abstr., 1894, i, 468) by the action of *isobutyl* chloride or bromide on naphthalene dissolved in carbon disulphide in presence of aluminium chloride, probably contains the tertiary butyl group; its *picrate* has m. p. 96°. T. H. P.

Equilibrium of Hydrogenation. MAURICE PADOA and UGO FABRIS (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 125—132. Compare this vol., i, 255).—The authors have made experiments to ascertain whether hydrogenated hydrocarbons, capable of giving up their hydrogen in several stages, can be made to do so by heating in presence of nickel at suitable temperatures.

When phenanthrene is hydrogenated in presence of nickel at 200°, dihydrophenanthrene and tetrahydrophenanthrene are obtained; at 175—200°, α -tetrahydrophenanthrene is formed; at 175°, dodecahydrophenanthrene is given, and at 150° a small quantity of a liquid which does not form a *picrate* and was not identified (compare Schmidt and Mezger, Abstr., 1907, i, 1022).

Dodecahydrophenanthrene only loses its hydrogen when heated with nickel at about 220°, at which temperature hexahydrophenanthrene also loses hydrogen, forming gaseous hydrocarbons and β -tetrahydrophenanthrene. At 280°, tetrahydrophenanthrene loses its hydrogen, yielding phenanthrene. In a closed tube at 250°, dodecahydrophenanthrene yields phenanthrene and gaseous hydrocarbons; at 330°, tetrahydrophenanthrene yields dihydrophenanthrene and gaseous hydrocarbons.

When heated in an open tube, decahydronaphthalene begins to lose hydrogen at 250°, naphthalene and gaseous hydrocarbons being formed. In a closed tube at 250°, decahydronaphthalene undergoes little change; at 300°, naphthalene is formed, together with gaseous hydrocarbons. When heated in a closed tube at 250° in presence of nickel, tetrahydronaphthalene is only partially dehydrogenated, gaseous hydrocarbons being formed, and probably also benzene or its homologues.

When decahydrofluorene is heated with nickel in an open tube at 250°, a slow evolution of gas is observed; at 300°, a more copious evolution of gas, mostly hydrogen, occurs. At 300° in a closed tube, hydrogen and gaseous hydrocarbons are evolved.

In an open tube at 250°, *cyclohexene* gives a large amount of gas, but in a closed tube at the same temperature, very little gas, mainly methane, is formed.

Thus, with hydrocarbons yielding several hydrogenated products, those most readily dehydrogenated by the action of nickel are those containing most hydrogen. Of the hydrocarbons examined, the only ones not attacked in this way are tetrahydronaphthalene at ordinary pressure and tetra- and di-hydrophenanthrene under ordinary or increased pressure. The pressure has a marked influence on the dehydrogenating action of nickel, increased pressure generally causing increased action; with tetrahydronaphthalene, however, hydrogen is

eliminated at ordinary pressure, and gaseous hydrocarbons at about three atmospheres pressure. Gradual elimination of the hydrogen of a highly hydrogenated hydrocarbon cannot, as a rule, be effected by gradual rise of temperature; further, the elimination of hydrogen commences only at a temperature considerably higher than that at which the inverse change begins, and is complete, yielding the least highly hydrogenated compound. Hydrogenation and the inverse phenomenon are thus two distinct processes; in some cases, nickel can effect both these changes, but in others, it only acts as a catalyst for the reaction in one direction. With increase of pressure, however, the maximum temperature at which hydrogenation is possible, and the minimum temperature necessary for the inverse change, approach one another, so that hydrogenation becomes possible at temperatures at which it does not take place under ordinary pressure. Under increased pressure, then, the phenomenon becomes one of equilibrium, both hydrogenation and dehydrogenation taking place. Whether the nature of the catalyst influences this equilibrium is unknown. T. H. P.

Triphenylindene and Some of its Derivatives. ELMER P. KOHLER (*Amer. Chem. J.*, 1908, 40, 217—233).—In the preparation of diphenylbenzylideneacetophenone by boiling α -bromotriphenylpropiofenone with alcoholic potash (Abstr., 1907, i, 1054), a small amount of 1-ethoxy-1:2:3-triphenylindene is produced. This is formed by loss of water from the bromo-ketone and substitution of ethoxyl for bromine in the bromoindene obtained, a process involving the shifting of the bromine atom from the α - to the β -position. 1-Bromo-1:2:3-triphenylindene, $C_6H_4 \begin{smallmatrix} \text{CBrPh} \\ \diagup \quad \diagdown \\ \text{CPh} \end{smallmatrix} \text{CPh}$, is prepared by heating α -bromotriphenylpropiofenone (for which an improved method of preparation is given; compare Abstr., 1906, i, 754) to 150—160°. It separates from ether in large, transparent plates, m. p. 129°, and forms with aluminium bromide a dark red, crystalline compound, $C_{27}H_{19}Br, AlBr_3$.

1-Hydroxy-1:2:3-triphenylindene, prepared by adding water or sodium acetate to a hot solution of the bromo-derivative in acetic acid, forms lustrous prisms, m. p. 129°; the methyl ether crystallises in tablets, m. p. 153°, and the ethyl ether separates in large, lustrous prisms, m. p. 172°. On oxidation with a glacial acetic acid solution of chromic acid, the latter furnishes phthalophenone, colourless tablets, m. p. 148° (Zincke, Abstr., 1876, i, 703, gives yellow plates, m. p. 146°). 1:2:3-Triphenyl-1-ethylindene is obtained by the action of magnesium ethyl bromide on bromotriphenylindene; it crystallises in plates, m. p. 108°, and, on oxidation with cold chromic and acetic acids, yields phenyl α -benzoylphenyl- α -phenyl-*n*-propyl ketone, $C_6H_4Bz \cdot CEtPhBz$, crystallising in large, shining tablets, m. p. 180°, and giving phthalophenone and *o*-benzoylbenzoic acid when boiled with the oxidising agent. When a solution of bromotriphenylindene in benzene is shaken with zinc amalgam and the red solution allowed to evaporate in dry air, triphenylindanyl peroxide, $(C_{27}H_{19}O)_2$, is formed. It crystallises in small, shining prisms, decomposing at about 155°. From its sulphuric acid solution, water precipitates some hydroxytriphenylindene and

alcohol, ethoxytriphenylindene. 1:2:3-*Triphenylindene* is prepared by treating an ethereal solution of the bromo-derivative with magnesium and a trace of iodine in an atmosphere of hydrogen and dissolving the excess of magnesium with hydrochloric acid. It crystallises from ether or acetone in large, colourless prisms, m. p. 135°. When treated with bromine vapour at 150—160°, the bromo-derivative is regenerated. On oxidation with chromic and acetic acids, at the ordinary temperature the chief product is the hydroxy-derivative, but when the mixture is boiled, phthalophenone is exclusively formed. 1:1:3-*Triphenylindene* is the hydrocarbon obtained by Vorländer and Siebert (Abstr., 1906, i, 346) from tetraphenylallene, and the constitution suggested by these authors is now shown to be correct. The oxidation product obtained by them is phthalophenone; when, however, the oxidation with chromic and acetic acids is carried out in the cold, *o*-benzoyltriphenylacetic acid, $C_6H_4Bz \cdot CPh_2 \cdot CO_2H$, is formed. This crystallises in small prisms, m. p. 230° (decomp.); the sodium salt crystallises in small, colourless prisms, m. p. 130° (decomp.).

J. C. C.

Studies in Nitration. III. Nitration of Aniline and of Certain of its *N*-Alkyl, *N*-Aryl, and *N*-Acyl Derivatives. J. BISHOP TINGLE and F. C. BLANCK (*J. Amer. Chem. Soc.*, 1908, 30, 1395—1412. Compare Abstr., 1907, i, 120; this vol., i, 408).—The authors have extended their work on nitration with 80% nitric acid (D 1.46) in presence of acetic, oxalic, trichloroacetic, or 92% sulphuric acid (D 1.83). Except when sulphuric acid is used, methyl- or ethylaniline yields tars, and the formation of tar was the general result of the nitration of dimethyl- or diethyl-aniline under similar conditions. Dimethylaniline, when nitrated in presence of a mixture of oxalic and acetic acid, gives *p*-nitrodimethylaniline. Formanilide yields *p*-nitroformanilide when nitrated in the presence of sulphuric acid, and, under the same conditions, acetanilide gives *m*-nitroacetanilide, but in the presence of oxalic or trichloroacetic acid, *p*-nitroacetanilide is formed. On nitrating benzanilide in the presence of sulphuric acid or a mixture of oxalic and acetic acids, the para-derivative is obtained, but in the presence of acetic acid the meta-derivative results. The products of nitration of a number of other anilides have not yet been identified.

J. C. C.

Iodination of *m*-Nitroaniline by means of Iodine and Potassium Iodate. WILHELM KÖRNER and BELASIO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 679—690).—*m*-Nitroaniline is readily iodinated by adding iodine dissolved in 25% aqueous potassium hydroxide to a solution of the base in hydrochloric acid containing potassium iodate; using 1 mol. of iodine per mol. of base, a mixed product is obtained containing 8% of 4-iodo-3-nitroaniline, 36% 6-iodo-3-nitroaniline, 17% 4:6-di-iodo-3-nitroaniline, and 39% of 2:4-di-iodo-3-nitroaniline. The structure of these substances follows from the facts given below.

4-Iodo-3-nitroaniline crystallises from alcohol in orange needles, m. p. 142°, and gives an *acetyl* derivative, m. p. 136.5°; the two substances are isomorphous with 4-bromo-3-nitroaniline and its acetyl

derivative respectively. On replacing the amino-group by hydrogen, *o*-iodonitrobenzene is obtained; on replacing the same group by iodine, 1:4-di-iodo-2-nitrobenzene (Brenans, Abstr., 1902, i, 673) is formed.

6-Iodo-3-nitroaniline crystallises from alcohol in orange-yellow needles, m. p. $160\cdot4^{\circ}$, and is convertible into *p*-iodonitroaniline by the diazo reaction. 6-Iodo-3-nitroacetanilide crystallises from alcohol in slender, white needles, m. p. 199° .

2:4-Di-iodo-3-nitroaniline (Brenans, Abstr., 1904, i, 661), m. p. 125° , gives an *acetyl* derivative crystallising in white, nacreous prisms, m. p. 168° .

4:6-Di-iodo-3-nitroaniline forms stellate aggregates of slender, pale yellow needles, m. p. 149° , and gives 1:3-di-iodo-4-nitrobenzene on eliminating the amino-group; replacing the same group by iodine, 1:2:4-tri-iodo-5-nitrobenzene, m. p. 178° , is obtained. This crystallises from carbon disulphide in yellow needles, and, on reduction with ferrous sulphate and ammonia, gives 2:4:5-tri-iodoaniline, which crystallises from a mixture of alcohol and ether in long, white, silky needles, m. p. $117\cdot8^{\circ}$, gives an *acetyl* derivative, m. p. $241\cdot5^{\circ}$, and, on eliminating the amino-group, is converted into the 1:2:4-tri-iodobenzene, m. p. $91\cdot4^{\circ}$; the latter substance is also obtained from 1:4-di-iodo-2-nitrobenzene by reduction and the diazo-reaction, thus confirming its structure. The same 1:2:4-tri-iodobenzene can also be obtained from 2:4-di-iodo-3-nitroaniline (*supra*) by replacing the amino-group by iodine, reducing the nitro-group, and then replacing the amino-radicle by hydrogen.

When 4-iodo-3-nitroaniline is iodinated by means of iodine and potassium iodate, 65% of the product consists of 2:4-di-iodo-3-nitroaniline and 35% of 4:6-di-iodo-3-nitroaniline.

1:2:3-Tri-iodobenzene is obtained by converting 2:4-di-iodo-3-nitroaniline into 1:3-di-iodo-2-nitrobenzene (Brenans, *loc. cit.*) by the diazo-reaction, reducing the product to 2:6-di-iodoaniline, m. p. 122° , and decomposing the diazo-sulphate derived from the latter by potassium iodide; 1:2:3-tri-iodobenzene crystallises in small, white prisms, m. p. 116° .

1:2:4:5-Tetraiodobenzene, obtained by replacing the amino-group of 2:4:5-tri-iodoaniline by iodine, crystallises from acetic acid or benzene in white needles, m. p. 254° .

1:3:4-Tri-iodo-2-nitrobenzene, prepared from 2:4-di-iodo-3-nitroaniline by the diazo-reaction, crystallises from carbon disulphide in long, white prisms, m. p. 137° , and, on reduction with ferrous sulphate and ammonia, gives 2:3:6-tri-iodoaniline, crystallising in stellate aggregates of needles and melting at $116\cdot8^{\circ}$. 1:2:3:4-Tetra-iodobenzene, obtained from this by the diazo-reaction, crystallises from carbon disulphide and melts at 136° . W. A. D.

[Preparation of 3-Chloro-4-aminodimethylaniline.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197035).—3-Chloro-4-aminodimethylaniline, white crystals, m. p. 42° , b. p. $158^{\circ}/15$ mm., is prepared by reducing the nitroso-derivative of 3-chlorodimethylaniline; its diazo-salt couples with 1:8-dihydroxynaphthalene:3:6-

disulphonic acid, giving rise to a blue colouring matter. 3-Chloro-4-aminodimethylaniline, colourless liquid, b. p. $285^{\circ}/760$ mm., forms a similar blue azo-dye.
G. T. M.

Characteristic Colour Reactions Produced by Sodium Hypobromite. WILLIAM M. DEHN and SILAS F. SCOTT (*J. Amer. Chem. Soc.*, 1908, 30, 1418—1423. Compare this vol., ii, 907).—Sodium hypobromite solution, either alone or preceded by ammonia, gives characteristic colorations with phenols and aromatic amines. The reactions of a large number of phenols, aromatic amines, and alkaloids are described. Isomeric compounds may readily be distinguished by this means.
J. C. C.

Action of Bromine and Chlorine on Phenols. Substitution Products, ψ -Bromides, and ψ -Chlorides. XXIII. Action of Bromine on Di-*p*-hydroxyphenylmethylethylmethane; ψ -Bromides and Quinones of *p*-sec.-Butylphenol. THEODOR ZINCKE and J. GOLDEMANN (*Annalen*, 1908, 362, 201—220. Compare Zincke and von Hohorst, *Abstr.*, 1907, i, 614).—The interesting results obtained during the investigation on the behaviour of di-*p*-hydroxyphenylmethylethylmethane towards bromine (compare Zincke and Grütters, *Abstr.*, 1906, i, 172) have led to a similar investigation on di-*p*-hydroxyphenylmethylethylmethane. The two compounds behave in the same manner; the heptabromide obtained from the higher homologue is, however, far more stable than the corresponding compound derived from the lower homologue.

Di-*p*-hydroxyphenylmethylethylmethane, $\text{CMeEt}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, is prepared by the action of hydrogen chloride on a mixture of methyl ethyl ketone (1 part) and phenol (3 parts); it crystallises in colourless needles or prisms, m. p. 124 — 125° ; the *dibenzoate*, $\text{C}_{30}\text{H}_{26}\text{O}_4$, crystallises in white needles, m. p. 140 — 141° ; the *diacetate* could not be obtained in a solid state.

3 : 5 : 3' : 5'-Tetrabromo-di-*p*-hydroxyphenylmethylethylmethane,
 $\text{CMeEt}(\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2$,

prepared by the action of bromine in glacial acetic acid on the parent phenol, crystallises in thick, white needles, m. p. 155° ; the *diacetate*, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Br}_4$, crystallises in white needles, m. p. 174° . The tetrabromide is converted by nitric acid (D 1.4—1.5) in acetic acid into 2 : 6-dibromo-4-nitrophenol, $\text{C}_6\text{H}_3\text{O}_3\text{NBr}_2$, m. p. 139 — 140° , and 2-bromo-4 : 6-dinitrophenol, pale yellow needles, m. p. 118 — 119° . Boiling nitric acid converts the tetrabromide into picric acid.

3 : 3'-Dibromo-5 : 5'-dinitro-di-*p*-hydroxyphenylmethylethylmethane,
 $\text{C}_{16}\text{H}_{14}\text{O}_6\text{N}_2\text{Br}_2$,

is formed by adding solid sodium nitrite to a solution of the tetrabromide in glacial acetic acid; it forms small, compact, yellow crystals, m. p. 146 — 147° , and yields soluble, yellowish-red alkali and ammonium salts and insoluble, intensely red barium and calcium salts; the *diacetate*, $\text{C}_{20}\text{H}_{18}\text{O}_8\text{N}_2\text{Br}_2$, crystallises in yellowish-white needles, m. p. 144 — 145° .

ψ -*p*-Tribromo-sec.-butyltribromophenol (ψ -hexabromo-*p*-sec.-butyl-

phenol), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}=\text{CH} \end{smallmatrix} \text{CH} \cdot \text{CBrEt} \cdot \text{CHBr}_2$, is formed together with tribromophenol when the tetrabromide described above is treated with bromine at the ordinary temperature; it crystallises in small, colourless, glistening prisms, m. p. 154—155°. *Acetylhexabromo-p-sec.-butylphenol*, $\text{C}_{12}\text{H}_{10}\text{O}_2\text{Br}_6$, crystallises in colourless prisms, m. p. 142°.

p-Dibromo-sec.-butylidenetribromoquinone (*pentabromo-sec.-butylidenequinone*), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}=\text{CH} \end{smallmatrix} \text{C}:\text{CEt} \cdot \text{CHBr}_2$, prepared by shaking an ethereal solution of the hexabromide just described with a 10% aqueous solution of sodium acetate, crystallises in yellow prisms, m. p. 182—183°. It is converted by acetic anhydride and strong sulphuric acid at the ordinary temperature into *p-α-dibromo-β-acetoxy-sec.-butyltribromophenyl acetate*, $\text{OAc} \cdot \text{C}_6\text{HBr}_3 \cdot \text{CEt}(\text{OAc}) \cdot \text{CHBr}_2$, which crystallises in colourless, glistening prisms or plates, m. p. 164—165°.

ψ-p-Tribromo-sec.-butyltetrabromophenol (*ψ-heptabromo-p-sec.-butylphenol*), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CH} \cdot \text{CBrEt} \cdot \text{CHBr}_2$, is formed together with tribromophenol by the action of bromine on the tetrabromide described above at 100°; it crystallises in brilliant, colourless needles, m. p. 190—191° (decomp.); the *acetate*, $\text{C}_{12}\text{H}_9\text{O}_2\text{Br}_7$, crystallises in colourless, glistening prisms, m. p. 130—131°.

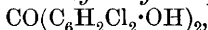
p-Dibromo-sec.-butylidenetetrabromoquinone (*hexabromo-sec.-butylidenequinone*), $\text{CO} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{C}:\text{CEt} \cdot \text{CHBr}_2$, may be prepared by shaking an ethereal solution of the heptabromide with an aqueous solution of sodium carbonate, but not sodium acetate; it is obtained in a purer state by boiling a solution of the heptabromide in benzene with anhydrous sodium carbonate; it crystallises in small, yellow prisms, m. p. 174—175°. Acetic anhydride and concentrated sulphuric acid convert it into *α-dibromo-β-acetoxy-p-sec.-butyltetrabromophenyl acetate*, $\text{OAc} \cdot \text{C}_6\text{HBr}_4 \cdot \text{CEt}(\text{OAc}) \cdot \text{CHBr}_2$; it forms small, granular crystals, which soften at 70°, m. p. 90°. W. H. G.

Action of Bromine and Chlorine on Phenols; Substitution Products, ψ-Bromides, and ψ-Chlorides. XXIV. Tetrachloro- and Tetrabromo-dihydroxybenzhydrol and their Transformation Products. THEODOR ZINCKE and E. BIRSCHER (*Annalen*, 1908, 362, 221—241. Compare preceding abstract).—It has been shown by Zincke and Krügener (*Abstr.*, 1904, i, 401) that a hexabromohydroxybenzylidenequinone can be prepared from 2 : 3 : 5 : 2' : 3' : 5'-hexabromo-4 : 4'-dihydroxybenzhydrol. Attempts were therefore made to prepare, by similar means, a hydroxybenzylidenequinone, but without success, since 4 : 4'-dihydroxybenzhydrol could not be prepared (compare von Baeyer and Burkhardt, *Abstr.*, 1882, 657). 3 : 5 : 3' : 5'-Tetrabromo-4 : 4'-dihydroxybenzhydrol and the corresponding tetrachloro-compound were, however, prepared, and were found to behave like the hexabromo-derivative.

3 : 5 : 3' : 5'-Tetrabromo-4 : 4'-dihydroxybenzophenone has m. p. 225—226°; von Baeyer and Burkhardt give m. p. 213—214° (*loc. cit.*)

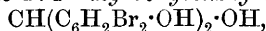
It is converted by bromine at 150—160° into pentabromophenol, and by nitric acid in acetic acid into 2-bromo-4:6-dinitrophenol. 3:3'-*Dibromo-5:5'-dinitro-4:4'-dihydroxybenzophenone*, $C_{13}H_6O_7N_2Br_2$, is prepared by adding solid sodium nitrite to a solution of the tetrabromide in glacial acetic acid; it crystallises in yellow needles, m. p. 246°, and forms orange alkali salts; the *diacetate*, $C_{17}H_{10}O_9N_2Br_2$, forms small, compact, pale yellow crystals, m. p. 165°.

3:5:3':5'-*Tetrachloro-4:4'-dihydroxybenzophenone*,



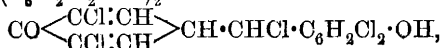
obtained by passing chlorine into a solution of 4:4'-dihydroxybenzophenone in acetic acid, crystallises in colourless leaflets or needles, m. p. 231—232°; the *diacetate*, $C_{17}H_{10}O_5Cl_4$, forms slender needles, m. p. 196—197°.

3:5:3':5'-*Tetrabromo-4:4'-dihydroxybenzhydrol*,



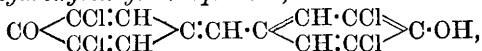
is obtained by reducing the tetrabromodihydroxybenzophenone with zinc dust and acetic acid; it crystallises in colourless needles, m. p. 173—174° (decomp.), and is oxidised by bromine or calcium hypobromite to the parent substance.

3:5:3':5'-*Tetrachloro-4:4'-dihydroxybenzhydrol*, $C_{13}H_8O_3Cl_4$, crystallises in small, compact needles, m. p. 179° (decomp.); the *triacetate*, $C_{19}H_{14}O_6Cl_4$, crystallises in small, glistening plates, m. p. 123—124°. Tetrachlorodihydroxybenzhydrol is converted by a solution of hydrogen chloride in glacial acetic acid into ψ -pentachloro-*p*-dihydroxydiphenylmethane, $CHCl(C_6H_2Cl_2 \cdot OH)_2$ or



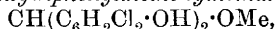
crystallising in colourless needles, m. p. 134—135°. It is reduced by zinc and hydrogen chloride in ethereal acetic acid to tetrachloro-*p*-dihydroxydiphenylmethane. The *diacetate*, $CHCl(C_6H_2Cl_2 \cdot OAc)_2$, prepared by the action of acetyl chloride on the ψ -pentachloride, crystallises in small, thick, colourless needles, m. p. 93°.

Tetrachlorohydroxybenzylidenequinone,

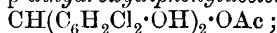


prepared by shaking with warm water a solution of the ψ -pentachloride in a mixture of benzene and light petroleum, is obtained as a red powder, which sinters at 200°, m. p. about 220°. The product so obtained is not quite pure, and apparently contains $1H_2O$, which is slowly liberated in a vacuum at 80—90°; it quickly becomes yellowish-white under the action of light, due to the absorption of water. The sodium salt is deep violet.

*Tetrachloro-*p*-dihydroxydiphenylmethoxymethane*,



is formed by dissolving the ψ -pentachloride described above in methyl alcohol; it crystallises in thick, colourless needles, m. p. 142°; the *diacetate*, $C_{18}H_{14}O_5Cl_4$, forms small prisms or plates, m. p. 155°. The ψ -pentachloride is converted by boiling acetic acid and sodium acetate into *tetrachloro-*p*-dihydroxydiphenylacetoxymethane*,



it forms compact, colourless crystals, m. p. 171° (decomp.); the *sodium* salt is brownish-red with a green reflex.

ψ -Pentabromo-*p*-dihydroxydiphenylmethane, $\text{CHBr}(\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2$, obtained by the addition of hydrogen bromide to the tetrabromodihydroxybenzhydrol described above, crystallises in small, colourless plates, m. p. 164 — 165° . It is not converted by acetic anhydride into the normal acetyl derivative, but into *tetrabromo-p-dihydroxybenzhydrol triacetate*; this substance could not be obtained pure.

Tetrabromohydroxybenzylidenequinone, $\text{O}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH}$, prepared by adding water to a solution of the ψ -pentabromide in acetone, is a red powder, m. p. 205° ; the *sodium* salt is deep violet. The tetrabromoquinone, when warmed with aqueous acetone, readily combines with water, forming the corresponding tetrabromodihydroxybenzhydrol. It is also converted by methyl alcohol into *tetrabromodihydroxydiphenylmethoxymethane*, $\text{CH}(\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2\cdot\text{OMe}$, colourless crystals, m. p. 143 — 144° .
W. H. G.

Oxidation of *iso*Eugenol. Dehydrodi*iso*eugenol. HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1908, 147, 247—249; *J. Pharm. Chim.*, 1908, [vi], 28, 193—199. Compare *ibid.*, 146, 1413).—When *iso*eugenol (20 c.c.), dissolved in 95% alcohol (180 c.c.), is treated with 40 c.c. ferric chloride solution (D 1.26) and with 120 c.c. of water, the greenish-blue mixture gradually becomes lighter in colour, and deposits light rose-coloured needles, which become colourless when washed with alcohol. The substance crystallises in long, colourless needles or rosettes of flat plates, m. p. 133° , which dissolve in alkali hydroxide solutions. The alcoholic solution gives a greenish-blue coloration with ferric chloride. Results of analysis and a cryoscopic determination of the molecular weight indicate that the substance is *dehydrodiiso*eugenol, $\text{C}_{20}\text{H}_{22}\text{O}_4$. The oxidation can be effected with ferric chloride in aqueous solution, but with less satisfactory results, and by the action of a current of air on an aqueous solution of the phenol containing a small proportion of a maceration of *Russula delica* in glycerol.

*Dimethyldehydrodiiso*eugenol, obtained by the action of methyl sulphate on the phenol in the presence of potassium hydroxide, crystallises in thin, nacreous, colourless lamellæ, m. p. 126° (corr.).

*Diacetyldehydrodiiso*eugenol, prepared by heating *dehydrodiiso*eugenol with acetic anhydride and fused sodium acetate, forms dense, massive, white crystals, m. p. 114° (corr.).

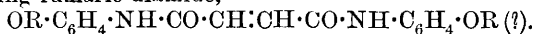
*Dibenzoyldehydrodiiso*eugenol, obtained by treating the phenol with benzoyl chloride in the presence of potassium hydroxide, crystallises in spheres of colourless, radiate needles, m. p. 119 — 120° (corr.).

The three ethers are insoluble in water and alkalis, do not give any coloration with ferric chloride, but reduce an aqueous solution of potassium permanganate.
E. H.

Maleic and Fumaric Derivatives of *p*-Aminophenols. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 635—641).—In benzene solution, maleic anhydride, like other anhydrides of dibasic

acids, reacts with *p*-aminophenols, forming additive compounds, substituted amic acids, which, unlike the corresponding compounds formed with saturated aliphatic and aromatic anhydrides, are yellow and give a violet coloration with ferric chloride in aqueous-alcoholic solution when the hydrogen of the phenolic hydroxyl is replaced by an alkyl radicle. It is hence probable that these amic acids have the enolic constitution $\text{OR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$. They do not, however, yield substituted carbamates when treated with phenyl-carbimide in presence of toluene in the cold, whilst, when heated, decomposition occurs with formation of maleic anhydride and a mono-substituted diphenylcarbamide: $\text{OR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H} + \text{NPh} : \text{CO} = \begin{array}{c} \text{CH} \cdot \text{CO} \\ || \\ \text{CH} \cdot \text{CO} \end{array} \text{O} + \text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OR}$. This reaction does not exclude the possibility of the presence of a hydroxyl group, since hydroxylic compounds are known which do not react with phenyl-carbimide, and it is also possible that the above reaction represents the decomposition of the carbamate at the high temperature used.

When maleic anhydride or acid is fused with a *p*-aminophenol at $125-130^\circ$, a small quantity of the maleinamate or fumaramate of the aminophenol is formed, together with a large proportion of the corresponding fumaric diamide,



These compounds may undergo transformation into the enolic forms, $\text{OR} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{C}(\text{OH}) : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OR}$, and they can, indeed, be obtained in two modifications, one white and the other yellow. But these two forms can be readily converted into one another, the white into the yellow by trituration in a mortar, and the yellow into the white by the addition of water to its sulphuric acid solution, so that they are best regarded as physical or enantiotropic isomerides. That these compounds are fumaric derivatives is shown by the fact that they are also obtained by heating the acid or normal fumarates of the amino-phenols.

When heated, the amic acids obtained from maleic anhydride and *p*-aminophenols yield, not the corresponding imides, but fumaric diamides. The imides of these amic acids, which can be obtained in presence of dehydrating agents, cannot be converted into their enantiotropic forms either mechanically or by crystallisation, and, even at 360° , are not appreciably decomposed or converted into the isomeric compounds. But when the white imides are kept fused at $130-140^\circ$ in a current of dry carbon dioxide, they are partly transformed into yellow isomeric imides, which have higher melting points than the white modifications, and can be readily obtained by heating the corresponding maleinamino-acids at $170-180^\circ$ in a stream of dry carbon dioxide. Since mixtures of these imides melt at a lower temperature than either separately, they are not enantiotropic forms, but chemical isomerides. Assuming that the action of acetyl chloride or phosphoryl chloride on amic acids yields asymmetric imides or *iso*-imides (compare Hoogewerff and van Dorp, Abstr., 1893, i, 599; 1894,

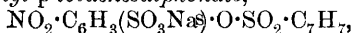
i, 594), the white imides would have the constitution $\begin{array}{c} \text{CH} : \text{C} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OR} \\ || \quad > \text{O} \\ \text{CH} \cdot \text{CO} \end{array}$,

and the yellow ones, $\begin{matrix} \text{CH}\cdot\text{CO} \\ | \\ \text{CH}\cdot\text{CO} \end{matrix} > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$. The yellow imides dissolve in alkali alkoxide solutions, giving a faint yellow coloration, whilst the white isomerides yield an intense violet coloration, due to the formation of additive products containing 1 mol. of imide to 1 mol. of alkoxide.

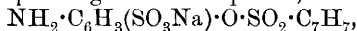
Acetic anhydride decomposes the maleinamic acids into maleic anhydride and acetyl derivatives of the aminophenols. The phenacetin obtained in this way from *p*-ethoxyphenylmaleinamic acid always contains an orange-yellow compound, m. p. 155—157°, with which it forms a solid solution. T. H. P.

Preparation of 2-Aminophenol-5-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 197496).—The sulphonation of *o*-aminophenol with fuming sulphuric acid yields exclusively 2-aminophenol-4-sulphonic acid. An isomeric 2-aminophenol-5-sulphonic acid, white needles, is obtained by sulphonating carboxy-*o*-aminophenol and hydrolysing the product with aqueous sodium hydroxide. The diazo-derivative, yellow needles, is only moderately soluble in water, and, on boiling with alcohol, yields phenol-3-sulphonic acid. G. T. M.

Preparation of Arylsulphonates of 2-Aminophenol-4-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 195226).—Sodium 4-sulpho-2-nitrophenyl-*p*-toluenesulphonate,



prepared from sodium *o*-nitrophenol-4-sulphonate and *p*-toluenesulphonyl chloride in aqueous sodium hydroxide, crystallises in yellow leaflets. The corresponding amino-compound,



leaflets, is obtained by reducing the foregoing compound with iron and dilute acetic acid, and treating the products with sodium carbonate; it forms a very reactive, insoluble diazo-derivative. G. T. M.

Preparation of 3-Nitro-6-aminophenol-4-sulphonic Acids. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 197807).—6-Chloro-2-aminophenol-4-sulphonic, 2-amino-*o*-cresol-4-sulphonic, and 2-amino-*p*-cresol-2-sulphonic acids readily yield carbonyl derivatives on treatment with carbonyl chloride in alkaline solutions. The sodium salts of these carbonyl compounds are colourless, soluble, crystalline substances, which, on nitration, furnish nitro-derivatives containing the nitro-group in the para-position to the amino-group. These products, on hydrolysis with aqueous calcium hydroxide, give rise to 2-chloro-3-nitro-6-aminophenol-4-sulphonic, 6-nitro-3-amino-*o*-cresol-5-sulphonic, and 2-nitro-5-amino-*p*-cresol-3-sulphonic acids, which form yellow, soluble alkali salts and diazo-derivatives. G. T. M.

Preparation of the Leuco-derivative of Colouring Matter obtained by Oxidation from 3-Hydroxy-(1)-thionaphthens. KALLE & Co. (D.R.-P. 196501).—When reduced with alkali hyposulphite or dextrin, the colouring matter derived from 3-hydroxy-(1)-thionaphthen furnishes a leuco-derivative, soluble in alkalis, but

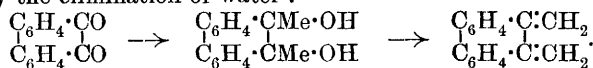
precipitated by acids. The leuco-compound is sparingly soluble in water, and oxidises only slowly to the colouring matter on exposure to the atmosphere; it forms a soluble sodium salt, crystallising in lustrous, colourless leaflets. G. T. M.

Leucoalizarin (1:2-Dihydroxyanthranol). EUGÈNE GRAND-
MOUGIN (*Chem. Zentr.*, 1908, i, 2179; from *Rev. Gén. Mat. color.*, 1908,

12, 44).—This substance, $C_6H_4 \begin{smallmatrix} C(OH) \\ C(OH) \end{smallmatrix} > C_6H_2(OH)_2$, is prepared by reducing alizarin in very dilute sodium hydroxide solution by means of sodium hydrogen sulphite; it crystallises in small, brown plates, m. p. 150°. J. V. E.

Preparation of *o*-Nitrosobenzyl Alcohol and Anthranil. KALLE & Co. (D.R.-P. 194811).—*o*-Nitrotoluene when heated with aqueous sodium hydroxide at 170°, and subsequently distilled, furnishes an oil which, on treatment with alcoholic mercuric chloride, gives rise to a white, flocculent precipitate, which probably consists of the mercurichloride of *o*-nitrosobenzyl alcohol, from which the latter substance can be liberated by the successive action of concentrated hydrochloric acid and water. The filtrate from the foregoing precipitate contains anthranil, which is set free by strong hydrochloric acid from the concentrated solution. G. T. M.

Ditertiary Alcohols from Phenanthraquinone. THEODOR ZINCKE and W. TROPP (*Annalen*, 1908, 362, 242—259).—From the investigations of Zincke and Buff (Abstr., 1905, i, 880), it seemed probable that quinonoid hydrocarbons might be obtained from the ditertiary alcohols derived from phenanthraquinone (dihydroxydialkyl-dihydrophenanthrenes; compare Werner and Grob, Abstr., 1904, i, 864) by the elimination of water:



The hydroxy-derivatives do not, however, lose $2H_2O$, but pass into oxides with the elimination of $1H_2O$. That the compounds so formed

have the formula $\begin{array}{c} C_6H_4 \cdot CR \\ C_6H_4 \cdot CR \end{array} > O$ is supported by the fact that they do not yield hydrazones or oximes, and are converted on reduction into 9:10-dialkylphenanthrenes. The latter are oxidised by chromic acid to diketones, $R \cdot CO \cdot C_6H_4 \cdot C_6H_4 \cdot CO \cdot R$; the same diketones are formed by oxidising the parent dihydroxy-compounds. Dihydroxydimethyldihydrophenanthrene is converted by phosphorus pentachloride into the corresponding oxide and a chloride which probably has the formula $\begin{array}{c} C_6H_4 \cdot CMeCl \\ C_6H_4 \cdot C : CH_2 \end{array}$. The analogous ethyl, propyl, and benzyl compounds, when similarly treated, yield only oxides.

9:10-Dihydroxydimethyldihydrophenanthrene, $C_{12}H_8 \begin{array}{c} CMe \cdot OH \\ CMe \cdot OH \end{array}$, prepared by adding an ethereal solution of phenanthraquinone to an

etheral solution of magnesium methyl iodide and treating the additive product so formed with dilute sulphuric acid, crystallises in large, colourless, pointed prisms, m. p. 164° ; neither an acetyl nor a benzoyl derivative could be prepared. It loses H_2O when treated with concentrated sulphuric acid in acetic acid, yielding the oxide,

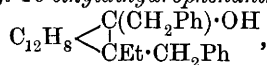
$\text{C}_{12}\text{H}_8 \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{CMe} \end{smallmatrix} \text{O}$, which crystallises in stout, colourless needles or prisms, m. p. 75° . The oxide is reduced by red phosphorus and hydriodic acid to 9:10-dimethylphenanthrene, $\text{C}_{16}\text{H}_{14}$, crystallising in colourless, pointed prisms, m. p. 139° . 9:10-Dihydroxydimethyldihydrophenanthrene is converted by phosphorus pentachloride into the oxide just described and a chloride, $\text{C}_{16}\text{H}_{13}\text{Cl}$, obtained as colourless, spear-shaped crystals, m. p. 155° . It loses hydrogen chloride when heated with an alcoholic solution of potassium hydroxide, yielding a substance which crystallises in white needles, m. p. $94\text{--}95^{\circ}$.

The following compounds are obtained by the same methods as the corresponding methyl derivatives.

9:10-Dihydroxydiethyldihydrophenanthrene, $\text{C}_{18}\text{H}_{20}\text{O}_2$, crystallises in microscopic, delicate needles, m. p. $120\text{--}122^{\circ}$. The corresponding oxide, $\text{C}_{18}\text{H}_{18}\text{O}$, crystallises in large plates or long, thin prisms, m. p. 65° ; it yields, on reduction, 9:10-diethylphenanthrene (?), crystallising in silvery leaflets, m. p. $105\text{--}106^{\circ}$.

9:10-Dihydroxydipropyldihydrophenanthrene, $\text{C}_{20}\text{H}_{24}\text{O}_2$, forms large, hard prisms, m. p. $155\text{--}156^{\circ}$. The oxide, $\text{C}_{20}\text{H}_{22}\text{O}$, crystallises in prisms, m. p. 83° ; it is not reduced by hydriodic acid and red phosphorus.

9:10-Dihydroxydibenzylidihydrophenanthrene, $\text{C}_{28}\text{H}_{24}\text{O}_2$, crystallises in asymmetric prisms, m. p. 175° . The oxide, $\text{C}_{28}\text{H}_{22}\text{O}$, forms compact needles and pointed prisms, m. p. 143° ; it is not attacked by phosphorus pentachloride under pressure at 150° , but is reduced by hydriodic acid and red phosphorus at 160° to phenanthrene. The oxide reacts with magnesium ethyl bromide, forming an additive product which, when treated with dilute sulphuric acid, yields 9-hydroxy-9:10-dibenzyl-10-ethyldihydrophenanthrene,



crystallising in slender, white needles, m. p. $186\text{--}187^{\circ}$. W. H. G.

Comparative Experiments on the Basicity and Strength of Acids and Phenols. ALFRED THIEL and HERMANN RÖMER (*Zeitsch. physikal. Chem.*, 1908, 63, 711—761. Compare Thiel, Schumacher, and Römer, Abstr., 1906, i, 22).—The method used by the authors consists in studying the changes in conductivity which result from the gradual addition of sodium hydroxide to a standard quantity (generally 1 millimolecule) of an acid in dilute solution (compare Miolati, Abstr., 1900, ii, 214; Küster and Grüters, Abstr., 1903, ii, 611; Küster, Grüters, and Geibel, Abstr., 1905, ii, 55). If the value of the conductivity is plotted against the number of c.c. of sodium hydroxide added, the curve obtained in the case of a strong monobasic acid falls rapidly to a minimum, which coincides with the neutralisation point.

If the monobasic acid is of medium strength, the curve falls a little to a rounded minimum and then rises to the neutralisation point, which is marked by a break in the curve; if the monobasic acid is very weak, no minimum at all is observed, the curve rising from the beginning, and the neutralisation point being marked by a break. It is pointed out that in the case of monobasic acids of medium strength, the weaker the acid the nearer must the minimum lie to the beginning of the curve. Each such acid must at the minimum point be dissociated to the extent of about 15%; the more dilute the solution in which any one such acid is examined the less is the distance between the point of minimum conductivity and the neutralisation point.

The authors discuss also the form of curve which is to be expected when a mixture of two monobasic acids of different strengths or a dibasic acid is gradually neutralised by sodium hydroxide. In the latter case, it is sometimes advantageous to titrate back with a strong acid, as the neutralisation point is then less liable to be obscured by hydrolysis. These more complicated types of curve are illustrated by the authors' experiments with hydrochloric acid + acetic acid, monochloroacetic acid + acetic acid, oxalic, fumaric, maleic, succinic, and phosphoric acids. It is noteworthy that phosphoric acid is found to behave as a dibasic acid (contrast Küster, Grütters, and Geibel, *loc. cit.*).

The authors have made an exhaustive study of the behaviour of aromatic hydroxylic compounds on the lines just indicated, and they draw conclusions as to the way in which the acidic character of the -OH group is modified by the introduction of other substituent groups into the molecule. The following are some of the main conclusions reached.

A compound containing two -OH groups in the *o*-position is monobasic, and the strength is only very slightly greater than that of the corresponding compound with one such group. When the second -OH group is in the meta- or para-position, the substance is dibasic, but the acidic character of the second group is exceedingly feeble. The introduction of nitro-groups markedly increases the acidic power of the -OH group, and the curves obtained by the gradual neutralisation of *o*-nitrophenol, 2:4-dinitrophenol, and picric acid may be taken as examples of the three types mentioned in the beginning of this abstract.

The introduction of a sulphonic group (as in sodium phenol-sulphonate) in the ortho- or para-position immensely strengthens the acidic character of the -OH group. In nitro-derivatives of the phenol-sulphonic acids, the acidic character of the -OH group is notably greater than in the corresponding nitrophenols. The -CHO group, as shown for example by the behaviour of salicylaldehyde, makes a phenol more distinctly acid. An -OH group in the ortho-position to a carboxyl group is indifferent; in the meta- and para-positions it has an appreciably acid character. For further information as to the influence of these substituents on the acidic character of one or more -OH groups, the original must be consulted.

In one or two favourable cases where the phenolic substance is an acid of medium strength, it is possible to calculate its dissociation constant from the position of the point of minimum conductivity. J. C. P.

Influence of Catalytic Agents in Ester Formation. Hydrogen Bromide and Zinc Bromide in the Formation of Ethyl Benzoate. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], **26**, 281—289).—The rate of esterification of benzoic acid by ethyl alcohol in presence of hydrogen chloride and hydrogen bromide has been studied by Goldschmidt (*Abstr.*, 1896, i, 229) at a temperature of 25°. The results obtained at this temperature were so nearly alike that the conclusion was drawn that hydrogen chloride and hydrogen bromide are of equal efficiency under the conditions of the experiments. Goldschmidt and Sunde (*Abstr.*, 1906, ii, 219) and other authors have recorded physico-chemical measurements which seem to indicate that the efficiency of a catalytic agent depends on its concentration and its degree of dissociation in alcoholic solution.

In an investigation (this vol., i, 166) on the amount of ethyl benzoate formed from benzoic acid in presence of sulphuric acid, hydrogen chloride, or hydrogen chloride and zinc chloride as catalytic agents, with different quantities of alcohol acting for different lengths of time, it was found that the amount of ester produced was increased by increasing the concentration of the catalysts up to a certain limit, but that beyond this point the quantity was decreased. It was also found that the yields of ester did not bear any relation to the degree of ionisation of the catalyst. In the present paper, the catalytic action of hydrogen bromide alone and in presence of zinc bromide at different temperatures on the formation of ethyl benzoate is compared with that of hydrogen chloride and zinc chloride.

The results show that hydrogen bromide varies in its efficiency as a catalytic agent according to its concentration and the temperature at which esterification takes place. The amount of ethyl benzoate formed increases with the time of reaction. Zinc bromide also exerts a catalytic action. The greater the amount of either catalyst present, the greater is the yield of ester. It is found that esterification is retarded by raising the temperature above a certain point, and that a similar effect is produced when hydrogen chloride and zinc chloride are employed, but in this case only at such temperatures as are most unsuitable for esterification. The failure of zinc bromide to act efficiently at the higher temperatures is due to the action of hydrogen bromide on alcohol to form ethyl bromide and water. Hydrogen chloride is therefore more efficient than hydrogen bromide as a catalyst for esterification, although, as Goldschmidt has shown, at as low a temperature as 25°, they are of equal efficiency. The amount of ester produced is not proportional to the concentration of the hydrogen ions. Although, in all cases, the esterification proceeds more completely as the amount of the catalytic agent is increased up to a certain limit, any further increase causes a reduction in the quantity of ester produced. This seems to be due to the fact that all the catalysts employed have a strong affinity for water, and consequently, when they are present in large quantities, absolute alcohol is not able to effect dehydration as thoroughly as is necessary for complete esterification.

E. G.

Influence of Catalytic Agents in Ester Formation. Effect of Certain Sulphates on Benzoic and Succinic Acids. ISAAC K. PHELPS, H. E. PALMER, and R. SMILLIE (*Amer. J. Sci.*, 1908, [iv], 26, 290—295).—It has been shown previously (Abstr., 1907, i, 823; this vol., i, 166) that almost theoretical yields of ethyl succinate can be obtained by the action of hydrogen chloride and alcohol on succinic acid, and that quantitative yields of ethyl benzoate can be obtained from benzoic acid when sulphuric acid is used as a catalytic agent. Bogojawlensky and Narbutt (Abstr., 1905, i, 864) have investigated the influence of various inorganic sulphates on the esterification of certain organic acids.

In the present paper, the effect of the hydrogen sulphates of potassium, ammonium, sodium, pyridine, and aniline on the esterification of benzoic and succinic acids is recorded, and the results are compared with those obtained with sulphuric acid. It is found that none of these acid sulphates is so efficient as sulphuric acid. The sodium salt is nearly equal as a catalyst, the ammonium salt is less efficient, the potassium salt considerably less, whilst the pyridine and aniline salts are very poor catalysts. The pyridine salt is more efficient than the aniline salt in the esterification of succinic acid, but in the case of benzoic acid they produce nearly equal effects.

The catalytic action of these sulphates might be due to the dissociation of the sodium and potassium salts into the neutral sulphates and sulphuric acid, and of the pyridine and aniline sulphates into the free base and sulphuric acid, but this explanation fails in the case of the latter salts. Since, in most cases, the salt does not go into solution and an increase in the quantity of salt employed produces a marked effect, it is considered possible that the undissolved salts behave as contact agents. This question is being further investigated.

E. G.

Influence of Catalytic Agents in Ester Formation. Esterification of Benzoic Acid with Certain Chlorides. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], 26, 296—300).—The catalytic actions at 100—110° of the chlorides of sodium, potassium, lithium, ammonium, copper, calcium, strontium, barium, mercury, aluminium, manganese, tin, lead, antimony and bismuth in presence of small quantities of hydrogen chloride are compared with those of zinc chloride with hydrogen chloride and of hydrogen chloride alone.

The results show that zinc chloride is the most efficient, although copper and tin chlorides are not much less so. The higher chlorides of bismuth, antimony, and mercury are about equally efficient, and nearly as active as zinc, copper, and tin chlorides. Small quantities of calcium chloride are without effect, but large quantities hinder esterification to a marked extent. Strontium chloride retards the action to a smaller degree, and barium chloride hinders esterification but slightly. The chlorides of manganese and potassium, and the lower chlorides of lead and mercury, seem to be without effect. Sodium chloride hinders esterification slightly, lithium chloride more. ammonium chloride still

more, and aluminium chloride more than any of the chlorides studied, except calcium chloride when present in large quantities. E. G.

New Method of Preparing Mixed Organic Acid Anhydrides. J. BOUGAULT (*Compt. rend.*, 1908, 147, 249—251).—It has been shown previously (Abstr., 1905, i, 9; 1906, i, 848; this vol., i, 537) that an aqueous solution of sodium phenylisocrotonate (or generally the salt of any β -ethylenic acid) when treated with iodine gives an iodolactone, and that in the presence of a large excess of sodium carbonate the product consists of benzoylacrylic acid (this vol., i, 179, 269). It is now stated that if an aqueous solution of sodium phenylisocrotonate containing excess of sodium carbonate is treated with an equivalent quantity of an aromatic acid and then with iodine, the mixed anhydride of benzoylacrylic acid and the acid added is precipitated. In this manner the following anhydrides have been prepared: *Benzoylacrylic benzoic anhydride*, $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{COPh}$, slender colourless needles, m. p. 158° , which are not attacked by cold sodium carbonate solution, but are slowly acted on when heated on a water-bath with the alkali carbonate, acetophenone being evolved. Alkali hydroxide acts more rapidly. Addition of a small quantity of sodium carbonate solution to the boiling alcoholic solution of the anhydride causes the formation of ethyl benzoate. The anhydride is completely hydrolysed by fifteen minutes' boiling with 50% acetic acid. In the presence of zinc, the latter reaction gives benzoic and benzoylpropionic acids. *Benzoylacrylic cinnamic anhydride*, $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}:\text{CHPh}$, has m. p. 154° ; *benzoylacrylic phenylacetic anhydride*, $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, m. p. 118° ; and *benzoylacrylic benzoylpropionic anhydride*, $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{COPh}$, m. p. 156° . The essential conditions of the reaction seem to be the insolubility of the anhydride and the nascent state of the benzoylacrylic acid.

The author points out that the exclusion of water and alkali, usually essential to the preparation of anhydrides, is unnecessary in this method. E. H.

Strength of the Second Stage [of the Dissociation] of Phenolcarboxylic and Phenolsulphonic Acids. ALFRED THIEL (*Zeitsch. anorg. Chem.*, 1908, 59, 371—372).—In reference to the observations of Ley and Erler (this vol., i, 177) and Obermiller (this vol., i, 634), it is pointed out that, whilst the approximation of the carboxyl group to the phenolic hydroxyl results in a diminution of the acidity of the latter group, the reverse holds good in reference to the influence of the sulphonic group on the acidity of phenolic hydroxyl. As a consequence of this relationship, the strength of the second stage of the hydrogen dissociation of *o*-phenolsulphonic acid is greater than that of *p*-phenolsulphonic acid. H. M. D.

Constitution of 1-Phenylnaphthalene-2:3-dicarboxylic Acid. JOHN E. BUCHER (*J. Amer. Chem. Soc.*, 1908, 30, 1244—1264).—Michael and Bucher (Abstr., 1898, i, 256) have shown that by the

action of acetic anhydride on phenylpropionic acid, 1-phenylnaphthalene-2:3-dicarboxylic anhydride is produced. This substance has also been studied by Linsler (Abstr., 1899, i, 916), Mauthey (Abstr., 1901, i, 31), and Linsler and Halvorsen (Abstr., 1902, i, 458). Stobbe (Abstr., 1907, i, 769) obtained the anhydride by the action of light on dibenzylidenesuccinic anhydride, and confirmed the constitution assigned to it by Michael and Bucher. In certain points, however, his conclusions differed from those of the latter authors, particularly with reference to the oxidation and reduction of the compound. A brief discussion of Stobbe's results has already been given (Michael and Bucher, this vol., i, 89). The results of a further study are now given in detail and confirm the previous work.

Stobbe (Abstr., 1907, i, 765) has stated that when 1-phenylnaphthalene-2:3-dicarboxylic acid is treated with concentrated sulphuric acid, a compound is produced which he termed *allochrysoketonecarboxylic acid*. It is now shown that this compound is isomeric with 1-phenylnaphthalene-2:3-dicarboxylic acid, and has the constitution $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{CO}-\text{C} \end{matrix} > \text{C}_{10}\text{H}_5(\text{CO}_2\text{H})$; it melts at 288° without decomposition, and forms potassium and sodium salts containing water of crystallisation. On oxidation with potassium permanganate, it yields a yellow *diphenyleneketonecarboxylic acid*, $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{CO}-\text{C} \end{matrix} > \text{C}_6\text{H}(\text{CO}_2\text{H})_3$, and when fused with potassium hydroxide is converted into a phenylnaphthalenedicarboxylic acid. The diphenyleneketonecarboxylic acid, on fusion with alkali hydroxide, yields a white *diphenyl-2:3:5:6'-tetracarboxylic acid*, $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_3 \cdot \text{C}_6\text{H}_4(\text{CO}_2\text{H})$, together with a small quantity of diphenyl-2:3:5:6-tetracarboxylic acid.

The action of acetic anhydride on piperonylpropionic acid, *o*-, *m*-, and *p*-chloro-, *o*- and *p*-bromo-, *m*- and *p*-nitro-, *p*-iodo-, and *p*-methoxyphenylpropionic acids has been studied. In each case an anhydride is produced which does not reduce alkaline permanganate solution, and is therefore a saturated compound, presumably a derivative of 1-phenylnaphthalene. The constitution of most of these compounds has been proved by transforming them into diphenyltetracarboxylic acid or by oxidising them to benzenepentacarboxylic acid.

*iso*Phthalic and terephthalic acids, when heated with acetic anhydride, are converted quantitatively into the corresponding *anhydrides*, which are almost insoluble in most organic solvents. E. G.

Esterification of Unsymmetrical Di- and Poly-basic Acids.

XVIII. Esterification of Dibasic Acids by Diazomethane. RUDOLF WEGSCHEIDER and HEINRICH GEHRINGER (*Monatsh.*, 1908, 29, 525—530. Compare Abstr., 1907, i, 850).—The acid (2 mols.) and diazomethane (1 mol.) react in ether. The main products are usually the normal ester and unchanged acid; in addition to these, 3-nitrophthalic acid, hemipinic acid, and nitroterephthalic acid yield small quantities of the α -methyl ester, whilst 4-hydroxyphthalic acid and camphoric acid give mixtures of the two acid esters. The method is unsuitable for the production of acid esters. C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.

XIX. Esterification of Phthalonic Acid. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 531—534).—A theoretical discussion of the partial esterification of phthalonic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, showing that the aliphatic carboxyl group, being the more strongly acidic, should be first esterified, a result which has been already established by Glogau (*Abstr.*, 1904, i, 673). C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.

XX. Methyl Esters of 3-Nitrophthalic Acid. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 535—539).—The m. p. of the α -methyl ester of 3-nitrophthalic acid ($\text{CO}_2\text{Me}:2$), dried at 100° , is given by different investigators as $144\text{--}145^\circ$ or $152\text{--}153^\circ$ (compare McKenzie, *Trans.*, 1901, 79, 1141). The suggestion of decomposition during dehydration is negatived by the fact that, after being maintained at 100° for 363 hours, the ester has practically the same m. p. as after fifteen hours' heating. Rapidity of heating in the m. p. determination or the existence of mixed crystals of the α and the β methyl esters is not the explanation of the difference. The author suggests the possibility of polymorphism, but satisfactory evidence of it was not obtainable.

The α methyl ester, m. p. $149\text{--}151^\circ$, forms short, monoclinic prisms containing H_2O [$a:b:c=0.5883:1:0.6731$]. The β ester ($\text{CO}_2\text{Me}:1$) forms anhydrous, monoclinic crystals [$a:b:c=0.2678:1:0.2260$].

C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids.

XXI. Nitrohemipinic Acid. RUDOLF WEGSCHEIDER and PETER VON RUŠNOV (*Monatsh.*, 1908, 29, 541—555).—Of the two carboxyl groups in hemipinic acid (3:4-dimethoxybenzene-1:2-dicarboxylic acid), that in position 2 is the more strongly acidic and the more subject to steric hindrance. By nitration, a nitro-group enters position 6, and in the resulting nitrohemipinic acid the two preceding characteristics are more pronounced in the carboxyl group in position 1, owing to the influence of the nitro-group. Partial esterification of the two acids by the same method gives, accordingly, acid esters in which different carboxyl groups have been attacked. Both acids yield chiefly the α methyl ester by the action of methyl alcohol on the anhydrides or from methyl iodide and the potassium hydrogen salts, whilst the β ester is the chief product of esterification by an alcohol and mineral acid. (In accordance with the authors' notation, the more strongly acidic carboxyl group is denoted by α ; this prefix, therefore, designates different carboxyl groups in the two acids in question.) The neutral esters of the two acids behave differently on partial hydrolysis; whilst dimethyl hemipinate yields entirely the α methyl ester, the neutral ester of 6-nitrohemipinic acid, which, contrary to expectation, is obtained without much difficulty by methyl-alcoholic hydrogen chloride, gives about equal quantities of the α and the β esters. Similarly, hemipinic acid and methyl alcohol at 100° give the α ester, whilst nitrohemipinic acid heated with methyl alcohol in an open vessel gives both α and β esters, the latter in larger amount.

[With LEO KUSY VON DÚBRAV.]—6-Nitrohemipinic acid, m. p.

155—156° (decomp.), is obtained by oxidising nitro-opianic acid by hot dilute, alkaline potassium permanganate, or, better, by nitrating hemipinic acid in glacial acetic acid at 90—100° by fuming nitric acid. *a*-Methyl 6-nitrohemipinate ($\text{CO}_2\text{Me}:1$) has m. p. 147—149°, and can also be obtained by nitrating *b*-methyl hemipinate. *b*-Methyl 6-nitrohemipinate ($\text{CO}_2\text{Me}:2$) has m. p. 115—117°.

Nitration of *a*-methyl hemipinate gives a substance, m. p. 142—144°, not identical with, but of the same composition as, *a*- or *b*-methyl nitrohemipinate. The substance, which is being investigated, is apparently a ψ -ester, $\text{NO}_2 \cdot \text{C}_6\text{H}(\text{OMe})_2 \begin{smallmatrix} \text{CO} \\ \text{C}(\text{OH})(\text{OMe}) \end{smallmatrix} \text{O}$, since it yields nitrohemipinic acid by hydrolysis. C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXII. Isomerism of Methyl Nitrohemipinates. RUDOLF WEGSCHEIDER and HUGO STRAUCH (*Monatsh.*, 1908, 29, 557—572).— ψ -Methyl 6-nitrohemipinate, m. p. 142—144° (preceding abstract), can also be obtained by nitrating either of the polymorphous forms of *a*-methyl hemipinate at 0° without a solvent. A by-product, which becomes the main product when the nitration is performed at 30—50°, is methyl dinitrodimethoxybenzoate, m. p. 89—90°, the orientation of which is being investigated.

That the ψ -ester is a derivative of 6-nitrohemipinic acid is proved by hydrolysis, the resulting acid being identical with this acid in all respects. (6-Nitrohemipinic anhydride, obtained by heating the acid at 160—165° in carbon dioxide, has m. p. 155°, not 145° as usually given.) The remarkable fact that 6-nitrohemipinic acid forms three acid methyl esters cannot be explained by polymorphism, since the three esters are precipitated unchanged by acidification of their solutions in alkalis. Experiments for the mutual interconversion of the esters have been unsuccessful. The author revives the old speculation of Roser and Anschütz that dicarboxylic acids may exist in the forms $\text{R}(\text{CO}_2\text{H})_2$ and $\text{R} \begin{smallmatrix} \text{C}(\text{OH})_2 \\ \text{CO} \end{smallmatrix} \text{O}$. This theory, unnecessary in the case

of the great majority of dicarboxylic acids, may serve to account for the occasional abnormally small affinity constants of some dibasic acids and acid esters, and is applicable to opianic and hemipinic acids. The former shows the conductivity of an aldehyde-acid, and yields both normal and ψ -esters. Nitro-opianic acid and its ester exist in the ψ -forms. The nearly related hemipinic acid shows no tendency to exist in the ψ -form. The introduction of the nitro-group, however, increases its tendency to the latter form, so that, whilst nitrohemipinic acid itself has the normal structure, it is capable of yielding a stable ψ -acid ester, $\text{NO}_2 \cdot \text{C}_6\text{H}(\text{OMe})_2 \begin{smallmatrix} \text{CO} \\ \text{C}(\text{OH})(\text{OMe}) \end{smallmatrix} \text{O}$. C. S.

Synthesis of Some Aromatic Acids. JOHAN F. EYKMAN (*Chem. Weekblad*, 1908, 5, 655—666. Compare this vol., i, 22).—A continuation of the author's work on the synthesis of aromatic acids by the action of aromatic hydrocarbons on unsaturated acids in presence of aluminium chloride. Most of the reactions were

carried out by maintaining the mixtures at 30° for about four weeks.

β -Phenyl-*n*-butyric acid, $\text{CPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (Schroeter, Abstr., 1907, i, 531), is obtained from crotonic acid and benzene; it has b. p. 140—145°/3 mm. It crystallises from light petroleum in monoclinic, columnar crystals [$a:b:c=1.22:1:1.08$; $\beta=90.52^\circ$], m. p. 37—38° (Schroeter: 39—40°). The *amide* forms colourless needles, m. p. 106—107°. The *anilide* has m. p. 136—137°. The refractometric constants of the acid are given. Toluene does not yield a similar condensation product with crotonic acid.

α -Phenyl- β -methylbutyric acid, $\text{CHMe}_2\cdot\text{CPh}\cdot\text{CO}_2\text{H}$, is obtained from $\beta\beta$ -dimethylacrylic acid and benzene. It separates from light petroleum in large crystals, m. p. 58—59° (freezing point, 57.4°). The constitution indicated is supported by the fact that the sodium salt has no action on benzaldehyde in presence of either acetic anhydride or the acid chloride, which points to the absence of the group $-\text{CH}_2\cdot\text{CO}_2\text{H}$, and therefore excludes the alternative formula $\text{CPhMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The *amide* has m. p. 68°; the *anilide* 121°. Nitric acid yields a crystalline nitro-acid, m. p. 175° (from alcohol). With toluene, $\beta\beta$ -dimethylacrylic acid yields an *acid*, b. p. 178°/21 mm., which has not been obtained crystalline.

A phenylhydrotiglic acid is formed from tiglic acid and benzene. Crystallised from a mixture of benzene and light petroleum, it has m. p. 132°. Its constitution has not been established, but it may be α -phenyl- α -methylbutyric acid, $\text{CPhMeEt}\cdot\text{CO}_2\text{H}$.

$\alpha\alpha$ -Diphenylacetic acid, $\text{CHPh}_2\cdot\text{CO}_2\text{H}$ (compare Symons and Zincke, this Journ., 1874, 162; Friedel and Bahlsohn, Abstr., 1881, 273; Anschütz and Romig, Abstr., 1886, 1033; Zinser, Abstr., 1892, 344; Michael and Jeanprêtre, Abstr., 1892, 1088; Klingemann, Abstr., 1893, i, 590; Fritsch and Feldmann, Abstr., 1899, i, 600), is formed from $\alpha\alpha$ -bromophenylacetic acid and benzene. It separates from a mixture of benzene and light petroleum in crystals, m. p. 148—149°.

Cinnamic acid and benzene yield $\beta\beta$ -diphenylpropionic acid,
 $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$

(Henderson, Trans., 1891, 784; Liebermann and Hartmann, Abstr., 1892, 848, 1228), which crystallises from benzene, m. p. 154—155° (corr.). The oxidation of the acid by permanganate to benzophenone, and its formation from $\beta\beta$ -bromophenylpropionic acid, establish its constitution. The *amide* crystallises from benzene in glistening leaflets, m. p. 125—126°; the *anilide* from alcohol, m. p. 177—178°.

$\alpha\alpha$ -Diphenylpropionic acid, $\text{CPh}_2\text{Me}\cdot\text{CO}_2\text{H}$ (Thörner and Zincke, Abstr., 1879, 322; Böttlinger, Abstr., 1881, 1035), is formed from α -phenylacrylic acid and benzene. It separates from benzene in crystals, m. p. 173—174°. α -Phenylcrotonic acid does not condense with benzene in presence of aluminium chloride.

$\beta\beta$ -Diphenyl- α -methylpropionic acid, $\text{CHPh}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is prepared from α -methylcinnamic acid and benzene, and separates from benzene in crystals, m. p. 161°. Permanganate oxidises it to benzophenone. The *amide* has m. p. 123°; the *anilide* 181°. The *methyl*

ester is obtained by saturating a solution of the acid in methyl alcohol with hydrogen chloride. After distillation in a vacuum and recrystallisation from light petroleum, it has m. p. 84—85°.

α -Ethylcinnamic acid and benzene yield an acid, which from analogy to that obtained from the corresponding methyl derivative is probably $\beta\beta$ -diphenyl- α -ethylpropionic acid, $\text{CHPh}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$. Crystallised from benzene, it has m. p. 167—168°. The *amide* has m. p. 150°; the *anilide* 211°.

$\alpha\beta\beta$ -Triphenylpropionic acid, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, is obtained from α -phenylcinnamic acid and benzene. It is freed from a yellow by-product by dissolving in alcohol and saturating with hydrogen chloride. On diluting with water, the bulk of the acid separates unchanged, along with a small proportion of the *ethyl* ester. The mixture is agitated with dilute caustic alkali, the alcoholic solution extracted with ether, and acidified. The pure acid separates in fine, white needles, m. p. 222—223°. After distillation in a vacuum and recrystallisation from alcohol, the ester is obtained in glistening leaflets, m. p. 122—123°.

A. J. W.

Oxidation and Reduction of γ -Cyano- $\beta\gamma$ -diphenylbutyric Acid. SAMUEL AVERY and GUY R. MCDOLE (*J. Amer. Chem. Soc.*, 1908, 30, 1423—1425. Compare this vol., i, 343).—Additional evidence of the correctness of the constitution of γ -cyano- $\beta\gamma$ -diphenylbutyric acid is afforded by its behaviour on oxidation and reduction. When the acid is oxidised with neutral potassium permanganate, desylacetic acid, $\text{CHPhBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained, whilst, on reduction with hot sodium ethoxide and subsequent addition of hydrochloric acid, a mixture of $\beta\gamma$ -diphenylbutyric acid and the *hydrochloride* of δ -amino- $\beta\gamma$ -diphenylvaleric acid, white, blunt needles, m. p. 256°, is formed.

J. C. C.

Nitration of β -*p*-Tolylglutaric Acid. SAMUEL AVERY and FRED W. UPSON (*J. Amer. Chem. Soc.*, 1908, 30, 1425—1429).—When β -*p*-tolylglutaric acid (Avery and Parmelee, *Abstr.*, 1902, i, 679) is added to ten times its weight of fuming nitric acid, 3 : 5-dinitro- β -*p*-tolylglutaric acid, pale yellow, microscopic plates, m. p. 182°, is obtained. The *anhydride*, hard, white, glistening plates, has m. p. 230—231°, and gives with aniline the *anilic acid*, white, microscopic needles, m. p. 169—170°. On reduction with ammonium sulphide, the glutaric acid furnishes 3-nitro-5-amino- β -*p*-tolylglutaric acid, yellowish-brown needles, m. p. 201°, the *silver* salt of which was analysed, and, on oxidation, 3 : 5-dinitroterephthalic acid is formed. The constitution of 3 : 5-dinitro- β -*p*-tolylglutaric acid was proved by the following synthesis: methyl *m*-nitro-*p*-tolylacrylate (Hanzlik and Bianchi, *Abstr.*, 1899, i, 891) is condensed with ethyl malonate, and the product hydrolysed to 3-nitro- β -*p*-tolylglutaric acid, m. p. 198.5°. On nitration this yields a dinitro-acid identical with the above.

J. C. C.

Fixation of Acetophenone by Benzoylacrylic Acid. J. BOUGAULT (*Compt. rend.*, 1908, 147, 476—478. Compare this vol., i, 179, 269, 422).—When an alkaline solution of benzoylacrylic acid is

allowed to remain in the cold for twenty-four hours and then acidified with acetic acid, diphenacylacetic acid is obtained. As von Pechmann found (Abstr., 1882, 1074) that boiling alkalis decompose benzoylacrylic acid with the formation of glyoxylic acid and acetophenone, it is probable that the same reaction proceeds more slowly in the cold, and that the acetophenone formed combines with still undecomposed benzoylacrylic acid in equimolecular proportions. This is proved to be the case by adding acetophenone to an alkaline solution of benzoylacrylic acid, when an increased yield of diphenacylacetic acid, $(\text{CH}_2\text{Bz})_2\text{CH}\cdot\text{CO}_2\text{H}$, is invariably obtained. J. C. C.

Preparation of Alkylthiosalicylic [2-Alkylthiolbenzoic] Acids. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 197520).—When *o*-thiocyanobenzoic acid and its derivatives are treated either with alkyl iodides or alkali alkyl sulphates, they yield *o*-alkylthiolbenzoic acids of the general formula $\text{R}(\text{S}\cdot\text{Alkyl})\cdot\text{CO}_2\text{H}$.

o-Methylthiolbenzoic acid, $\text{C}_6\text{H}_4(\text{SMe})\cdot\text{CO}_2\text{H}$, m. p. 168—169°, is obtained by heating together in aqueous sodium hydroxide, *o*-thiocyanobenzoic acid and sodium methylsulphate. *o*-Ethylthiolbenzoic acid, $\text{C}_6\text{H}_4(\text{SEt})\cdot\text{CO}_2\text{H}$, m. p. 134—135°, is produced from *o*-thiocyanobenzoic acid, ethyl iodide, and potassium hydroxide in alcoholic solutions; the ethyl ester which is first formed is an oil, b. p. 152—153°/10 mm. G. T. M.

[Preparation of 8-Carboxymethylthiolnaphthoic Acid.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 198050).—

8-Carboxymethylthiolnaphthoic acid, colourless leaflets, m. p. 175—176°, is prepared by treating the diazo-derivative of 8-aminonaphthoic acid successively with potassium xanthate and sodium chloroacetate. Blue colouring matters are produced by heating this substance with aqueous alkali hydroxides, nitrobenzene, acetic anhydride, acid sulphites, thiosulphates, or sulphur; these dyes are suitable for the hyposulphite vat (compare this vol., i, 451, and preceding abstract). G. T. M.

Preparation of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid. KALLE and Co. (D.R.-P. 196016. Compare this vol., i, 451).—A good yield of 3-hydroxy-(1)-thionaphthen-2-carboxylic acid is obtained by heating at 150—200° a mixture of phenylthioglycol-*o*-carboxylic (*o*-carboxymethylthiobenzoic) acid and sodium hydroxide, and acidifying the product at the ordinary temperature. If the mixture becomes heated, carbon dioxide is evolved, and 3-hydroxy-(1)-thionaphthen is produced. G. T. M.

Preparation of Indoxyl and its Derivatives. LEON LILIENFELD (D.R.-P. 195352).—Comparative experiments on Heumann's indigo synthesis have shown that the addition of magnesium powder to the alkali fusion of phenylglycine and its homologues considerably increases the yield of indigotin. Thus a mixture of potassium phenylglycine, sodium and potassium hydroxides, and barium oxide furnished

only 27% of indigotin, whereas the addition of magnesium raised the yield to 60%.
G. T. M.

Preparation of Tri-, Tetra-, and Hexa-halogenated Derivatives of Indigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 195085 and 195291. Compare this vol., i, 695).—*Chlorodibromindigotin*, $C_{16}H_7O_2N_2ClBr_2$, is obtained by heating chloroindigotin with bromine in nitrobenzene at 226—228°. With a larger proportion of bromine, a chlorotribromindigotin, $C_{16}H_6O_2N_2ClBr_3$, is produced. These products give leuco-derivatives in the hyposulphite vat, which dye cotton in bright blue shades of extraordinary fastness. *p*-Dichloroindigotin, prepared from 4-chloro-2-aminobenzoic acid, when heated at 225° with bromine in nitrobenzene solution, gives rise to a *dichlorotetrabromindigotin*, which yields a yellow *leuco*-derivative. When *p*-dibromindigotin is employed in this reaction, *hexabromindigotin* is obtained.
G. T. M.

Preparation of Succinylsalicylic Acid and its Methyl Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 196634).—*Succinylsalicylic acid*, $C_2H_4(CO \cdot O \cdot C_6H_4 \cdot CO_2H)_2$, white, tasteless, colourless needles, m. p. 176—178°, produced by the interaction of succinyl chloride, salicylic acid, and dimethylaniline in benzene solution, dissolves very sparingly in water, and is only slightly soluble in cold alcohol or glacial acetic acid.

Succinyl-o-cresotic acid, $C_2H_4(CO \cdot O \cdot C_6H_3Me \cdot CO_2H)_2$, tasteless, crystalline powder, m. p. 163—164°. *Succinyl-m-cresotic acid*, m. p. 195—197°, and *succinyl-p-cresotic acid*, colourless crystals, m. p. 193—195°, are prepared by the foregoing reaction, and resemble the preceding compound.
G. T. M.

Arylsulphonated Acetonitriles. II. Condensation of the Nitriles with Aromatic Aldehydes and with Amyl Nitrite and Sodium Ethoxide. JULIUS TRÖGER and ADOLF PROCHNOW (*J. pr. Chem.*, 1908, [ii], 78, 123—138).—The similarity between arylsulphonated acetonitriles (Abstr., 1905, i, 336, 870; this vol., i, 633), on the one hand, and ethyl acetoacetate, ethyl cyanoacetate, or benzyl cyanide, on the other, is further illustrated by the readiness with which the nitriles condense with aromatic aldehydes and with amyl nitrite and sodium ethoxide. The RSO_2 group in combination with a nitrile group has much the same effect on the methylene group as carbonyl and carboxy radicals. The condensation with aldehydes takes place readily in the presence of a few drops of aqueous sodium hydroxide; the reaction is of the type $R \cdot CH : O + R' \cdot SO_2 \cdot CH_2 \cdot CN \rightarrow R \cdot CH : C(SO_2R') \cdot CN + H_2O$. The following condensation products (arylsulphonearylideneacetonitriles) have been prepared. The temperatures are melting points:

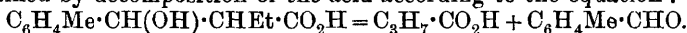
$R = R' = Ph$, colourless needles, 135°; $R = o-C_6H_4 \cdot OH$, $R' = Ph$, microcrystalline needles, 160°; $R = o-C_6H_4 \cdot OMe$, $R' = Ph$, yellow needles, 113°; $R = p-C_6H_4 \cdot NO_2$, $R' = Ph$, yellow needles, 159°; $R = C_6H_5 \cdot CH : CH$, $R' = Ph$, yellow needles, 146°; $R = Ph$, $R' = p-C_6H_4Me$, colourless needles, 114°; $R = o-C_6H_4 \cdot OH$, $R' = p-C_6H_4Me$, 152°; $R = o-C_6H_4 \cdot OMe$, $R' = p-C_6H_4Me$, yellow needles, 110°; $R = p-C_6H_4 \cdot NO_2$, $R' = p-C_6H_4Me$,

yellow needles, 198° ; $R = \text{Ph}$, $R' = \beta\text{-C}_{10}\text{H}_7$, 122° ; $R = o\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = \beta\text{-C}_{10}\text{H}_7$, microcrystalline needles, 173° ; $R = o\text{-C}_6\text{H}_4\cdot\text{OMe}$, $R' = \beta\text{-C}_{10}\text{H}_7$, pale yellow needles, 117° ; $R = p\text{-C}_6\text{H}_4\cdot\text{NO}_2$, $R' = \beta\text{-C}_{10}\text{H}_7$, yellow needles, 187° ; $R = \text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}$, $R' = \beta\text{-C}_{10}\text{H}_7$, yellow needles, 157° ; $R = \text{Ph}$, $R' = p\text{-C}_6\text{H}_4\text{Br}$, large needles, 119° ; $R = o\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = p\text{-C}_6\text{H}_4\text{Br}$, needles, 143° ; $R = o\text{-C}_6\text{H}_4\cdot\text{OMe}$, $R' = p\text{-C}_6\text{H}_4\text{Br}$, yellow needles, 146° ; $R = p\text{-C}_6\text{H}_4\cdot\text{NO}_2$, $R' = p\text{-C}_6\text{H}_4\text{Br}$, yellow needles, 210° ; $R = \text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}$; $R' = p\text{-C}_6\text{H}_4\text{Br}$, yellow needles, 176° .

The condensation between the arylsulphonated nitriles, amyl nitrite, and sodium ethoxide may be represented by the equation $\text{C}_5\text{H}_{11}\text{ONO} + \text{RSO}_2\cdot\text{CH}_2\cdot\text{CN} + \text{NaOEt} \rightarrow \text{C}_5\text{H}_{11}\text{OH} + \text{EtOH} + \text{NaO}\cdot\text{N}:\text{C}(\text{SO}_2\text{R})\text{CN}$, the methylene hydrogen atoms being replaced by the bivalent oxime group. The free oximes are obtained when the sodium salts are decomposed with hydrochloric acid. The following oximes (*isonitroso*-compounds) have been prepared: $R = \text{Ph}$, colourless crystals from water, 140° ; $R = p\text{-C}_6\text{H}_4\text{Me}$, colourless crystals, 129° ; $R = \beta\text{-C}_{10}\text{H}_7$, 80° ; $R = p\text{-C}_6\text{H}_4\text{Br}$, 163° .
J. J. S.

Synthesis and Properties of β -Hydroxy- β -*m*-tolyl- α -ethylpropionic Acid. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 761—769).—Ethyl β -hydroxy- β -*m*-tolyl- α -ethylpropionate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, prepared by the action of zinc on a mixture of ethyl α -bromobutyrate and *m*-tolualdehyde, is a viscous, colourless liquid, b. p. $187.5\text{—}188^{\circ}/31\text{ mm.}$, and has the normal molecular weight in boiling ether or freezing benzene.

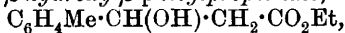
The acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$, separates from water in colourless, acicular crystals, m. p. $109.5\text{—}110^{\circ}$, and exhibits normal ebullioscopic behaviour in ether. When boiled with 10% sulphuric acid, the acid decomposes in two ways: (1) giving CO_2 , H_2O and α -*m*-tolyl- Δ^{α} -butylene, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CHEt}$, which is a colourless, mobile liquid, b. p. 208° , $D_{20}^{25} 0.8901$, $n_D^{25} 1.5365$, and forms the dibromide, $\text{C}_{11}\text{H}_{14}\text{Br}_2$; (2) giving *m*-toluic acid, which probably results from *m*-tolualdehyde obtained by decomposition of the acid according to the equation:



The potassium, $\text{C}_{12}\text{H}_{15}\text{O}_3\text{K}\cdot\text{H}_2\text{O}$, barium, $(\text{C}_{12}\text{H}_{15}\text{O}_3)_2\text{Ba}\cdot 8\text{H}_2\text{O}$, copper, silver, $\text{C}_{12}\text{H}_{15}\text{O}_3\text{Ag}$, iron, lead, zinc, and platinum salts of the acid were prepared.

The properties of the acid are compared with those of β -hydroxy- β -*p*-tolyl- α -ethylpropionic acid (compare Mazurewitsch, *Abstr.*, 1907, i, 623).
T. H. P.

Action of a Mixture of Ethyl Bromoacetate and *p*-Tolualdehyde on Zinc. Synthesis of β -Hydroxy- β -*p*-tolylpropionic Acid. W. ANDRIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 770—782).—Ethyl β -hydroxy- β -*p*-tolylpropionate,



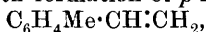
obtained by the action of zinc on a mixture of ethyl bromoacetate and *p*-tolualdehyde, is a yellow, viscous liquid, b. p. $178\text{—}180^{\circ}/19\text{ mm.}$

The corresponding acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, separates from aqueous alcohol in acicular crystals, m. p. $94\text{—}95^{\circ}$, and has the normal molecular weight in boiling ether. The potassium, silver, and

barium (+ 2H₂O) salts were analysed, and the ammonium, mercury, zinc, copper, iron, lead, and nickel salts prepared.

When boiled with 10% sulphuric acid solution, the acid is decomposed mainly in accordance with the equation :

$C_6H_4Me \cdot CH(OH) \cdot CH_2 \cdot CO_2H = H_2O + C_6H_4Me \cdot CH : CH \cdot CO_2H$,
yielding *p*-methylcinnamic acid, a small part of which undergoes further decomposition with formation of *p*-methylstyrene,



and carbon dioxide. When subjected to dry distillation at 130°, the acid decomposes into water and *p*-methylcinnamic acid (compare Bronstein, Abstr., 1907, i, 848). T. H. P.

Preparation of Aromatic *o*-Hydroxyaldehydes. HUGO WEIL (D.R.-P. 196239).—A solution of a salicylate when shaken with sodium amalgam shows no apparent change, but when boric acid is first added, the introduction of the amalgam develops immediately an odour of salicylaldehyde.

When *p*-toluidine is also present, *o*-hydroxybenzylidene-*p*-toluidine is produced. The reduction may be carried out electrolytically by using a mercury cathode and a solution containing a sodium salt.

G. T. M.

Derivatives of Phenyl α -Naphthyl Ketone. E. CAILLE (Bull. Soc. chim., 1908, [iv], 3, 916—919).—When an alcoholic solution of phenyl α -naphthyl ketone is treated with sodium amalgam, it yields *phenyl- α -naphthylcarbinol*, which crystallises from alcohol in white, orthorhombic prisms, m. p. 85°, and gives a violet coloration with sulphuric acid; the *benzoyl* derivative, m. p. 106°, crystallises from alcohol in colourless plates, giving a violet coloration with sulphuric acid. The oxime of phenyl α -naphthyl ketone, described by Spiegler (Abstr., 1884, 1182) as a yellow oil, when prepared by the action of hydroxylamine on the ketone, with the addition of zinc chloride, forms white, silky needles, m. p. 73°, and gives an orange coloration with sulphuric acid. The *phenylhydrazone*, m. p. 189°, forms a yellow mass, which reddens on exposure to air and gives a green coloration with sulphuric acid. J. C. C.

Formation of Oximes. UGO GRASSI (Gazzetta, 1908, 38, ii, 32—40).—The formation of *l*-menthoneoxime from *l*-menthone and free hydroxylamine is accelerated by raising the temperature and also by increasing the proportion of alcohol in the solution. In some cases, the optical activity of the solution diminishes considerably instead of increasing, as it should do were the oxime formed. This cannot be due to inversion of the menthone, since the solutions employed were quite neutral to litmus and phenolphthalein, and the proportion of alcohol present was too small to produce rapid inversion. The author therefore assumes the formation of an intermediate compound, which is probably a simple additive compound, $OH \cdot CRR' \cdot O \cdot NH_2$, analogous to those formed by the hydrogen sulphites, or by ammonia with aldehydes, and stable at low temperatures. This compound then passes into the oxime by a process of dehydration, which may well be

accelerated by rise of temperature or by alcohol. Some of the solutions of *l*-menthone and hydroxylamine were found to attain a final rotation higher than that calculated for the oxime from the values given by Beckmann (Abstr., 1889, 721).

With regard to the acceleration of the formation of oximes by dehydrating agents, it is found that camphoroxime is formed much more rapidly in absolute alcohol containing anhydrous sodium sulphate than in absolute alcohol alone.

The distribution of hydroxylamine between two ketones has been studied in 94% alcohol at 35°. Under these conditions, hydroxylamine combines with acetone in preference to menthone, but acetone in large excess is unable to remove hydroxylamine from menthoneoxime, at any rate in neutral solutions. Even oximes, such as that of pinacolin, which Stewart's investigations (Trans., 1905, 87, 185, 410) show to be the weakest, resist energetically the action of other ketones.

T. H. P.

2' : 4'-Dihydroxyhydrochalkone. GUIDO BARGELLINI and M. MARANTONIO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 119—125).—**2' : 4'-Dihydroxyhydrochalkone** [*o* : *p*-dihydroxyphenyl phenylethyl ketone], $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, prepared by the condensation of hydrocinnamic acid and resorcinol in presence of zinc chloride, crystallises from dilute acetic acid in needles, m. p. 88°, dissolves in alkali hydroxide solutions or in concentrated sulphuric acid, giving pale yellow solutions, and in aqueous solution gives a yellow coloration with ferric chloride. The acetyl derivative was obtained as a pale yellow resin which could not be purified. The *monomethyl ether*, $\text{C}_{16}\text{H}_{16}\text{O}_3$, crystallises from water in white needles, m. p. 74—75°, and the *dimethyl ether*, $\text{C}_{17}\text{H}_{18}\text{O}_3$, from dilute acetic acid in long needles, m. p. 103—104°. The *oxime*, $\text{C}_{15}\text{H}_{15}\text{O}_3\text{N}$, crystallises from benzene as a white powder, m. p. 171—172°. The ketone is not attacked when heated for several hours with 70% potassium hydroxide solution (compare Weisl, Abstr., 1905, i, 904; Finzi, Abstr., 1905, i, 906).

2' : 4'-Dihydroxychalkone [*o* : *p*-dihydroxyphenyl styryl ketone],

$\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$,

prepared by the condensation of cinnamic acid and resorcinol in presence of zinc chloride, crystallises from water in needles, m. p. 175°.

T. H. P.

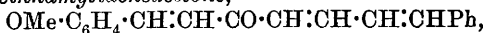
Coloured Hydrohalides of Unsaturated Aromatic Ketones. LUIGI FRANCESCONI and G. CUSMANO (*Gazzetta*, 1908, 38, ii, 70—97).—The authors have prepared a number of aromatic ketones containing various substituent groups and from one to four double linkings in different positions with respect to the carbonyl group. The ketones have been subjected to the action of dry hydrogen chloride, the derivatives obtained being unstable towards water (compare Baeyer and Villiger, Abstr., 1901, i, 659; 1902, i, 355; Vorländer and Mumme, Abstr., 1903, i, 495; Straus and Ecker, Abstr., 1906, i, 859). Certain of the ketones containing three double linkings have been treated with bromine, the addition of which is only partial in some

cases and total in others; the behaviour of some of these bromo-derivatives towards hydrogen chloride has been studied.

Methylvanillylideneacetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, prepared by the interaction of methylvanillin and aqueous acetone in presence of sodium hydroxide or by methylating vanillylideneacetone, crystallises from ethyl acetate in yellow needles, m. p. 168° .

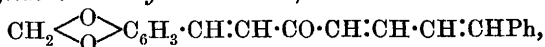
Benzylidenecinnamylideneacetone (compare Scholtz, Abstr., 1896, i, 368) has m. p. $109-110^\circ$.

Anisylidenecinnamylideneacetone,



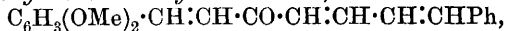
separates from a mixture of ether and ethyl acetate in pale yellow crystals, m. p. 138° .

Piperonylideneacinnamylideneacetone,



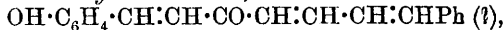
is deposited from ethyl acetate in shining, pale yellow crystals, m. p. 127° .

Methylvanillylideneacinnamylideneacetone,



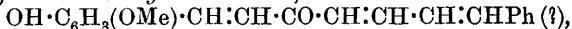
crystallises from ether in pale yellow leaflets, m. p. 110° .

Salicylideneacinnamylideneacetone,



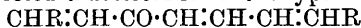
obtained by condensing salicylaldehyde with cinnamylideneacetone in presence of sodium hydroxide, crystallises from chloroform in pale yellow leaflets, m. p. 163° .

Vanillylideneacinnamylideneacetone,

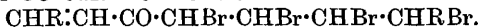


obtained only in small quantity, is a pale yellow compound.

It would be expected that ketones of the type



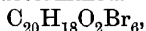
would yield two dibromides, $\text{CHRBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CHR}$ and $\text{CHR} : \text{CH} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH} : \text{CH} \cdot \text{CHRBr}$, and two tetrabromides, $\text{CHRBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH} : \text{CH} \cdot \text{CHRBr}$ and



By the action of two or four atoms of bromine on anisylidenecinnamylideneacetone or piperonylideneacinnamylideneacetone, however, only one di- or tetra-bromide could be isolated. Like the unsaturated aromatic ketones themselves, the dibromides and monohydrobromides of ketones of the type of dibenzylideneacetone give colorations with concentrated sulphuric acid, but no coloration is given by the coloured tetrabromides or dihydrobromides. A coloration is hence only obtained when an ethylene linking is present, and when it is next to the double linking of the carbonyl group. From their ability or inability to give a coloration with sulphuric acid, it is therefore possible to decide the constitution of the tetrahalogenated derivatives, and, since these, with one exception, give no coloration, they must have the structure $\text{CHRBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CH} : \text{CH} \cdot \text{CHRBr}$; dibromides of either of the constitutions given above would give a coloration with sulphuric acid, so that in their case the structure cannot be settled.

Anisylidenecinnamylideneacetone dibromide, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Br}_2$, m. p. $135-136^\circ$ (decomp.), does not increase in weight or become coloured in

contact with dry hydrogen chloride, but gives a peacock-blue coloration with concentrated sulphuric acid. The *tetrabromide*, $C_{20}H_{18}O_2Br_4$, m. p. 146—147°, which gradually gives a violet coloration with sulphuric acid, was obtained together with another compound, m. p. 131—133°, the nature of which was not determined. The *hexabromide*,



separating from ether as a white, microcrystalline powder, m. p. 144°, and gradually giving a violet coloration with sulphuric acid, was obtained together with a whitish-violet, microcrystalline powder, m. p. 172.5°.

Piperonylidene-cinnamylideneacetone dibromide, $C_{20}H_{16}O_3Br_2$, separates from chloroform in faintly yellow, microscopic crystals, m. p. 149—150°, and gives an intense coloration with sulphuric acid, but is not affected by hydrogen chloride. The *tetrabromide*, $C_{20}H_{16}O_3Br_4$, m. p. 147—148°, obtained as a white powder becoming faintly rose-red in the light, gives no coloration with either sulphuric acid or hydrogen chloride. The hexabromide could not be prepared, an unsaturated compound derived from the hexabromide by elimination of hydrogen bromide being obtained.

The following hydrochlorides were prepared by the action of dry hydrogen chloride on the various ketones. They are all unstable in presence of water, with which they give the original ketones.

Benzylideneacetone hydrochloride, $C_{10}H_{10}O, HCl$, dense oil; the *dihydrochloride*, $C_{10}H_{10}O, 2HCl$, obtained by cooling with ice and salt, forms a dense, reddish-brown oil.

Salicylylideneacetone hydrochloride, $C_{10}H_{10}O_2, HCl$, is a dark reddish-violet oil; the *dihydrochloride*, $C_{10}H_{10}O_2, 2HCl$, forms an orange-yellow powder.

Anisylideneacetone hydrochloride, $C_{11}H_{12}O_2, HCl$, is dark green, and the *dihydrochloride*, $C_{11}H_{12}O_2, 2HCl$, an orange-yellow powder.

Vanillylideneacetone hydrochloride, $C_{11}H_{12}O_3, HCl$, has a dark peacock-blue colour, and decomposes slowly in the air, giving the ketone.

Methylvanillylideneacetone hydrochloride, $C_{12}H_{14}O_3, HCl$, has a garnet-red colour.

Cinnamylideneacetone hydrochloride, $C_{12}H_{12}O, HCl$, forms a semi-fluid mass with metallic, yellow reflection.

Benzylidenepiperonylideneacetone hydrochloride, $C_{18}H_{14}O_3, 2HCl$, resembles colcothar in appearance.

Benzylidenecinnamylideneacetone hydrochloride, $C_{19}H_{16}O, 2HCl$, is a peacock-blue compound, and the free ketone dissolves in concentrated sulphuric acid, giving a cochineal-red solution.

Anisylidenecinnamylideneacetone dissolves in concentrated sulphuric acid, giving an intense peacock-blue coloration, and forms two hydrochlorides: the *dihydrochloride*, $C_{20}H_{18}O_2, 2HCl$, which is a green powder with metallic lustre, and the *trihydrochloride*, $C_{20}H_{18}O_2, 3HCl$, which is dark grey.

Piperonylidene-cinnamylideneacetone forms a dark violet solution in sulphuric acid, and yields the *hydrochloride*, $C_{20}H_{16}O_3, 2HCl$, m. p. 97° (decomp.), which is a green powder with metallic lustre.

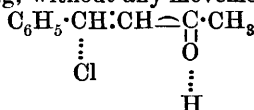
The following general conclusions are drawn from the results obtained by the authors and by Vorländer and Mumme (*loc. cit.*).

With ketones of the types $\text{CHR}:\text{CH}\cdot\text{CO}\cdot\text{R}$, $\text{CHR}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{R}$,
 $\text{CHR}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CHR}$, $\text{CHR}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CHR}$,
 $\text{CHR}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CHR}$,

where R represents a substituted aryl or alkyl residue, the number of mols. of hydrogen chloride added at the ordinary temperature is, in general, the same as the number of double linkings in the $\alpha\beta$ -position. But the reaction is influenced by the substituent groups of the ketone molecule.

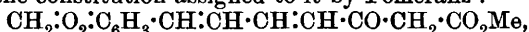
If, in dibenzylideneacetone, which unites readily and in definite molecular proportions with hydrogen chloride, the two hydrogen atoms combined with the carbon atom adjacent to the carbonyl group are replaced by methyl groups, no definite addition of hydrogen chloride occurs either at the ordinary temperature or at 0° . The introduction of methoxyl groups into the ketone molecule also favours the combination with hydrogen chloride. The substituent groups also influence the colour of the hydrochlorides, which, with colourless ketones, are yellow; with yellow ketones containing one double linking and of the type of benzylideneacetone, red, and with ketones containing two or three double linkings, green.

The formation of two series of compounds, one stable and colourless and the other unstable and coloured, by the action of halogen hydracids on unsaturated aromatic ketones cannot be explained either by a difference in the positions assumed by the atoms in the molecule or by a different spacial arrangement of the atoms. The colourless, stable derivatives behave like additive halogen compounds, and are formed according to Thiele's law (Abstr., 1899, i, 554), the application of which to ketones of the types under consideration shows that, if the addition of the hydracid is effected successively, it can only result in the formation of derivatives with one mol. of the acid for ketones with only one double linking and of derivatives with two mols. of acid in the case of ketones with two double linkings. The unstable, coloured additive derivatives are formed by the engaging of the partial valencies due to the double linking, without any movement of the latter, thus :

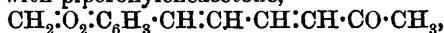


These compounds hence represent the first phase of the reaction of addition of the halogen hydracids. T. H. P.

Kawa Root [of *Piper methysticum*]. E. WINZHEIMER (*Arch. Pharm.*, 1908, 246, 338—365).—Besides confirming and extending the results of Pomeranz, the author has mainly investigated the constitution of yanonin. The root contains: resins, 5.3% (of which 23% acids, 77% esters); methysticin, 0.30%; ψ -methysticin, 0.268%; yanonin, 0.184%; an alkaloid, 0.022%; two glucosides, 0.69%; an amorphous acid, insoluble in water, 0.7—0.8%, and sugar. Methysticin has the constitution assigned to it by Pomeranz :

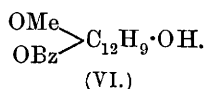
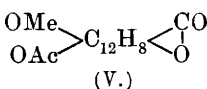
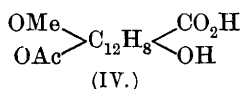
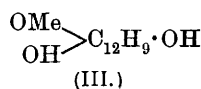
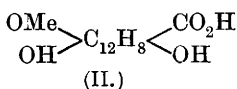
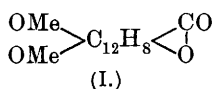


or a very similar one, since methysticol, obtained from it, is now proved to be identical with piperonyleneacetone,

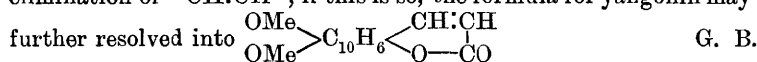


previously synthesised by Scholtz. The *phenylhydrazone* of methysticol melts at 152—152·5°; the *p-bromophenylhydrazone* at 162—163°; the *semicarbazone* at 199—199·5°; *benzylidenemethysticol*, $C_{20}H_{16}O_3$, at 110—111°; its *phenylhydrazone* at 187·5—188°, and *piperonylidene-methysticol* at 195—195·5°. ψ -*Methysticin* is, like methysticin, an ester of methystic acid; pale yellow leaflets, m. p. 113—114°; the analytical results are doubtful.

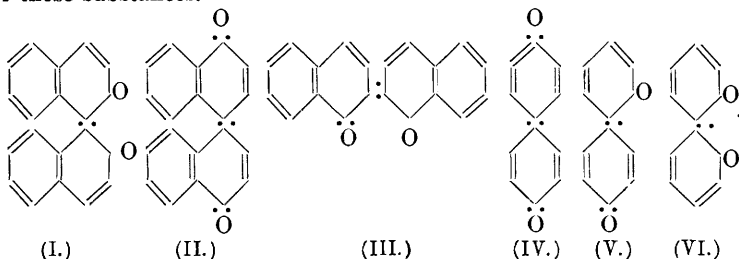
Yanگونin (I) has the composition $C_{15}H_{14}O_4$ (and not $C_{17}H_{12}O_5$, or $C_{10}H_8O_3$, as previously supposed). It contains two methoxyl groups, and appears to be a lactone; potassium hydroxide transforms it into *yangonic acid* (II), needles, m. p. 126—126·5°. At its melting point, or in boiling alcohol, this acid loses carbon dioxide, being converted into *yangonol* (III), yellow leaflets, m. p. 92—92·5°. When yangonic acid is heated with acetic anhydride, *acetylyangonic acid* (IV), m. p. 230°, and *acetylyangonic lactone* (V), m. p. 131—132°, are formed.



Yangonol forms a *monobenzoyl* derivative (VI), yellow plates, m. p. 103°. On fusion with potassium hydroxide, yangonin yields a small quantity of a crystalline *acid*, m. p. 210—211°, free from methoxyl and probably having the composition $C_{11}H_{10}O_5$. It is regarded as being derived from yangonic acid (like benzoic from cinnamic acid) by the elimination of $-\text{CH}:\text{CH}-$; if this is so, the formula for yangonin may be



Binuclear Quinones as Chromogens. HERMAN DECKER (*Annalen*, 1908, 362, 320—324).—Of the six formulæ below, only I, III, and VI can form indigoid dyes according to Friedländer's view of these substances.



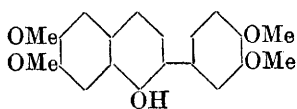
Nevertheless, two strongly coloured derivatives of (II) have now been obtained (see following abstract), and the strong dye, cedrret, is a derivative of (IV). The author proposes therefore to group all such substances under the name of "binuclear quinonoid dyes." The

meaning of the term quinonoid must be widened to include substances in which a group, $-S-$, $-O-$, $-NH-$, or $-CH_2-$, is substituted for $-C:C-$, as also those in which the quinonoid

oxygen atom is displaced by a bivalent imine or hydrocarbon group. The binuclear quinonoid dyes fall then into place between the quinonoid and the triphenylmethane dyes. In this new group, the dye and leuco-compounds form two reciprocal systems of conjugated double linkings.

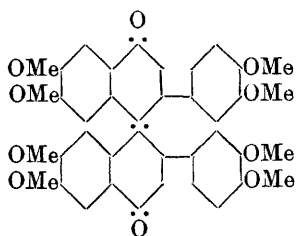
G. Y.

Formation of Naphthol Derivatives from Papaverine and the Binuclear Quinones of the Naphthalene Series. HERMAN DECKER (*Annalen*, 1908, 362, 305—319).—Decker and Dunant's



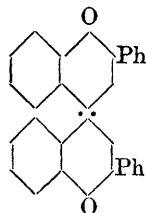
suggestion that the phenolic compound, m. p. 180° , formed by the action of alkalis on papaverinium methyl haloids, has the annexed constitution (this vol., i, 204) is now confirmed, and the mechanism of the reaction by which it is formed is discussed.

6:7-Dimethoxy-2-mp-dimethoxyphenyl- α -naphthol gives a light green coloration with sulphuric acid, becoming violet when heated, forms crystalline alkali salts, and couples with α -diazonaphthalenes, forming insoluble, brownish-red azo-dyes. The pentamethoxy-compound,



$C_{10}H_4(OMe)_3 \cdot C_6H_3(OMe)_2$, formed by the action of methyl sulphate and alkali on the naphthol, crystallises in white leaflets, m. p. $162-163^\circ$, and sublimes unchanged. The blue dye, formed together with tetramethoxyphenylnaphthol by the action of alkalis on papaverinium methyl haloids in presence of air, or by the action of air on the impure naphthol containing veratraldehyde, but not on the pure

naphthol or by the action of oxidising agents on the naphthol in alkaline or acid solution, is considered to have the annexed constitution. It is obtained as a dark blue, glistening mass resembling indigotin, m. p. $225-235^\circ$, gives a green coloration with concentrated sulphuric acid, is decolorised by hot concentrated or alcoholic potassium hydroxide, and again forms the naphthol when treated with reducing agents.



When boiled with alcoholic potassium hydroxide in an atmosphere of hydrogen in a reflux apparatus, 1-phenylisoquinolinium methiodide evolves methylamine and yields 2-phenyl- α -naphthol, which is obtained as a resinous mass, gives the phenol reaction with diazo-solutions, forms a methyl and a crystalline acetyl derivative, and on oxidation yields a violet dye, m. p. about 220° , annexed constitution. This forms a bluish-red solution in alcohol, or a violet-red in benzene or chloroform.

G. Y.

The Replacement of a Sulphonic Group by Hydroxyl in Anthraquinone- α -sulphonic Acid and its Derivatives. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197649).—It has been found that by heating anthraquinone- α -sulphonic acid and its more highly sulphonated derivatives with aqueous sodium carbonate at 190—200°, the sulphonyl groups in α -positions are replaced by hydroxyl. Anthraquinone-1:5- and -1:8-disulphonic acids yield respectively anthrarufin and chrysazin, with small quantities of 1-hydroxyanthraquinone-5- and -8-sulphonic acids as intermediate products. Anthraquinone- α -sulphonic acid itself furnishes erythrohydroxyanthraquinone. G. T. M.

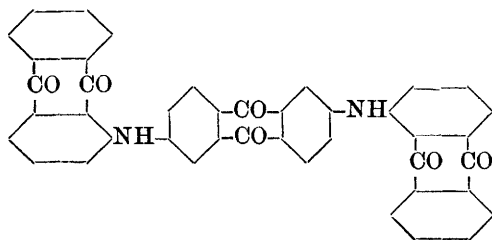
Preparation of Hydroxyanthrarufin and Hydroxychrysazin. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 196980).—1:2:5-Trihydroxyanthraquinone is readily obtained by heating anthrarufin with a mixture of sodium and potassium hydroxides in the presence of water and sodium nitrate. The employment of the mixture of alkali hydroxides gives a much better result, the oxidation to the trihydroxy-derivative being complete and without production of 1:2:5:6-tetrahydroxyanthraquinone. G. T. M.

Preparation of 1:5- and 1:8-Hydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197607).—When heated with a mixture of calcium hydroxide and water at 140—150°, 1:5- and -1:8-anthraquinonedisulphonic acids are readily converted into 1-hydroxyanthraquinone-5- and -8-sulphonic acids, which are obtained in the form of their sodium salts. G. T. M.

Preparation of Hydroxyanthrarufin and Hydroxychrysazin. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 195028).—1:2:5-Trihydroxyanthraquinone (*hydroxyanthrarufin*), m. p. 273—274°, triacetyl derivative, m. p. 228°, was obtained by fusing anthrarufin with sodium nitrate and aqueous sodium hydroxide at 180—185°. 1:2:8-Trihydroxyanthraquinone (*hydroxychrysazin*), orange needles, m. p. 230°, triacetyl derivative, m. p. 219°, was obtained under similar conditions from chrysazin. G. T. M.

Preparation of Complex Dianthraquinonyldiaminoanthraquinones. BADISCHE ANILIN UND SODA-FABRIK (D.R.-P. 197554. Compare this vol., i, 456).—Complex anthracene colouring matters suitable for vat-dyeing are produced by condensing the amino- and diamino-anthraquinones with $\beta\beta$ -dihalogenated anthraquinones containing the two halogen atoms in different rings.

Di-1'-anthraquinonyl-2:6-diaminoanthraquinone is obtained by

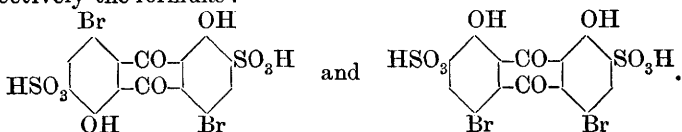


condensing 2:6-dichloro-anthraquinone and 1-aminoanthraquinone with anhydrous sodium acetate and cuprous chloride in boiling nitrobenzene. Similar compounds are produced from 2:7-dibromoanthraquinone and 1-aminoanthraquinone,

and 2:6-dichloroanthraquinone and 1:5-diaminoanthraquinone; they dissolve in concentrated sulphuric acid to green solutions, and furnish yellow or brownish-red leuco-derivatives in the hyposulphite vat.

G. T. M.

Preparation of *p*-Dibromoanthrarufin- and Dibromochrysazindisulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197082).—The sodium hydrogen salts of anthrarufindisulphonic and chrysazindisulphonic acids when treated with bromine in aqueous solution furnish the corresponding salt of dibromoanthrarufindisulphonic and dibromochrysazindisulphonic acids, which have respectively the formulæ:



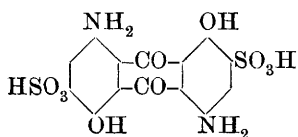
These products are yellow, crystalline salts moderately soluble in water.

G. T. M.

Preparation of Phenanthroanthraquinone. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 194328).—*Phenanthroanthraquinone*, yellow needles, m. p. 234°, is obtained by heating equal parts of phenanthrylbenzoyl-*o*-carboxylic acid and phosphoric oxide at 150° until the product is no longer soluble in aqueous alkalis. The crude quinone is dissolved in the form of its dihydro-derivative by alkaline hyposulphite and re-precipitated from this solution by aerial oxidation.

G. T. M.

Preparation of Diaminoanthrarufindisulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 195139).—



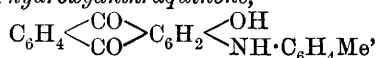
Diaminoanthrarufindisulphonic acid, blue needles, is readily obtained by stirring together sodium *p*-dibromoanthrarufindisulphonate, aqueous ammonia (20%), and a small amount of copper powder at 30—40°. Other halogenated anthra-

quinonesulphonic acids behave in a similar manner.

G. T. M.

Condensation of Quinizarin with Aromatic Amines. EUGÈNE GRANDMOUGIN (*Chem. Zentr.*, 1908, i, 2178—2179; from *Rev. Gén. Mat. color*, 1908, 12, 37—39).—Quinizarin is readily reduced to *leucoquinizarin* by moistening it with alcohol, dissolving in very dilute sodium hydroxide solution, and treating with sodium hydrogen sulphite at the boiling temperature. It crystallises in yellow to orange needles, m. p. 155°.

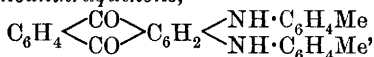
1: *o*-Toluidino-4-hydroxyanthraquinone,



is prepared by heating leucoquinizarin with *o*-toluidine and acetic

acid to 120—125°; dark violet crystals, m. p. 166°. The *acetate* is a violet-black, crystalline substance, m. p. 149°.

1 : 4-*Di-o-toluidinoanthraquinone*,



is obtained by heating leucoquinizarin with *o*-toluidine, acetic acid, and anhydrous boric acid; it crystallises in small, dark brown needles, m. p. 223°. The *di-m-toluidine* derivative of quinizarin, prepared in a similar manner, crystallises in small, dark blue needles, m. p. 183°, and the *di-diethyl-p-phenylenediamine* derivative, $\text{C}_{34}\text{H}_{36}\text{O}_2\text{N}_4$, nearly black needles, m. p. 234—235°. The *mono-p-toluidine* derivative is violet-black, m. p. 183°; *di-p-toluidine* derivative, m. p. 218°.

J. V. E.

Preparation of Alkyl Camphorates. J. D. RIEDEL (D.R.-P. 196152. Compare this vol., i, 352).—Inactive camphoric acid, like its dextrorotatory constituent, reacts in alkaline solution either with methyl sulphate or the alkyl arylsulphonates to furnish its normal esters. *Methyl dl-camphorate*, colourless oil, D 1·073/22°, and b. p. 145—147°/20 mm., is thus obtained by adding alternately potassium hydroxide and methyl sulphate to an aqueous solution of potassium *dl*-camphorate.

G. T. M.

Preparation of *iso*Bornyl Esters of the Fatty Acids from Pinene Hydrochloride or Hydrobromide. CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 196017. Compare this vol., i, 351).—*iso*Bornyl esters of the fatty acids are produced by heating together pinene hydrochloride or hydrobromide, the requisite mineral acid, and a zinc salt of some acid, other than a halide or an oxidising agent. Thus *isobornyl formate* is derived from pinene hydrochloride, formic acid, and anhydrous zinc sulphate. *iso*Bornyl acetate is produced by the interaction of pinene hydrochloride, acetic acid, and zinc *p*-toluenesulphonate.

G. T. M.

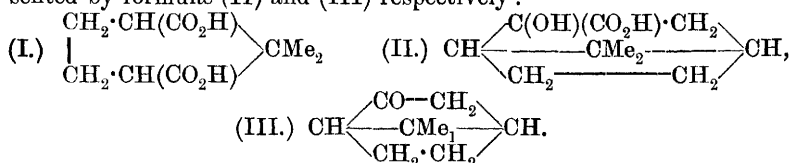
Preparation of the *iso*Bornyl Esters of Fatty Acids from Pinene Hydrochloride or Hydrobromide. CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 194767. Compare this vol., i, 351).—Although zinc chloride and other metallic salts, such as cobalt or cuprous chloride, when heated separately with pinene hydrochloride and glacial acetic acid, give rise only to small yields of *isobornyl acetate*, yet when a mixture of the zinc salt and that of another heavy metal is employed, a good yield of the required ester is obtained.

Thus good yields of *isobornyl acetate* are obtained by boiling a mixture of pinene hydrochloride, glacial acetic acid, and zinc chloride with cuprous, cupric, ferrous, aluminium, cadmium, cobalt, or nickel chloride. *iso*Bornyl formate results in a similar manner from pinene hydrochloride, formic acid, manganous chloride, and zinc chloride.

G. T. M.

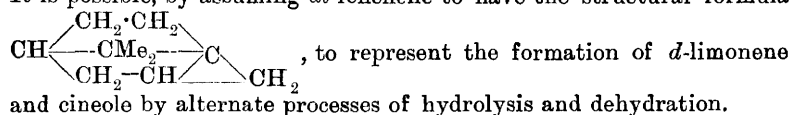
Terpenes and Ethereal Oils. XCIV. The Fenchone Series. OTTO WALLACH [with PAUL VIVCK] (*Annalen*, 1908, 362, 174—200. Compare Wallach, this vol., i, 429; Abstr., 1898, i, 486; 1899, i, 65; 1901, i, 331; 1907, i, 541).—The oxidation of *dl*-fenchene by an

aqueous alkaline solution of potassium permanganate has been re-investigated, and the results obtained previously (Abstr., 1899, i, 65) confirmed. The hydrocarbon is exceedingly stable towards this oxidising agent, yielding *dl*-hydroxyfenchenic acid, m. p. 154°, and *apocamphoric acid*. *dl*-Hydroxyfenchenic acid is oxidised by lead peroxide and sulphuric acid to fenchocamphorone, which latter is converted by alkaline potassium permanganate into *apocamphoric acid*. Assuming *apocamphoric acid* to have the generally accepted formula (I), then *dl*-hydroxyfenchenic acid and fenchocamphorone must be represented by formulæ (II) and (III) respectively:



The conclusion might also be drawn that *dl*-fenchene has the structural formula $\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{C} : \text{CH}_2 \\ | \quad | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \end{array}$, but the great stability of the hydrocarbon towards permanganate is not in agreement with this formula.

The *dl*-fenchene used in this investigation was obtained by adding sodium nitrite and acetic acid to an aqueous solution of fenchylamine hydrochloride. An oil, b. p. 175—178°, was obtained together with the fenchene, and was found on investigation to be a mixture of *d*-limonene, cineole, and dipentene; the latter substance was probably formed as a secondary product from either the *d*-limonene or cineole. It is possible, by assuming *dl*-fenchene to have the structural formula



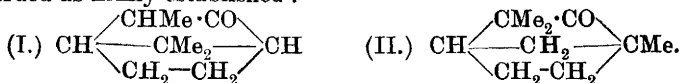
and cineole by alternate processes of hydrolysis and dehydration.

The "*isofenchene*" obtained by Bertram and Helle (Abstr., 1900, i, 398) from *isofenchyl alcohol* is shown to be identical with *dd*-fenchene obtained from fenchyl alcohol (compare Wallach, Abstr., 1899, i, 65).

isoFenchone, derived from *isofenchyl alcohol*, is oxidised by permanganate to an acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, which, since it is isomeric with camphoric acid, is named *isofenchocamphoric acid*. It is therefore

evident that *isofenchone* must contain the grouping $\text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \text{C} \\ \text{C} \end{array} \text{C}$;

further, since fenchone and *isofenchone* behave so differently on oxidation, they must have widely different constitutions. Neither the author's fenchone formula (I) nor Semmler's formula (II) is to be regarded as firmly established:



dl-Fenchene, prepared from fenchylamine, is the purest as yet obtained; it has b. p. 156—157°, D_{19} 0.869, n_D^{19} 1.4724, and α_D^{18} -32.2° (in 1-dcm. tube). The *dibromide*, $C_{10}H_{16}Br_2$, prepared by acting on the hydrocarbon with bromine in acetic acid, forms colourless crystals, m. p. 87—88°, $[\alpha]_D^{11} + 42.83^\circ$ (in ethyl acetate).

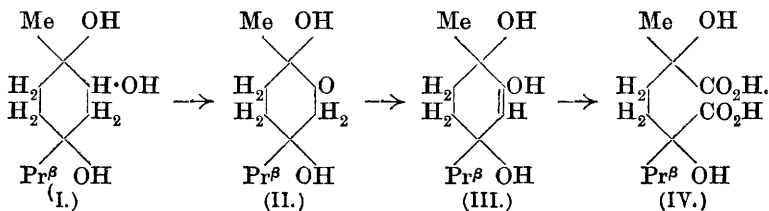
dl-Hydroxyfenchenic acid is now found to have m. p. 154°, $[\alpha]_D^{13} - 62.98^\circ$ (in ether).

*iso*Fenchone readily forms a *semicarbazone*, $C_{11}H_{19}ON_3$, which crystallises in needles, m. p. 221—222°, $[\alpha]_D^{11} - 8.27^\circ$ (in methyl alcohol). *Bromoiso*fenchone, $C_{10}H_{15}OBr$, is readily formed by the action of bromine on *iso*fenchone at the ordinary temperature; it forms colourless crystals, m. p. 56—57°, $[\alpha]_D^{15} - 164.1^\circ$ (in ethyl alcohol).

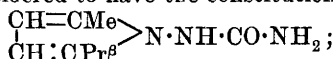
*iso*Fenchocamphoric acid, $C_{10}H_{16}O_4$, obtained by oxidising *iso*fenchone or *iso*fenchyl alcohol with an aqueous alkaline solution of potassium permanganate, has m. p. 158—159°, $[\alpha]_D^{11} - 12.75^\circ$ (in ether); the *silver* salt, $C_{10}H_{14}O_4Ag_2$, was prepared and analysed.

The following derivatives of *l*-fenchone were prepared; they melt at the same temperatures as the corresponding *d*-fenchone derivatives; the values in brackets are the m. p.'s of the racemic compounds: *iso*-fenchyl phenylcarbamate, m. p. 107° (94°); *iso*fenchone *semicarbazone*, m. p. 221—222° (223—224°); *iso*fenchoneoxime, m. p. 82° (133°); *bromoiso*fenchone, m. p. 56—57° (46—47°); *iso*fenchocamphoric acid, m. p. 158—159° (174—175°).
W. H. G.

Terpenes and Ethereal Oils. XCV. Alcohols of the Terpinene Series (Terpinenols). OTTO WALLACH (*Annalen*, 1908, 362, 261—284. Compare this vol., i, 429).—I. *Degradation Products of Terpinene-4-ol* (Δ^1 -Menthene-4-ol). [With FRITZ MEISTER.]—It was shown previously (Abstr., 1907, i, 943) that, on oxidation with alkaline permanganate, trihydroxyterpane yields an optically active acid, m. p. 205—206°, and an optically inactive isomeric acid, m. p. 188—189°. It is found now that, when heated with permanganate and dilute sulphuric acid at 60—70°, both acids yield dimethyl-acetylacetone, and must therefore have the constitution (IV). The oxidation of the trihydroxyterpane (I) is considered to lead in the first place to the formation of a dihydroxyketone (II), which changes in the alkaline solution into the enolic form (III), and then undergoes further oxidation with resolution of the ring between the carbon atoms 2 and 3. Such a reaction may take place also in other cases, and may explain the difference in the oxidation products sometimes obtained on resolution of cyclic compounds with permanganate and with chromic acid:

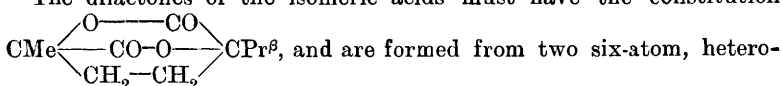


The semicarbazone of dimethylacetylacetone (Posner, Abstr., 1902, i, 82) is considered to have the constitution



it does not yield the ketone when heated with 10% sulphuric acid, is resinified by boiling with strong acids, and when heated alone evolves vapours giving the pyrrole reaction.

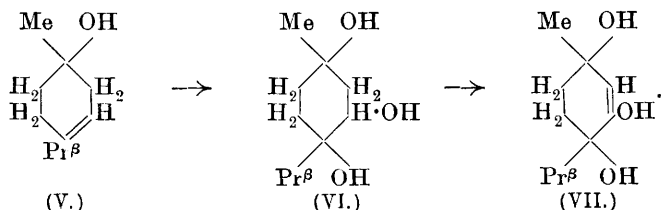
The dilactones of the isomeric acids must have the constitution



cyclic nuclei (compare Le Sueur, Trans., 1907, 93, 716).

II. *Synthesis of $\alpha\alpha'$ -Dihydroxy- α -methyl- α' -isopropyladipic Acid.* [With FRITZ MEISTER.]—With the object of confirming the constitution ascribed to the isomeric acids obtained by oxidation of trihydroxyterpane, dimethylacetylacetone was treated with potassium cyanide and hydrochloric acid at 0° , and subsequently on the water-bath; on distillation with steam, the product yielded the dilactone, m. p. $72\text{--}73^\circ$, which on hydrolysis with boiling alkali was converted into the optically inactive acid, m. p. $188\text{--}189^\circ$.

III. *Terpinene-1-ol [Δ^3 -p-Menthene-1-ol] and its Degradation Products.* [With FRITZ MEISTER.]—The unsaturated alcohol, $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$, b. p. $208\text{--}210^\circ$, obtained from the fractions of commercial terpineol boiling at low temperatures cannot be, as was thought (*loc. cit.*), identical with terpinene-4-ol, as the trihydroxyterpane, m. p. 120° , obtained from it yields when heated with acids, not carvenone, but a ketone with an odour of menthone. The alcohol is now considered to be terpinene-1-ol (V). This, on oxidation, must yield 1:3:4-trihydroxyterpane (VI), which, on further oxidation, should be converted by way of the enolic form (VII) into $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid (IV). The identity of the acid thus obtained has been confirmed by its conversion into the dilactone, m. p. 72° , and into dimethylacetylacetone.



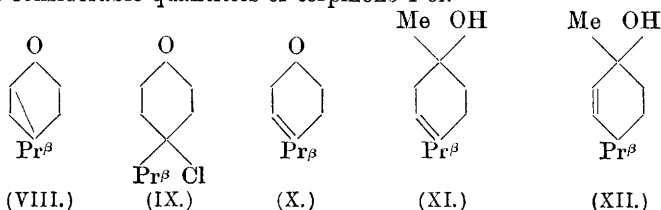
The ketone (Δ^1 -menthenone), $\text{CMe} \begin{array}{c} \diagup \text{CH} \text{---} \text{CO} \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CHPr}^\beta$, formed from 1:3:4-trihydroxyterpane, has b. p. $235\text{--}237^\circ$, $D_{19}^{20} 0.9375$, $n_D^{20} 1.4875$, and forms a sparingly soluble semicarbazone, m. p. $224\text{--}226^\circ$, which yields the ketone again when heated with sulphuric acid. When treated with sodium in ethereal solution, the ketone yields a *pinacone* and an *alcohol*, which is oxidised by chromic acid, forming *i*-menthone. The semicarbazone of this has m. p. $210\text{--}212^\circ$. A comparison of the physical properties of Δ^1 -menthenone with those of carvenone,

carvotanacetone, Δ^4 -menthenone, and Callenbach's menthenone (see Rabe and Rahm, Abstr., 1904, i, 757; Merling, Abstr., 1905, i, 349), shows that the new ketone most closely resembles carvenone.

Δ^4 -Menthenone, purified by conversion into its oxime and liberation by means of sulphuric acid, has b. p. 213° , D^{21}_D 0.918, n^{21}_D 1.4720; the semicarbazone has m. p. 142° ; the dibromide, $C_{10}H_{16}OBr_2$, m. p. 36° . On reduction, menthenone yields a mixture of stereoisomeric menthols, including *i*-menthol, which forms a semicarbazone, m. p. 212° .

IV. *Synthesis of the Two Tertiary Alcohols of the Terpinene Series, Terpinene-4-ol (Δ^1 -Menthene-4-ol) and Terpinene-1-ol (Δ^3 -Menthene-1-ol).*—The formation of terpinene-4-ol from sabinene hydrate was described previously (this vol., i, 430). The crystalline sabinene hydrate, formed by the action of magnesium methyl iodide on sabina ketone, has $[\alpha]_D +53.67^\circ$, and when shaken with sulphuric acid yields terpinene-4-ol, which has $[\alpha]_D +10.53^\circ$, and is identical with the terpinenol from cardamom and majorana oils, but may contain small amounts of the inactive alcohol.

[With RICHARD HEYER.]—Terpinene-1-ol (XI) is prepared from sabinaketone (VIII) by conversion of this by way of its hydrochloride (IX) into Δ^3 -isopropylhexenone (X) and treatment of the product with magnesium methyl iodide. Δ^3 -isoPropylhexenone has b. p. $95-96^\circ/12$ mm., D^{22}_D 0.944, n^{22}_D 1.4817. Terpinene-1-ol has b. p. $92-97^\circ/14$ mm., D^{24}_D 0.9210, n^{24}_D 1.4778, and loses water when distilled under the ordinary pressure, forming phellandrene. The ethylene linking undergoes transmigration during the decomposition of the terpinenol, or Δ^3 -isopropylhexenone isomerises to Δ^2 -isopropylhexenone during the Grignard reaction, in which case the resulting alcohol must be phellandrene hydrate (XII). As on oxidation the synthetic alcohol yields 1:3:4-trihydroxyterpane, it must contain at least considerable quantities of terpinene-1-ol.

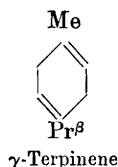
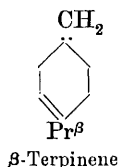
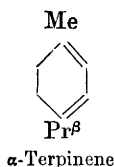


V. *Other Syntheses in the Terpinene Group.*—The action of magnesium isopropyl iodide on sabina ketone leads to the formation of a tertiary alcohol, which is obtained as a viscid oil, b. p. $102-107^\circ/14$ mm., and, when shaken with dilute sulphuric acid, slowly forms the *terpin*, $OH \cdot CPr^\beta < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > CPr^\beta \cdot OH$. This crystallises in plates, m. p. 139° , and reacts readily with hydrogen haloids in glacial acetic acid solution. The dichloride, $C_{12}H_{22}Cl_2$, has m. p. $111-112^\circ$; the dibromide, m. p. $120-121^\circ$. G. Y.

Terpenes and Etheral Oils. XCVI. Terpinene and its Modifications. OTTO WALLACH (*Annalen*, 1908, 362, 285—304).—I. β -Terpinene.— β -Terpinene (Abstr., 1907, i, 1058) is now found

to have b. p. $173-174^{\circ}$, D_4^{20} $0.838-0.840$, n_D^{20} $1.4751-1.4754$. With bromine in alcoholic-etheral solution, it forms a sparingly soluble *tetrabromide*, $C_{10}H_{16}Br_4$, crystallising in prisms, m. p. $154-155^{\circ}$, and when treated with water and oxygen in presence of sunlight is converted into dihydrocuminaldehide, which is further oxidised to cuminaldehide. Oxidation of β -terpinene with permanganate in aqueous solution leads to the formation of a neutral *product*, which distils at $225^{\circ}/10$ mm., yielding small amounts of a crystalline *substance*, and when treated with dilute sulphuric acid, without previous distillation, yields an oil having a strong odour of cuminaldehide and forming a *semicarbazone*, m. p. $201-202^{\circ}$.

II. *Constitution of Ordinary Terpinene*.—It has been shown previously (Abstr., 1907, i, 943) that terpinene must be one of, or a mixture of two or three of, the three substances having the annexed formulæ. These three substances yield the same dihydrohaloids.



Terpinene has now been obtained (a) from the dihydrochloride, m. p. 52° , (b) by inversion of pinene, and (c) synthetically from sabinaketone. Ordinary terpinene, b. p. $179-181^{\circ}$, cannot contain β -terpinene, as this has now been found to boil at a lower temperature than limonene, to form terpinene nitrosite only slowly and incompletely, and to yield oxidation products; moreover, ordinary terpinene does not form a crystalline tetrabromide. α -Terpinene, on oxidation with permanganate, must form 1:2:3:4-tetrahydroxyterpane (erythritol), which, on further oxidation, yields $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid (see preceding abstract). It is found, however, that, on oxidation with permanganate, ordinary terpinene, prepared by method (a), (b), or (c), yields in addition to this acid an erythritol, m. p. $236-237^{\circ}$, which does not form the dihydroxyadipic acid on further oxidation; ordinary terpinene must therefore be a mixture of hydrocarbons, α -terpinene being the chief component. The other hydrocarbon present can be either γ -terpinene or terpinolene, and the latter on oxidation does not yield the erythritol, m. p. $236-237^{\circ}$. It is held that terpinene nitrosite is derived from α -terpinene.

G. Y.

Philippine Terpenes and Essential Oils. I. RAYMOND F. BACON (*Philippine J. Sci.*, 1908, 3, 49-64).—When a mixture of limonene hydrochloride and ether is treated with magnesium and the product decomposed with cold dilute sulphuric acid, a hydrocarbon, $C_{10}H_{18}$, b. p. $174-176^{\circ}$, is produced, which has D_4^{30} 0.8257 , n_D^{30} 1.4585 , and $[\alpha]_D^{30}$ 90.3° , and is probably identical with the dihydrolimonene obtained by Semmler (Abstr., 1903, i, 505) by the

reduction of limonene hydrochloride with sodium and alcohol. The hydrochloride of this compound was prepared and submitted to the Grignard reaction, when a *hydrocarbon*, $C_{10}H_{20}$, b. p. 171—174°, was obtained, which has D_4^{20} 0.8052, n_D^{20} 1.4459, and $[\alpha]_D^{20}$ 3.7°. When benzaldehyde is added to the product of the action of magnesium on limonene hydrochloride, the hydrocarbon, $C_{10}H_{18}$, is liberated, and a *compound*, $C_6H_5 \cdot COMgCl$, is produced, which is decomposed by dilute acids with formation of benzaldehyde, and is converted by heat into benzoin and other substances. Acetone reacts with the magnesium compound in a similar way.

When magnesium benzyl chlorid is treated with benzaldehyde, phenylbenzylcarbinol, m. p. 67—68°, is produced. E. G.

Philippine Terpenes and Essential Oils. II. Ylang-ylang Oil. RAYMOND F. BACON (*Philippine J. Sci.*, 1908, 3, 65—86).—Determinations have been made of the sp. gr., rotatory power, refractive index, and ester number of samples of Philippine ylang-ylang oil of different grades and origin. The ester number of first-grade oils is usually about 100, whilst that of second-grade oils rarely exceeds 80. The refractive index of the former is rarely more than 1.4900, whereas that of the latter approaches 1.5000. This difference is due to the fact that the second-grade oils contain more sesquiterpenes and resins. For the same reason, $[\alpha]_D$ of the first-grade oils is usually below -45° , whilst that of the second-grade is -60° or more.

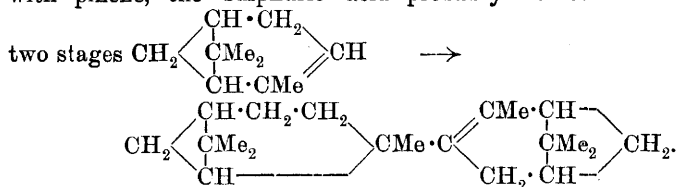
A study of the composition of the oil has confirmed, on the whole, the work of previous observers, and has shown that the following substances are present: esters of formic, acetic, valeric (?), benzoic, and salicylic acids; methyl and benzyl alcohols; pinene, cadinene, and other terpenes and sesquiterpenes; linalool, geraniol, and safrole; eugenol, isoeugenol, and *p*-cresol, probably as methyl ethers; and creosol.

The following esters have been prepared for comparison: *benzyl salicylate*, b. p. 186—188°/10 mm.; *benzyl benzoate*, b. p. 315—320°; *benzyl methyl ether*, b. p. 166—168°; *benzyl formate*, b. p. 84—85°/10 mm.; *geranyl methyl ether*, b. p. 100—105°/10 mm. and 208—212°/760 mm.; *linalyl methyl ether*, b. p. 189—192°, and *geranyl benzoate*, b. p. 198—200°/15 mm. E. G.

Method of Obtaining Resins from Turpentine and the Preparation from them of Lacs, Varnishes, &c. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 800—805).—This method consists in treating turpentine oil with sulphuric acid of 66° B. and formaldehyde, neutralising with ammonia, separating the ammonium sulphate, and heating with ammonia. After drying at 70—80°, a yellowish-brown resin is obtained, which is soluble in alcohol, benzene, toluene, ether, or acetic acid, giving yellow solutions. It also dissolves in solvent naphtha or ethyl acetate, and the solutions in these solvents form quick-drying, elastic lacs.

The chemical constituents of the lacs obtained were not determined, but it is probable that they consist of a hydrocarbon, or mixture of

hydrocarbons, produced by a series of condensations. For example, with pinene, the sulphuric acid probably causes condensation in



Continuation of this process would lead to still more complicated hydrocarbons. The formaldehyde probably reacts with the mobile hydrogen atoms, giving $\cdot\text{CH}_2\cdot\text{OH}$ groups. The alcohols so formed would lose water on heating, giving rise to methylene derivatives of terpenes and polyterpenes.

T. H. P.

Resins from Conifers, and Treatment of the Resinous Sap

from *Pinus maritima*, *P. sylvestris*, and other Species. W. SCHKATELOFF (*Chem. Zentr.*, 1908, i, 2097—2100; from *Moniteur scient.*, 1908, [4], 22, 217—227. Compare Abstr., 1907, i, 213).—From studying the composition of the resin from *Pinus sylvestris*, the author comes to the conclusion that in all ordinary resins, such as colophony, galipot, resinous saps, &c., the same resin acid is present in the following isomeric modifications: (1) α -Sylvic acid, a white, crystalline powder, m. p. 143—144°, $[\alpha]_D - 73.67^\circ$; (2) β -sylvic acid, crystallising in three-sided plates, m. p. 160°, $[\alpha]_D - 92.5^\circ$; (3) γ -sylvic acid, crystallising in long needles or three-sided plates, m. p. 179—180°, optically inactive. Of these modifications, β -sylvic acid appears to be identical with the abietic acid described by Mach and Levy, and γ -sylvic acid identical with pyromaric acid described by Laurents. A yellow, acid, uncrystallisable resin, called by Unverdorben pinic acid, was found accompanying these three isomeric acids in all crude products. It is produced from the isomeric resin acids by oxidation when exposed to the air. The evidence so far obtained indicates that the formula of the resin acids may be $\text{C}_{20}\text{H}_{28}\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, an unsaturated compound containing two double linkings. Considerable contradiction and confusion as to the properties of these resin acids is caused by the difficulty of investigating them. As an instance of this, it is stated that if α -sylvic acid from *P. sylvestris* is melted, a pale colophony is obtained, $[\alpha]_D - 73.5^\circ$; the same acid from *P. abies excelsa* gives a colophony, $[\alpha]_D - 74.1^\circ$, which, if heated in an air-oven to 170°, shows $[\alpha]_D - 60^\circ$, and $[\alpha]_D - 18^\circ$ after heating to 180—190°, finally becoming inactive.

The Properties of Resinous Saps from Various Pines.—(a) From *Pinus sylvestris*: gives, when steam-distilled, 15—16% turpentine oil, $[\alpha]_D + 22^\circ$ to $+ 24^\circ$, or rectified over sodium hydroxide, $[\alpha]_D + 25.1^\circ$, $D^{15} 0.867$. The acid present in the sap is α -sylvic acid. (b) From *P. abies excelsa*: gives very little resin; the resin sap contains about 13.4% oil, $D^{15} 0.873$, $[\alpha]_D - 13.2^\circ$, and also α -sylvic acid, m. p. 143° and $[\alpha]_D - 74.1^\circ$. (c) *Larix sibirica* gives very little resin sap, 14.13% oil of $D^{15} 0.870$, $[\alpha]_D - 14.3^\circ$, and β -sylvic acid. (d) *Pinus cembra* gives only 6% oil of $D^{15} 0.865$, $[\alpha]_D + 14.04^\circ$; another portion

contained 20% oil of b. p. 155—156° and $[\alpha]_D + 17^\circ$, and from the solid resin, β -sylvic acid was obtained. (e) *P. taurica* gave a quantity of the same resin as *P. maritima*; the resinous sap contained 20% oil of D^{19} 0.861 and $[\alpha]_D - 75.9^\circ$, and the solid resin, α -sylvic acid. (f) *Abies sibirica*: the resin sap is a very aromatic, clear liquid containing 28% oil, D^{19} 0.8751, $[\alpha]_D - 35.6^\circ$, but no crystallisable substance. (g) *Pinus strobus*: the resin sap is similar to that of ordinary pine, and contains α -sylvic acid. J. V. E.

Decomposition of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1908, 246, 365—366).—Feist (this vol., i, 437) regards *d*-benzaldehydecyanohydrin, formed when emulsin acts on amygdalin, as a primary product in the hydrolysis. The author, however, has now shown experimentally that *d*-benzaldehydecyanohydrin is formed from benzaldehyde and hydrocyanic acid by emulsin, and is therefore a secondary synthetic product. G. B.

Constitution of Vicianin. I. GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1908, 147, 252—254).—Vicianin (Abstr., 1907, i, 68), like amygdalin and Dakin's *isoamygdalin* (Trans., 1904, 85, 1512), when dissolved in concentrated sulphuric acid gives a carmin-red coloration, slowly whilst cold, rapidly on heating. Schiff (Abstr., 1900, i, 49) considered this reaction as characteristic of mandelonitrile. The presence of the group $\cdot O \cdot CHPh \cdot CN$ in vicianin is proved by two reactions: (1) When an aqueous solution of the crystallised glucoside is treated at 35° with an extract of the seeds of *Vicia angustifolia*, hydrogen cyanide (estimated by Denigès' method, Abstr., 1896, ii, 385) and benzaldehyde (estimated by conversion into the phenylhydrazone) are produced in equal molecular quantities. (2) By evaporating to dryness vicianin (4 grams) with fuming hydrochloric acid (25 c.c.), *l*-mandelic acid is produced. The acid obtained has m. p. 132—133° (on Maquenne block) and $[\alpha]_D - 153.3^\circ$ (at 1% and 1% solution), whilst Walden (Abstr., 1896, ii, 137) found m. p. 131—132° and $[\alpha]_D - 133.06^\circ$. The conclusion is drawn that vicianin, like amygdalin, is a derivative of *l*-mandelonitrile. E. H.

Action of Hydrochloric Acid on Santonin and its Derivatives. Mechanism of the Formation of Desmotroposantonin. LUIGI FRANCESCONI and G. CUSMANO (*Gazzetta*, 1908, 38, ii, 101—110).—It has been stated by Wedekind (*Chem. Zeit.*, 1902, No. 13), and by Wedekind and Schmidt (*Arch. Pharm.*, 1906, 244, 623), that santonin acid is transformed into desmotroposantonin by the action of hydrochloric acid. The authors show that no such change takes place, and that the method of preparation of santonin acid probably employed by Wedekind (Abstr., 1898, i, 596) gives mixtures of santonin acid with santoninic acid or santonin, which mixtures have, in some cases, a melting point practically the same as that given by Wedekind, and cannot be freed from impurity by crystallisation from a mixture of alcohol and ether.

Santonin acid and desmotroposantonin are not acted on by dry hydrogen chloride. When cooled with a mixture of ice and salt,

santonin absorbs 2 mols. of hydrogen chloride, one of which is eliminated rapidly at the ordinary temperature in an atmosphere of hydrogen chloride, and the other, slowly in presence of an extraneous gas. Both these hydrochlorides yield santonin when treated with water or sodium hydroxide, and are related to santonin in the same way as the coloured, unstable additive products of ketones with the halogen hydracids are related to the ketones themselves (compare this vol., i, 801). Both these hydrochlorides change gradually into a monohydrochloride, which is not capable of absorbing hydrogen chloride, and yields desmotroposantonin by the action of water or by spontaneous elimination of hydrogen chloride. The formation of these different hydrochlorides and that of desmotroposantonin from them are explained in the same way as the formation of the various hydrochlorides of the unsaturated, aromatic ketones (*loc. cit.*).

T. H. P.

Sapotoxin and Sapogenin from *Agrostemma githago*. II. J. BRANDL (*Arch. exp. Path. Pharm.*, 1908, 59, 245—268).—A second sapotoxin can be obtained from the lead acetate precipitate from the crude sapotoxin, which can be purified by precipitation by ethyl alcohol from the solution in methyl alcohol. It is designated *agrostemmic acid*. It has a considerably higher molecular weight than the *A*-sapotoxin. It yields on hydrolysis sapogenin, $C_{35}H_{54}O_{10}$, in a yield of 38%, and sugars, calculated as dextrose, in a yield of 50.67%. The sugars obtained by the hydrolysis of the saponins consist of dextrose and galactose, with possibly some arabinose.

The potassium salt of sapogenin methyl ester, when pure, has a composition corresponding with $C_{36}H_{55}O_{10}K$. By treating the potassium salt or its methyl esters with methyl sulphate, a series of methyl derivatives can be obtained, the yield of which varies with the conditions of experiment. The monomethyl derivative, which is crystalline, but has no definite m. p., corresponds with the formula $C_{36}H_{56}O_{10}$. The higher methyl derivatives are not crystalline.

By heating sapogenin with potassium hydroxide at 160—175°, an acid, $C_{30}H_{46}O_4$, is obtained, which does not melt at 290°, and yields a dimethyl ester, m. p. 231—232°. This acid is also obtained from dogs' faeces after ingestion of sapotoxin.

The toxic effects of the seeds of *Agrostemma githago*, of agrostemmic acid, and of the sapotoxin are similar. The seeds in quantities of 10 grams per kilo. in pigeons, and 15 grams per kilo. in hens, ingested *per os* cause death in two to three days. Vomiting, diarrhoea, salivary flow, and paralysis are the chief symptoms.

S. B. S.

Sweet Substances from *Eupatorium Rebaudianum* and Liquorice. PAUL RASENACK (*Chem. Zentr.*, 1908, ii, 78—79; from *Arb. Kais. Gesundh.-Amt.*, 1908, 28, 420—443).—The sweet material which is contained chiefly in the leaves of *Eupatorium Rebaudianum* was obtained by extracting with alcohol and then precipitating with ether. The crude product separates from methyl alcohol in slender, white needles, which shrink at 180—190°, m. p. 200—210° (decomp.). The

composition of this substance appears to be $C_{42}H_{72}O_{21}$, and its behaviour towards salt solutions differs from that of glycyrrhizin.

When boiled with dilute sulphuric acid, it gives dextrose and a tasteless substance, forming small, prismatic crystals, m. p. 226—227°, which are sparingly soluble in water, and appear to have the composition $C_{80}H_{40}O_5$. The author has investigated the sweet material from liquorice root, and detected the presence of saccharose therein. From the results of analysis, the formula for glycyrrhizic acid is considered to be $C_{44}H_{60}O_{18}$. J. V. E.

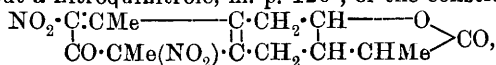
Aminolactones from Diacetone Alcohol. MORITZ KOHN (*Monatsh.*, 1908, 29, 509—518. Compare this vol., i, 829).—The use of diacetone alcohol (β -methylpentane- β -ol- δ -one) instead of diacetone-amine in the Bucherer and Zelinsky reaction (*loc. cit.*) leads in a similar manner to the formation of tetrahydrofuran derivatives in place of those of pyrrolidone.

4-Amino-5-keto-2:2:4-trimethyltetrahydrofuran, $O \begin{array}{l} \text{CO—CMe·NH}_2 \\ \text{CMe}_2 \cdot \text{CH}_2 \end{array}$, m. p. 30—34°, b. p. 122—124°/14—16 mm., yields a phenylthiocarbamide, m. p. 195—198°. 4-Methylamino-5-keto-2:2:4-trimethyltetrahydrofuran, $C_8H_{15}O_2N$, b. p. 108—111°/12 mm., forms a phenylthiocarbamide, m. p. 152—154°.

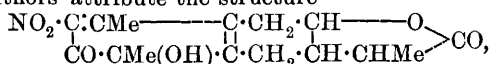
The reaction between the alcohol, potassium cyanide, and dimethylamine hydrochloride leads to the ultimate formation of a liquid, b. p. 113°/12 mm., which is a mixture of Franke and Kohn's 4-hydroxy-5-keto-2:2:4-trimethyltetrahydrofuran (*Abstr.*, 1907, i, 816) and 4-dimethylamino-5-keto-2:2:4-trimethyltetrahydrofuran, $C_9H_{17}O_2N$, of which the platinichloride, and the methiodide with its aurichloride and platinichloride are mentioned. C. S.

Action of Nitric Acid on Desmotroposantonin. GUIDO BARGELLINI and V. DACONTO (*Gazzetta*, 1908, 38, ii, 41—52. Compare *Abstr.*, 1907, i, 931).—When oxidised by means of chromic acid, desmotroposantonin yields a compound which, with phenylhydrazine in dilute acetic acid, gives an insoluble, red product, but the amount obtained was too small to admit of its further study.

On treating desmotroposantonin with nitric acid under the conditions given by Andreocci (*Abstr.*, 1898, i, 266), the authors find that the first compound formed is not the nitrodesmotroposantonin described by Andreocci, but a nitroquinitle, m. p. 120°, of the constitution



which decomposes readily into one or other of the three compounds described by Andreocci (*loc. cit.*), according to the conditions. To the compound, m. p. 240°, obtained by Andreocci by the action of hot dilute nitric acid or cold concentrated nitric acid on desmotroposantonin, the authors attribute the structure



which is more in accord with its mode of formation from the nitroquinitle and with its behaviour as a nitroquinol than is the con-

stitution suggested by Andreocci. The authors could not obtain Andreocci's third substance, m. p. 145° , in a pure state.

The *nitroquinitrole*, $C_{15}H_{16}O_7N_2$, obtained as an amorphous, white powder, m. p. about 120° (decomp.), like all quinitroles, decomposes readily with evolution of oxides of nitrogen. When decomposed by means of methyl or ethyl alcohol, it gives an almost quantitative yield of nitrodesmotroposantonin, $C_{15}H_{17}O_5N$, which separates from alcohol in trimetric crystals [A. ROSATI: $a:b:c=0.4133:1:2.2646$], m. p. $189-190^{\circ}$, $[\alpha]_D^{25} + 115.38^{\circ}$. Nitrodesmotroposantonin exhibits all the characters of the nitrophenols, and yields an *acetyl* derivative,

$C_{17}H_{19}O_6N$,

which crystallises from alcohol in white needles, m. p. $166-167^{\circ}$, $[\alpha]_D^{25} + 111.79^{\circ}$

The nitroquinol, m. p. $237-240^{\circ}$ (decomp.), which can also be obtained by heating the nitroquinitrole or nitrodesmotroposantonin on the water-bath with nitric acid (D 1.23), dissolves readily in concentrated sulphuric acid, giving a cherry-red solution, and yields an *acetyl* derivative, $C_{17}H_{19}O_7N$, m. p. $186-188^{\circ}$. When reduced by means of sulphuric acid, the nitroquinol is converted into nitrodesmotroposantonin, whilst reduction by zinc and acetic acid yields a red, amorphous substance, which appears to be analogous to that obtained by Wedekind (Abstr., 1905, i, 134) by reducing benzene azodesmotroposantonin with stannous chloride and hydrochloric acid.

[With A. MANNINO.]—*l*-Desmotroposantonin behaves towards nitric acid in the same way as desmotroposantonin, a nitroquinitrole being first formed. The *nitroquinol*, $C_{15}H_{17}O_6N$, crystallises from acetic acid in colourless needles, m. p. $218-220^{\circ}$ (decomp.), dissolves in concentrated sulphuric acid, giving a red coloration, and is *lævo*-rotatory.

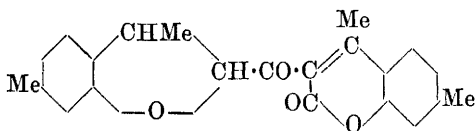
T. H. P.

Conversion of Coumarins into Coumarinic Acids and *o*-Coumaric Acids. KARL FRIES and W. KLOSTERMANN (*Annalen*, 1908, 362, 1—29).—It has been shown previously (Abstr., 1906, i, 276) that 7-methylcoumarin, 4:7-dimethylcoumarin, and 3:4:7-trimethylcoumarin differ in their behaviour towards aqueous alkalis. The rate of formation of coumarinic acids from these substituted coumarins, and also from 4:7-dimethyl-3-ethylcoumarin and 3-benzyl-4:7-dimethylcoumarin, on treatment with an aqueous solution of potassium hydroxide has now been measured. It is found that the velocity with which the coumarin is converted into the corresponding coumarinic acid decreases, not only with an increase in the number, but also in the size, of the alkyl or aryl group. This is shown by the following comparative values representing the velocity of formation of the coumarinic acid: 7-methylcoumarin = 150, 4:7-dimethylcoumarin = 100, 3:4:7-trimethylcoumarin = 75, 4:7-dimethyl-3-ethylcoumarin = 45, 3-benzyl-4:7-dimethylcoumarin = 35.

The behaviour of these substituted coumarins on treatment with sodium ethoxide is far more complicated. Ebert has shown (Abstr., 1885, 391) that coumarin and 7-methylcoumarin are converted into the corresponding *o*-coumaric acids when heated with sodium ethoxide. It has now been found possible to isolate the hitherto unknown ethyl

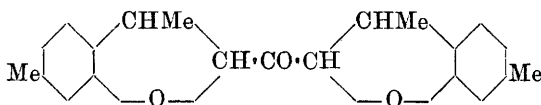
esters of these acids, formed as intermediate products during the reaction. The esters themselves are colourless, but their alkali salts are yellow; it is therefore not improbable that the salts have the quinonoid structure $O:C_6H_4:CH:CH:C(OEt)ONa$. This view receives support from the fact that an alcoholic ammoniacal solution of the ester reduces silver nitrate, whereas neither *o*-coumaric acid nor ethyl cinnamate reduces silver nitrate under similar conditions. The yellow, aqueous solutions of these salts are not fluorescent.

4:7-Dimethylcoumarin when heated with sodium ethoxide or



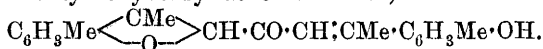
methoxide is not converted into the corresponding coumaric acid, but yields a ketone which probably has the annexed formula. It is

proposed to name the group $C_6H_4 \begin{smallmatrix} \diagup CH_2 \\ \diagdown O \end{smallmatrix} CH \cdot CO-$, hydrocoumarilyl, hence this ketone is 3-[2:5-dimethylhydrocoumarilyl]-4:7-dimethylcoumarin. It is converted by aqueous alkalis into another ketone, thus: $C_{22}H_{20}O_4 + H_2O \rightarrow C_{21}H_{22}O_3 + CO_2$. This new compound is



probably 1-[2:5-dimethylhydrocoumarilyl]-2:5-dimethylhydrocoumarone, having the annexed formula.

The solubility of this substance in alkalis and the formation of a methoxy-derivative on treating a solution in alcoholic sodium ethoxide with methyl iodide may be explained by assuming a transformation into an enolic form, but the compound does not give a coloration with ferric chloride and does not react with copper acetate. It is possible that in the formation of the salts, the hydrocoumarone ring opens, forming an *o*-hydroxybenzylidene derivative,



This would account for the yellow colour of the salts, but the fact that the methoxy-derivative is colourless then becomes remarkable.

4:6-Dimethylcoumarin, like the isomeric 4:7-dimethyl compound, is converted by sodium ethoxide into a ketone, $C_{21}H_{22}O_3$, similar to that just described.

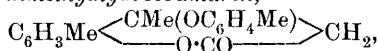
3:4:7-Trimethylcoumarin, 4:7-dimethyl-3-ethylcoumarin, and 3-benzyl-4:7-dimethylcoumarin are converted by sodium ethoxide into sodium salts of the corresponding coumarinic acids.

The effect of the presence of alkyl groups on the reconversion of coumaric acids into coumarins is very marked; thus β :4-dimethyl-*o*-coumaric acid and β :5-dimethyl-*o*-coumaric acid in acetic acid are converted by concentrated hydrochloric acid at the ordinary temperature into the corresponding coumarins in a few hours, whilst, under the same conditions, *o*-coumaric acid and 4-methyl-*o*-coumaric acid remain practically unchanged even during several days. The tendency of β -alkyl-*o*-coumaric acids to change into coumarins is shown

by the fact that the latter compounds slowly separate from solutions of the acids in aqueous sodium carbonate.

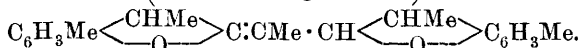
Ethyl o-coumarate, $C_{11}H_{12}O_3$, crystallises in small, compact plates, m. p. 87° ; the *sodium* salt crystallises in yellow leaflets. *Ethyl 4-methyl-o-coumarate*, $C_{12}H_{14}O_3$, crystallises in plates, m. p. 105° .

4-Tolyl-oxy-4 : 7-dimethylhydrocoumarin,



is formed together with 4 : 7-dimethylcoumarin if in the preparation of the latter from *m*-cresol and ethyl acetoacetate the quantity of the sulphuric acid employed is less than that previously given (Abstr., 1906, i, 276). It crystallises in long, glistening prisms, m. p. 220° , and is converted by strong acids into *m*-cresol and 4 : 7-dimethylcoumarin.

3-[2 : 5-Dimethylhydrocoumarilyl]-4 : 7-dimethylcoumarin, $C_{22}H_{20}O_4$, crystallises in slender, white needles, m. p. 257° (decomp.). 1-[2 : 5-Dimethylhydrocoumarilyl]-2 : 5-dimethylhydrocoumarone, $C_{21}H_{22}O_3$, crystallises in monoclinic prisms, m. p. 185.5° . The molten substance sets to a glassy mass, m. p. $93-95^\circ$; the liquefied substance again becomes solid at about 140° , and then has m. p. 185.5° . The *hydrobromide*, $C_{21}H_{22}O_3 \cdot HBr$, forms yellow crystals; the *oxime*, $C_{21}H_{23}O_3N$, crystallises in small plates, m. p. 220° ; the *phenylhydrazone*, $C_{27}H_{28}O_2N_2$, forms slender, pale yellow needles, m. p. 198° . The ketone, $C_{21}H_{22}O_3$, when treated with magnesium methyl iodide and then with dilute sulphuric acid, is converted into a substance, having the formula $C(C_6H_3Me \left\langle \begin{array}{c} CHMe \\ O \end{array} \right\rangle CH)_2 \cdot CH_2$ or



It forms large crystals, m. p. 145° . The ketone, $C_{21}H_{22}O_3$, yields a *methoxy*-derivative, $C_{22}H_{24}O_3$, crystallising in long, flat plates, m. p. 165° , and an *ethoxy*-derivative, $C_{23}H_{26}O_3$, crystallising in prisms, m. p. 156° .

4 : 6-Dimethylcoumarin is converted by a hot aqueous solution of potassium hydroxide into β : 5-dimethyl-*o*-coumaric acid, $C_{11}H_{12}O_3$; it crystallises in small leaflets, decomposing with evolution of carbon dioxide at about 138° .

A ketone, $C_{21}H_{22}O_3$, is formed by the action of sodium ethoxide on 4 : 6-dimethylcoumarin. It is very similar in properties to the isomeric ketone derived from the 4 : 7-compound, forming compact, colourless crystals, m. p. 199° ; the *oxime*, $C_{21}H_{23}O_3N$, crystallises in microscopic needles, m. p. 120° .

4 : 7-Dimethyl-3-ethylcoumarin, $C_{13}H_{14}O_2$, prepared by the action of concentrated sulphuric acid on a mixture of ethyl ethylacetoacetate and *m*-cresol, crystallises in long, spear-shaped needles, m. p. 87° .

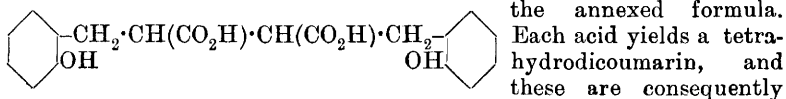
3-Benzyl-4 : 7-dimethylcoumarin, $C_{18}H_{16}O_2$, prepared from ethyl benzylacetoacetate and *m*-cresol, crystallises in long, white needles, m. p. 117° .

W. H. G.

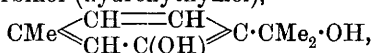
Reduction of Coumarins with Zinc Dust in Alkaline Solution. KARL FRIES and G. FICKEWIRTH (*Annalen*, 1908, 362, 30—48).—With the object of finding a simple method of preparing

hydrocoumarins from coumarins, reduction by means of zinc dust in alkaline solution was tried, but without success. The results obtained show, however, that derivatives of coumarin containing an alkyl group in the pyrone ring are quite different in their chemical behaviour from coumarin itself.

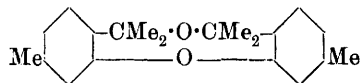
Coumarin is converted by zinc dust in alkaline solution chiefly into melilotic acid, but at the same time two isomeric tetrahydrodicoumaric acids are formed, namely, α - and β -tetrahydrodicoumaric acids, having the annexed formula.



α - and β -tetrahydrocoumarins, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \\ \text{O} \quad \text{CO} \quad \text{CO} \quad \text{O} \end{array} \text{C}_6\text{H}_4$ (compare Dyson, Trans., 1887, 51, 61). When 4:7-dimethylcoumarin is treated in the same way as coumarin, it yields 2-hydroxy-4-methylphenyldimethylcarbinol (hydroxythymol),



2-hydroxy- β :4-dimethylstyrene, and thymol; the quantity of each substance formed depends on the duration of the action, the first compound formed being hydroxythymol. The part played by the zinc dust in the formation of the latter substance is not yet clear, for, although the formation of this alcohol is not due to simple reduction, yet the reaction proceeds in a different direction when the zinc dust is not present. It is probable that at first the 4:7-dimethylcoumarin is converted into β :4-dimethyl-*o*-coumaric acid, which by the addition of water changes into β :2-hydroxy-4-methylphenyl- β -methylhydracrylic acid, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$; the latter substance then loses carbon dioxide, yielding hydroxythymol. Since hydroxythymol, when heated, readily loses water, yielding 2-hydroxy- β :4-dimethylstyrene or its polymeride (compare this vol., i, 160), it is evidently a tertiary alcohol having the formula given above. Although hydrochloric acid and hydrobromic acid convert hydroxythymol into the polymerised form of 2-hydroxy- α :4-dimethylstyrene, hydriodic acid acts on it, forming a substance identical with the condensation product obtained by Gaebel (*Diss.*, Marburg, 1903) from *m*-cresol and acetone, to which the annexed formula was assigned.



The normal reduction product of 4:7-dimethylcoumarin, namely, β :4-dimethylhydrodicoumaric acid, is obtained by using sodium amalgam as the reducing agent. This acid is very unstable, and readily changes into 4:7-dimethylhydrocoumarin.

4:6-Dimethylcoumarin is converted by zinc dust and alkali into 2-hydroxy-5-methylphenyldimethylcarbinol and 6-hydroxy- α :3-dimethylstyrene (compare this vol., i, 160). The compound corresponding with thymol, namely, 2-hydroxy-5-methylcumene, seems to be formed only with difficulty, and has not yet been obtained pure.

3:4:7-Trimethylcoumarin remains practically unattacked by zinc dust in alkaline solution.

α -Tetrahydrodicoumaric acid, $\text{C}_{18}\text{H}_{18}\text{O}_6$, crystallises in plates, m. p.

280—282°. When heated alone for some time at 280°, or in acetic acid, it is converted into α -tetrahydrodicoumarin, $C_{18}H_{14}O_4$, crystallising in glistening needles, m. p. 284°.

β -Tetrahydrodicoumaric acid, $C_{18}H_{18}O_6$, forms compact prisms, m. p. 158°.

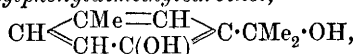
β -Tetrahydrodicoumarin, $C_{18}H_{14}O_4$, crystallises in glistening, slender needles, m. p. 256°.

2-Hydroxy-4-methylphenyldimethylcarbinol (*hydroxythymol*),
 $C_{10}H_{14}O_2$,

forms small, glistening, spear-shaped crystals, m. p. 64°. It is converted by hydriodic acid into a substance, $C_{20}H_{24}O_2$, crystallising in colourless, compact prisms, m. p. 132°. A substance, $(C_{10}H_{13}O)_n$, crystallising in small leaflets, m. p. 186°, is formed, together with hydroxythymol, by the action of zinc dust on 4:7-dimethylcoumarin in alkaline solution; mol.-wt. determinations by the boiling-point method point to n being 2.

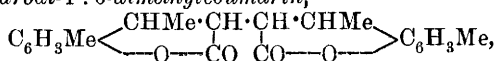
β :4-Dimethyl-o-hydrocoumaric acid, $C_{11}H_{14}O_8$, crystallises in hook-like needles, m. p. 98°; it loses water when heated, yielding 4:7-dimethylhydrodicoumarin, obtained as an oil. If, during the reduction of 4:7-dimethylcoumarin with sodium amalgam, the liquid is kept slightly acid by means of acetic acid, a small quantity of a substance, m. p. 250°, is obtained. It is probably a tetramethyltetrahydrodicoumarin.

2-Hydroxy-5-methylphenyldimethylcarbinol,



prepared from 4:6-dimethylcoumarin, crystallises in rosettes of small, glistening prisms, m. p. 82°.

α -Tetrahydrodi-4:6-dimethylcoumarin,



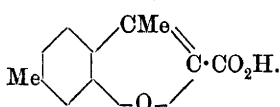
produced by the action of zinc dust on 4:6-dimethylcoumarin in alkaline solution, forms small needles, m. p. 284°. The β -isomeride is best prepared from β :5-dimethylcoumaric acid; it forms small, colourless crystals, m. p. 254°.

W. H. G.

Coumarone and Hydrocoumarone Derivatives from 4:7-Dimethylcoumarin. KARL FRIES and G. FICKEWIETH (*Annalen*, 1908, 362, 49—53).—The object of this investigation was the preparation of 2:5-dimethylhydrocoumarone, the latter being required for purposes of identification. This substance was first prepared by von Baeyer and Seuffert (*Abstr.*, 1901, i, 216) by a method which gives but a poor yield. It was therefore obtained by reducing 2:5-dimethylcoumarilic acid to 2:5-dimethylhydrocoumarilic acid, which, when distilled with soda-lime, yields 2:5-dimethylhydrocoumarone.

4:7-Dimethylcoumarin is converted by bromine in chloroform into 3-bromo-4:7-dimethylcoumarin, $C_{11}H_9O_2\text{Br}$; it crystallises in long, white, silky needles, m. p. 138°, and is converted by a boiling alcoholic

solution of potassium hydroxide into 2:5-dimethylcoumarilic acid.



The latter substance forms small, compact crystals or oblique-angled plates, m. p. about 212° (decomp.); the *ethyl* ester crystallises in small, slender needles, m. p. 38° . The acid, when distilled with soda-

lime, yields 2:5-dimethylcoumarone, b. p. 218° (compare Stoemer, Abstr., 1900, i, 650).

2:5-Dimethylhydrocoumarilic acid, $C_{11}H_{12}O_3$, is obtained by reducing 2:5-dimethylcoumarilic acid with sodium amalgam. It forms small crystals, m. p. 95° , and, when distilled with soda-lime, yields 2:5-dimethylhydrocoumarone, $C_{10}H_{12}O$, an oil, b. p. 222° .

W. H. G.

Preparation of Double Salts from Caffeine and Alkali Metaphosphates. F. HOFFMANN-LA ROCHE & CIE (D.R.-P. 194533).—Caffeine and the alkali metals form soluble, stable dimetaphosphates.

Caffeine sodium dimetaphosphate, $C_8H_{10}O_2N_4 \cdot NaHP_2O_6$, is prepared by adding caffeine to an aqueous solution of sodium hydrogen dimetaphosphate and evaporating to dryness under reduced pressure.

G. T. M.

The Alkaloids of Chinese Corydalis Tubers. K. MAKOSHI (Arch. Pharm., 1908, 246, 381—400).—After much labour, corydaline, corybulbine, protopine, dehydrocorydaline (not hitherto known to occur naturally), and two new alkaloids were isolated. The first new alkaloid, $C_{20}H_{17}O_4N$, is an isomeride of berberine, and a quaternary base; the *hydrochloride*, $C_{20}H_{18}O_4NCl \cdot 2H_2O$, forms red needles, resembling sanguinarine hydrochloride, but is not precipitated by ammonia; *aurichloride*, $C_{20}H_{18}O_4NCl \cdot AuCl_3$, reddish-brown needles, decomposing above 280° without melting. By zinc and hydrochloric acid, this alkaloid is reduced to a *substance*, $C_{20}H_{21}O_4N$, colourless needles, m. p. 218 — 219° , not identical with hydroberberine.

The second new alkaloid, greyish-white needles, m. p. 197 — 199° , was only obtained in minute quantity, and is not identical with bulbocapnine, since it gives different colour reactions.

G. B.

Does Crystallisable Cocaine Occur in Java Coca? ANNE W. K. DE JONG (Chem. Weekblad, 1908, 5, 666—668).—Samples of the alkaloid obtained from both the old and young leaves of Java coca contain cocaine, the percentage being higher in that derived from the former source.

A. J. W.

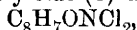
Oxidation by means of Picric Acid. Indulines from Aniline. A. BACOVESCU (Chem. Zentr., 1908, i, 2034—2035; from Buletinul d. Chimie, 1908, 10, 3—5).—When aniline is successively heated with picric acid to about 225° and the mass purified from chloroform and ether, two substances, probably indulines, are obtained.

The reaction also takes place in the presence of hydrogen chloride. One substance is greyish-black, the other brown, and both dissolve in concentrated sulphuric or acetic acid, giving a blue solution.

J. V. E.

Preparation of Halogenated Anilides. A. MANNINO and L. DI DONATO (*Gazzetta*, 1908, 38, ii, 20—31).—The authors have applied the method used by Verda (*Abstr.*, 1903, i, 21) to the preparation of halogenated derivatives of various acetanilides. The latter were treated with mixtures of nitric acid (D 1.398) and hydrochloric (D 1.19) or hydrobromic acid (D 1.48) in various proportions. As a rule, these acid mixtures effect only a chlorinating or brominating action, but in some cases, for example, aceto-*o*-naphthalide, a nitro-group is introduced into the molecule. It is remarkable that, in these reactions, hydrolysis of the acetyl group never occurs, although this takes place easily when the acetanilides are heated with hydrochloric acid alone. The products obtained are individual compounds in a pure state, and the yields are almost quantitative.

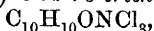
With acetanilide and nitric and hydrochloric acids, 2:4-dichloroacetanilide is obtained if the action is restricted, and 2:4:6-trichloroacetanilide if the action is prolonged. With nitric and hydrobromic acids, 2:4-dibromoacetanilide is formed. With *o*-chloroacetanilide, the product is 2:4:6-trichloroacetanilide or 2-chloro-4-bromoacetanilide. *m*-Chloroacetanilide yields (1) a *dichloroacetanilide*,



crystallising from alcohol in white needles, m. p. 187—188°, and probably not identical with 3:5-dichloroacetanilide, also melting at 187°, since under the above conditions the halogen generally enters in the *o*- or *p*-position to the NHAc group; (2) 3-chloro-2-bromoacetanilide (?), $\text{C}_8\text{H}_7\text{ONClBr}$, which crystallises from 60% acetic acid in needles, m. p. 105—107°. *p*-Chloroacetanilide yields 2:4:6-trichloroacetanilide or 4-chloro-2-bromoacetanilide. *m*-Bromoacetanilide gives 4:6-dichloro-3-bromoacetanilide (?), $\text{C}_8\text{H}_6\text{ONCl}_2\text{Br}$, which crystallises from alcohol in tufts of flesh-coloured needles, m. p. 194—195°, or 2:4:5-tribromoacetanilide. With *m*-nitroacetanilide a chlorodinitroacetanilide (?), m. p. about 200°, is formed. *p*-Nitroacetanilide yields 2-chloro-4-nitroacetanilide or a yellow bromo-derivative, m. p. about 115°, which was not obtained sufficiently pure to analyse.

Aceto-*o*-toluidide yields a dichloroaceto-*o*-toluidide, m. p. 155—156° (compare Verda, *loc. cit.*), or 5-bromo-2-acetotoluidide. Aceto-*p*-toluidide gives (1) 2:3:6- or 2:3:5-trichloroaceto-*p*-toluidide, $\text{C}_9\text{H}_8\text{ONCl}_3$, which separates from alcohol in crystals, m. p. 178—180°, and (2) 2:6-dibromoaceto-*p*-toluidide, $\text{C}_9\text{H}_8\text{ONBr}_2$.

Aceto-*m*-xylidide gives (1) 3:5:6-trichloroaceto-*m*-xylidide,



which crystallises from aqueous alcohol in white needles, m. p. 190—192°, and, when boiled with dilute hydrochloric acid, yields the corresponding trichloro-*m*-xylidine, m. p. 203°, or (2) 3:5:6-tribromoaceto-*m*-xylidide, $\text{C}_{10}\text{H}_{10}\text{ONBr}_3$, which separates from alcohol in crystals, m. p. 246—248°.

Aceto- α -naphthalide yields (1) the chloronitroaceto- α -naphthalide, m. p. 219°, which was prepared by Verda (*loc. cit.*), which, on boiling with dilute hydrochloric acid in alcoholic solution, gives a compound, $C_{10}H_7O_2N_2Cl$, crystallising from alcohol in yellow needles, m. p. about 230°, or (2) 3 : 8-dibromoaceto- α -naphthalide. Aceto- β -naphthalide gives (1) a red, oily chloro-derivative; (2) a tribromoaceto- β -naphthalide, m. p. 250° (decomp.), which gives, on hydrolysis, a compound, m. p. 125°; since 1 : 3 : 6-tribromo- β -naphthylamine has m. p. 143°, it is probable that the tribromoaceto- β -naphthalide is not the 1 : 3 : 6-compound which has been described as having the m. p. 250°.

T. H. P.

Resolution of Racemic Amines by means of Camphoramic Acids. MLLE. G. FREYLON (*Ann. Chim. Phys.*, 1908, [viii], 15, 140—144).—According to Wallach (*Abstr.*, 1906, i, 160), primary amines can be prepared by the addition of formic or acetic acid to a mixture of ammonium formate with an aldehyde or ketone. The author finds, however, that this method does not serve for the preparation of α -phenylethylamine, which can be obtained in a yield equal to 50% of the ketone employed by heating 10 grams of acetophenone with 20 grams of pure, dry ammonium formate to 180—190° for six hours.

When condensed with camphoric anhydride, α -phenylethylamine yields a mixture of the two stereoisomeric camphoramic acids, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NH \cdot CHMePh$, which, by fractional crystallisation, can be separated into: (1) a dextro-fraction, $C_{18}H_{25}O_3N$, $[\alpha]_D^{20} + 64.92^\circ$, and (2) a lævo-fraction, $[\alpha]_D^{20} - 50.52^\circ$, both of which have m. p. 161—162°. When boiled with 30% hydrochloric acid, the *d*-compound yields the amine, b. p. 81°/15 mm., which gives a dextrorotatory hydrochloride, m. p. 159—160°, but was obtained in quantity too small to admit of analysis.

Thus, although the α -camphoramic acids are easily and rapidly prepared, they do not afford a good means for resolving racemic bases into their optically active components. With bases containing only aliphatic radicles, the resolution is more difficult than with aromatic compounds, so much so that in no case has more than one derivative exhibiting a constant m. p. and rotatory power been obtained (compare Locquin, *Abstr.*, 1907, i, 593).

T. H. P.

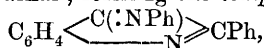
New Method of Preparing some Simple Ethers. II. TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1908, 540—551. Compare *Abstr.*, 1907, i, 173).—The author has extended his investigation on the preparation of ethers by the action of quinoline hydrochloride on primary alcohols to secondary and tertiary alcohols, with the results that, whereas the secondary alcohol yields the corresponding ether and ethylene hydrocarbon, the tertiary alcohol yields ethylene hydrocarbons only. When isopropyl alcohol (1 mol.) is heated with quinoline hydrochloride (0.2 mol.) in sealed tubes at 160° for eight days, the products consist of isopropyl ether, isopropyl chloride, and propylene, together with an isopropylquinoline and diisopropylquinoline. The isopropyl ether, b. p. 68—68.2°, $D^{16.2} 0.7349$ (Zander, *Abstr.*, 1882,

1259, gives D^{20}_{25} 0.7247), obtained amounted to 24.5% of the theoretical yield; the *isopropylquinoline*, b. p. 280—300°, yielded a *picrate*, m. p. 160—161°, and is therefore not identical with any of the *isopropylquinolines* already described (Widman, Abstr., 1886, 465; Döbner, Abstr., 1887, 504; Spady, Abstr., 1886, 263); *diisopropylquinoline*, b. p. 300—320°, forms a *picrate*, m. p. 226—228°.

When trimethylcarbinol is heated for three days at 160° with quinoline hydrochloride, the principal products consist of *isobutylene* and *diisobutylene*.
M. A. W.

Catalytic Action of Finely-divided Metals on Compounds containing Nitrogen. MAURICE PADOA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 728—731).—Whereas 2-methylindole is obtained on passing quinoline vapour over reduced nickel heated at 260—280° (Abstr., 1906, i, 765), 3-methylindole is formed together with a little quinoline when tetrahydroquinoline is similarly treated. The action probably occurs owing to the intermediate formation of propylaniline by the breaking of bond 4—5, or of 2-methylamino-1-ethylbenzene by the breaking of bond 2—3, probably the latter, because propylaniline does not produce a methylindole when heated with nickel at 300°.
W. A. D.

Indoles. ANGELO ANGELI and EUGENIO MORELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 697—702).—The view that 3-nitrosoindoles are true nitroso-derivatives, $C_6H_4 \begin{smallmatrix} C(NO) \\ \diagup \quad \diagdown \\ N-H \end{smallmatrix} > CR$, is improbable in view of the fact that either the silver or sodium salt gives with ethyl iodide only one ethyl derivative; that obtained from 3-nitroso-2-phenylindole is red, and has m. p. 45°. The structure of the nitroso-indoles is discussed at some length; they are probably best regarded as oximes, $C_6H_4 \begin{smallmatrix} C(:NOH) \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > CR$, derived from the tautomeric form, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > CR$, of the indoles. This view is confirmed by the fact that 2-phenylindole reacts with nitrosobenzene in alcoholic solution in presence of traces of alkali, forming the compound,



which crystallises from alcohol in crimson prisms, m. p. 155°. The action is compared with that of phenylacetonitrile and nitrosobenzene, $CH_2Ph \cdot CN + NO \cdot C_6H_5 = H_2O + NPh : CPh \cdot CN$.

The compound, $C_6H_4 \begin{smallmatrix} C(:NPh) \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > CMe$, prepared from 2-methylindole and nitrosobenzene, forms yellow crystals, m. p. 183°. The compound, $NMe_2 \cdot C_6H_4 \cdot N : C \begin{smallmatrix} CMe \\ \diagup \quad \diagdown \\ C_6H_4 \end{smallmatrix} > N$, obtained similarly from 2-methylindole and nitrosodimethylaniline, forms red needles, m. p. 185°.
W. A. D.

Preparation of Anthranil. KALLE & Co. (D.R.-P. 194364. Compare Abstr., 1907, i, 908).—The dimercure derivative of *o*-nitro-

toluene forms a yellow chloride when mixed with 10% hydrochloric acid, and this product, when added to stronger hydrochloric acid (D 1.185), furnishes the hydrochloride of anthranil, from which this amide can be purified by distillation in steam. G. T. M.

Aminopyrrolidone Derivatives from Mesityl Oxide and from Benzylideneacetone. MORITZ KOHN (*Monatsh.*, 1908, 29, 497—508).—Bucherer's and Zelinsky's modifications of Strecker's original method for the production of α -amino-acids have been applied by the author to β -amino-ketones, with the result that aminopyrrolidone derivatives are obtained instead of the expected α : γ -diamino-acids.

The interaction of aqueous methyldiacetonamine, powdered potassium cyanide (1 mol.), and concentrated aqueous ammonium chloride (1 mol.) at 5—10° leads, after hydrolysis of the diaminonitrile by concentrated hydrochloric acid, to the formation of 4-amino-5-keto-1:2:2:4-tetramethylpyrrolidine, $\text{NMe} \begin{matrix} \text{CO} - \text{CMe} \cdot \text{NH}_2 \\ | \\ \text{CMe}_2 \cdot \text{CH}_2 \end{matrix}$, b. p. 140—143°/17 mm., which is soluble in water, absorbs carbon dioxide, and forms a *phenylthiocarbamide*, m. p. 180—181°. By using methylamine hydrochloride in the place of ammonium chloride in the preceding reaction, 4-methylamino-5-keto-1:2:2:4-tetramethylpyrrolidine, $\text{C}_9\text{H}_{18}\text{ON}_2$, b. p. 128—130°/15—16 mm., is obtained, which also absorbs water or carbon dioxide, and yields a *phenylthiocarbamide*, m. p. 132—135°, and an *acetyl* derivative, m. p. 123—125.5°. 4-Dimethylamino-5-keto-1:2:2:4-tetramethylpyrrolidine, b. p. 130—140°/13 mm., obtained in a similar manner by using an aqueous-alcoholic solution of dimethylamine hydrochloride, forms a *platinichloride* and a *methiodide*, from which the corresponding *aurichloride* and *platinichloride* are obtained.

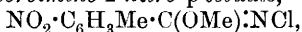
The constitution of the additive compound of benzylideneacetone and methylamine has been shown to be $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{NHMe}$, since it can be converted by potassium cyanide and methylamine hydrochloride and subsequent hydrolysis into 4-methylamino-5-keto-2-phenyl-1:4-dimethylpyrrolidine, $\text{NMe} \begin{matrix} \text{CO} - \text{CMe} \cdot \text{NHMe} \\ | \\ \text{CHPh} \cdot \text{CH}_2 \end{matrix}$, b. p. 181°/13 mm., a colourless, odourless, viscous liquid, which is soluble in water, absorbs carbon dioxide, and forms a crystalline *phenylthiocarbamide*. C. S.

Stereoisomeric Chloroimino-acid Esters. WILLIS STOSE HILPERT (*Amer. Chem. J.*, 1908, 40, 150—194).—Stieglitz and Earle (*Abstr.*, 1904, i, 39) have shown that methyl chloroimino-*m*-nitrobenzoate exists in two stereoisomeric modifications, and Stieglitz and Hale have recently found (unpublished) that the corresponding ethyl ester exhibits the same phenomenon. The author now finds that methyl and ethyl chloroimino-*p*-nitrobenzoates, methyl chloroimino-2-nitro-*p*-toluate, and methyl and ethyl chloroimino- β -naphthoates also exist in stereoisomeric modifications, but no stereoisomerides are obtainable in the case of methyl chloroimino-*p*-bromo-*m*-nitrobenzoate

and methyl chloroimino-*p*-bromobenzoate. In the case of the first three pairs of stereoisomerides, the less stable form can be transformed into the more stable one by the action of chlorine, and the converse process also is possible to a small extent. In the case of the naphthalene derivatives, the change is brought about by boiling water. Further details are given for the separation of α - and β -methyl chloroimino-*m*-nitrobenzoates and for the transformation of one form into the other.

When *p*-nitrobenzonitrile is treated with methyl alcohol in benzene solution, it yields *methyl imino-p-nitrobenzoate*, a white, crystalline substance, m. p. 93—94°, which, with hypochlorous acid, gives *methyl chloroimino-p-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$.

The crude substance is fractionally precipitated from its chloroform solution by light petroleum, whereby the α -(*syn*-)form is precipitated in needles, m. p. 99—100°, and the mother liquor yields the more stable β -(*anti*-)form in plates, m. p. 76°. *Ethyl chloroimino-p-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OEt}) \cdot \text{NCl}$, is prepared similarly by the action of hypochlorous acid on the imino-ester obtained from *p*-nitrobenzonitrile and ethyl alcohol. By the same process of fractionation as used for the methyl ester, the α -(*syn*-)form was almost exclusively obtained in needles, m. p. 98—99°. The β -(*anti*-)form, which crystallised only to a very small extent along with the α -form, was isolated mechanically; it occurs in plates, m. p. 90°, and is the more unstable modification, being readily transformed into the α -form by chlorine. *n-Propyl chloroimino-p-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OPr}^n) \cdot \text{NCl}$, is an oil. *Methyl imino-2-nitro-p-toluate*, prepared from 2-nitro-*p*-tolunitrile and methyl alcohol, is a white, crystalline solid, m. p. 60—61°; the *hydrochloride* was analysed. On treatment with hypochlorous acid, the free ester yields *methyl chloroimino-2-nitro-p-toluate*,



which, when fractionally precipitated by light petroleum from its chloroform solution, yielded a mixture of the α -(*syn*-)form in plates, m. p. 84—85°, and the β -(*anti*-)form in needles, m. p. 71°. The α -modification is readily transformed by chlorine into the more stable β -form.

Methyl chloroimino-p-toluate, $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, is a colourless oil.

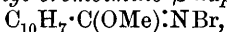
Methyl chloroimino- β -naphthoate, $\text{C}_{10}\text{H}_7 \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, prepared by chlorinating methyl imino- β -naphthoate, is separated into the two modifications by adding light petroleum to its chloroform solution. The α -form is precipitated in minute crystals, m. p. 125°, and from the filtrate is obtained the β -form in large, thin plates, m. p. 72°. By heating with water, each modification is partly transformed into the other, probably by the action of a trace of hypochlorous acid or chlorine liberated from the chloroimino-ester.

Ethyl chloroimino- β -naphthoate (Slosson, Abstr., 1903, i, 475), when prepared by the hypochlorous acid method, yields an α -(*syn*-)variety, m. p. 72°, and a substance crystallising in needles, m. p. 39°, which is probably a mixture of both forms.

Methyl chloroimino-p-bromobenzoate, $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, crystallises in plates and needles, m. p. 60°; it does not, however, occur in

two stereoisomeric modifications. *Methyl chloroimino-p-bromo-m-nitrobenzoate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, also crystallises in plates and needles, m. p. 95° , which are not stereoisomeric. *Methyl chloroimino-p-anisate*, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe}) \cdot \text{NCl}$, prepared from *methyl iminoanisate hydrochloride*, is a pale yellow oil with a sharp odour.

Methyl bromoimino-m-nitrobenzoate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OMe}) \cdot \text{NBr}$, prepared from methyl imino-*m*-nitrobenzoate and hypobromous acid, crystallises in plates, m. p. 99.5° , and needles, m. p. 101° , which are not stereoisomeric. *Methyl bromoimino- β -naphthoate*,

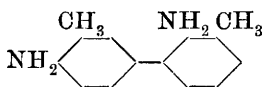


has m. p. $99-100^\circ$.

J. C. C.

The Transformation of Hydrazotoluene into Tolidine.

J. P. VAN LOON (*Chem. Weekblad*, 1908, 5, 689—698).—The transformation of hydrazotoluene into tolidine has been investigated quantitatively, and it has been found that 100 grams of hydrazotoluene yield



87.4 grams of tolidine, 2 grams of azotoluene, and 2 grams of toluidine. A small proportion of an isomeric tolidine, probably of the annexed formula, is also formed, but has not

been obtained free from tolidine. The estimation of the tolidine was effected by precipitation as sulphate from hydrochloric acid solution by magnesium sulphate, a correction being necessary on account of tolidine sulphate being appreciably soluble in cold water. The value of the correction factor was ascertained by experiments on the solubility of the sulphate at certain temperatures.

A. J. W.

Replacement of Hydroxyl Groups by Hydrazino-groups.

HARTWIG FRANZEN and TH. EICHLER (*J. pr. Chem.*, 1908, [ii], 78, 157—164. Compare *Abstr.*, 1905, i, 244, and following abstract).—It has not been found possible to replace the hydroxyl groups in catechol and quinol by hydrazino-residues, or yet to transform 1 : 3 : 4-tolylene-diamine into the corresponding hydrazine derivative.

Dibenzylidene-1 : 3-phenylenedihydrazine, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{N} \cdot \text{CHPh})_2$, obtained by the action of benzaldehyde on the crude product obtained by heating resorcinol, hydrazine sulphate, and a 50% solution of hydrazine hydrate for six hours to $110-120^\circ$ in an atmosphere of hydrogen, crystallises from xylene and has m. p. $247-248^\circ$.

Pyruvic acid reacts with the same condensation product, yielding *dipyrvic acid-m-phenylenedihydrazine*, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CO}_2\text{H})_2$, in the form of a yellow solid, m. p. 191° .

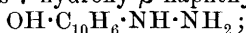
Hydrazine salicylate, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \cdot \text{N}_2\text{H}_4$, forms colourless crystals, m. p. 106° , which, when heated by means of nitrobenzene vapour, yield 3-keto-1 : 3-dihydroindazole (Fischer, *Abstr.*, 1882, 1068). Salicyl-hydrazide when heated in the same manner yields the indazole in addition to *disalicylhydrazide*, $\text{N}_2\text{H}_2(\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$, m. p. 301° .

Hydrazine-o-hydroxytoluate, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H} \cdot \text{N}_2\text{H}_4$ [$\text{Me} \cdot \text{OH} \cdot \text{CO}_2\text{H} = 1 : 2 : 3$], has m. p. $133-134^\circ$; the isomeric *meta*-compound [$1 : 3 : 4$] $137-138^\circ$, and the *para*-compound [$1 : 4 : 3$], 130° . When these salts are heated, they yield mixtures of hydrazino- and dihydroindazole derivatives, which so far have not been separated.

β -Hydrozynaphthoic acid hydrazide, $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ [$2 : 3$],

crystallises from alcohol in yellow plates, m. p. 203—204° (decomp.), and yields a *benzylidene* derivative, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, m. p. 224·5°. J. J. S.

7-Hydroxy- β -naphthylhydrazine. HARTWIG FRANZEN and W. DEIBEL (*J. pr. Chem.*, 1908, [ii], 78, 143—157).—Although 2:3-dihydroxynaphthalene yields 2:3-naphthylenedihydrazine when heated with hydrazine hydrate, the isomeric 2:7-dihydroxy-derivative, under similar conditions, yields 7-hydroxy- β -naphthylhydrazine,

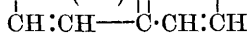


even when the latter compound is heated with hydrazine hydrate, a good yield of the dihydrazine derivative is not obtained.

This anomalous behaviour of the 2:7-dihydroxynaphthalene cannot be explained by supposing that one of the hydroxyl groups reacts as the tautomeric ketone, since ketones also condense readily with hydrazine.

The best yield of 7-hydroxy- β -naphthylhydrazine is obtained when the dihydroxy-derivative, hydrazine sulphate, and a 45% solution of hydrazine hydrate are heated at 120—125° for eight hours in an atmosphere of hydrogen. It crystallises from water or alcohol in colourless plates, m. p. 176° (decomp.), and, when exposed to the air, turns red. It dissolves in acids, but not in alkalis or ether. The *hydrochloride*, $\text{C}_{10}\text{H}_6\text{ON}_2\cdot\text{HCl}$, is readily soluble in water, and has m. p. 192°; the *sulphate* is somewhat less soluble, and has m. p. 232° (decomp.); the *nitrate* has m. p. 173° (decomp.), and also decomposes when kept for some time. When the finely-divided base, obtained by the addition of a little potassium hydroxide solution to its aqueous solution, is oxidised by aspirating air through the suspension, a dark red solution is formed, and this yields a red precipitate with carbon dioxide.

Nitrous acid transforms the base into a *dinitroso*-derivative, probably $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{NO})\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{N}(\text{NO})\cdot\text{NH}_2$; it has m. p. 124°.



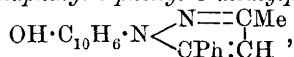
Benzaldehyde 7-hydroxy- β -naphthylhydrazone,



crystallises from benzene in pale yellow plates, m. p. 233°. The corresponding *o*-hydroxybenzaldehyde derivative, $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$, has m. p. 223°.

7-Hydroxy- β -naphthylsemicarbazide, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained by the action of a concentrated aqueous solution of potassium cyanate on the hydrazine derivative, crystallises from alcohol in reddish-violet needles, m. p. 228°. **7-Hydroxy- β -naphthylphenylthiosemicarbazide,** $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, obtained by the action of phenylthiocarbimide on the hydrazine, has m. p. 183°.

The base condenses with an alcoholic solution of benzoylacetone, yielding 7'-hydroxy- β -naphthyl-5-phenyl-3-methylpyrazole,



m. p. 199°, and with ethyl acetoacetate, yielding 7'-hydroxy- β -naphthyl-3-methylpyrazolone, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N} < \begin{array}{c} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{CH}_2 \end{array}$, m. p. 243°.

7-Chloro-β-naphthol, $C_{10}H_6Cl \cdot OH$, can be prepared by dropping a hot solution of the hydroxyhydrazine into a boiling solution of copper sulphate; it crystallises from light petroleum in colourless plates, m. p. 126·5°. The corresponding *acetyl* derivative, $C_{10}H_6Cl \cdot OAc$, crystallises from toluene in colourless plates, m. p. 104·5°.

An acetic acid solution of the hydroxyhydrazine is oxidised by copper sulphate solution to *β-naphthol*.

7-Amino-β-naphthol, $OH \cdot C_{10}H_6 \cdot NH_2$, obtained together with 2:7-naphthylenediamine by heating 2:7-dihydroxynaphthalene with ammonium sulphite and hydroxide in a reflux apparatus, has m. p. 201°.

In the preparation of 7-hydroxy-*β-naphthylhydrazine*, a small amount of 2:7-naphthylenedihydrazine is formed. This yields a *dibenzylidene* derivative, $C_{10}H_6(NH \cdot N : CHPh)_2$, m. p. 186·5°.

7-Amino-β-naphthylhydrazine, $NH_2 \cdot C_{10}H_6 \cdot NH \cdot NH_2$, obtained by the action of hydrazine hydrate and sulphate on 2:7-naphthylenediamine, has m. p. 184°, and yields a *dibenzylidene* derivative,

$CHPh : N \cdot C_{10}H_6 \cdot NH : N : CHPh$,
m. p. 201·5°, and a *di-o-hydroxybenzylidene* derivative,
 $OH \cdot C_6H_4 \cdot CH : N \cdot C_{10}H_6 \cdot NH : N : CH \cdot C_6H_4 \cdot OH$,
which begins to decompose at 169°.

J. J. S.

Action of Nitrogen Peroxide on Aldehyde Phenylhydrazones. ROBERTO CIUSA and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 840—846).—The action of nitrogen peroxide on aldehyde phenylhydrazones in ethereal solution yields the corresponding arylnitroformaldehyde phenylhydrazones in almost quantitative proportions: $CHAr : N_2HPh \rightarrow NO_2 \cdot CAr : N_2HPh$, small amounts of free aldehyde, diazobenzene nitrate, and oxidation products being also formed. The reaction affords a very convenient method of preparing arylnitroformaldehyde phenylhydrazones, being easier to carry out, and giving better yields of purer material, than the action of diazobenzene salts on the primary nitrohydrocarbons, or the action of nitrous acid on the phenylhydrazones. As regards the mechanism of the reaction, the nitro-group replaces the methinic hydrogen atom, a further proof being thus afforded of the peculiar activity of this hydrogen atom.

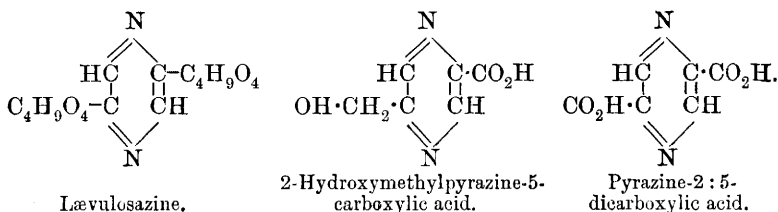
The phenylhydrazones on which the reaction was tried were those of benzaldehyde, *m*-nitrobenzaldehyde, anisaldehyde, and piperonal. The compound obtained in the last case was *nitromethylenedioxy-ω-benzaldehydephenylhydrazone*, $CH_2O_2 : C_6H_3 \cdot C(NO_2) : N_2HPh$, which crystallises from a mixture of benzene and alcohol in ruby-red, prismatic needles, m. p. 119°, and dissolves in concentrated sulphuric acid, giving a violet coloration changing to red, and with alkalis, forming dark red solutions, from which it is re-precipitated by the addition of acid; the *potassium* salt is obtained as a golden-yellow, crystalline powder.

T. H. P.

The Degradation of Lævulosazine (Ditetrahydroxybutylpyrazine) in the Animal Body. KARL STOLTE (*Biochem. Zeitsch.*, 1908, 12, 499—509).—After ingestion of lævulosazine, a product is

excreted in the urine which gives with ferrous sulphate in acetic acid solution a carmine-red colour. The substance causing this reaction was isolated from rabbits' urine by concentrating it to a syrup and precipitating the inorganic salts with alcohol. On addition of a concentrated aqueous solution of copper acetate acidified with acetic acid, a copper salt was precipitated. This was dissolved in sodium hydroxide solution and decomposed by hydrogen sulphide, the filtrate from the sulphide decolorised by charcoal, and copper acetate in aqueous solution added. A crystalline precipitate was thereby obtained, which was identified as the copper salt of 2-hydroxymethylpyrazine-5-carboxylic acid. On oxidation with hydrogen peroxide in alkaline solution, it yielded pyrazine-2:5-dicarboxylic acid, m. p. 272—273°.

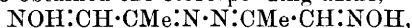
The relation of lævulosazine to these degradation products can be expressed as follows:



The constitution of the excreted product was also confirmed by the preparation of an acetyl derivative. The substance which sometimes in normal urine gives a red coloration with ferrous sulphate is not a pyrazine derivative.

S. B. S.

Preparation of Certain Azines. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1908, 38, ii, 123—126; *Atti R. Accad. Sci. Torino*, 1908, 43, 817—820).—The conclusion drawn by von Rothenburg (*Abstr.*, 1893, i, 701), that when hydrazine acts on compounds containing the group :NOH the latter is always replaced by :N·NH₂, is inaccurate. Thus, from isonitrosoacetone and hydrazine, the authors have obtained the corresponding azine,



and from the latter, by means of a simple and general reaction, the azines of mixed isonitroso-ketones, Me·CO·C·Ar:NOH, which cannot be prepared directly. The latter compounds crystallise well, and are converted into mixed diketones, CH₃·CO·CO·Ar, by the action of dilute acids, but are not transformable into pyrazines.

isoNitrosoacetoneazine, C₆H₁₀O₂N₄, prepared by the action of powdered hydrazine sulphate (1 mol.) on a solution of isonitrosoacetone (2 mols.) in 20% sodium hydroxide solution, separates from alcohol or water in crystals, m. p. 221° (decomp.).

isoNitrosophenylacetoneazine, (NOH:CPh·CMe·)N₂, obtained by the interaction of isonitrosoacetoneazine and diazobenzene chloride (2 mols.) in 10% sodium hydroxide solution, crystallises from alcohol in yellowish-red needles, m. p. 187—188°, and yields hydrazine sulphate and phenyl methyl diketone when heated with 10% sulphuric acid.

iso*Nitroso-p-tolylacetone*azine, $[\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NOH})\cdot\text{CMe}]_2\text{N}_2$, prepared by treating *isonitrosoacetone*azine in alkaline solution with diazo-*p*-toluene chloride, crystallises from alcohol in yellow laminae, m. p. 198—199° (decomp.).

iso*Nitrosoanisylacetone*azine, $[\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{CMe}]_2\text{N}_2$, prepared in a similar manner to the preceding compounds, crystallises from alcohol in yellow prisms, m. p. 193—194° (decomp.), and yields hydrazine sulphate and *p*-anisyl methyl diketone, m. p. 44—45°, when distilled with 10% sulphuric acid.

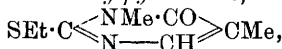
T. H. P.

Pyrimidines. XXXIII. Synthesis of *N*-Alkyl Derivatives of Cytosine, Thymine, and Uracil. TREAT B. JOHNSON and SAMUEL H. CLAPP (*J. Biol. Chem.*, 1908, 5, 49—70. Compare this vol., i, 692, 693).—Various *N*-alkyl derivatives of cytosine, thymine, and uracil have been synthesised on account of the occurrence of certain methyl-purines in nature, and also on account of the relationship between methyluracils and the purines, theobromine and caffeine.

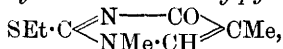
The introduction of methyl groups into these pyrimidine derivatives has a similar influence on their physical properties to that on the purines. They increase the solubility and lower the melting points. The 3-methyl pyrimidines melt at higher temperatures than the isomeric 1-methyl derivatives.

When 6-oxy-2-ethylthiol-5-methylpyrimidine is methylated by means of methyl iodide and alcoholic potassium hydroxide, a mixture of the two isomeric 1:5- and 3:5-dimethyl derivatives is obtained.

6-Oxy-2-ethylthiol-1:5-dimethylpyrimidine,

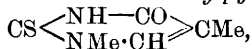


is less soluble, and crystallises from water in long, slender prisms, m. p. 65°. 6-Oxy-2-ethylthiol-3:5-dimethylpyrimidine,



crystallises from benzene in colourless prisms, m. p. 156°. When hydrolysed with hydrobromic acid, each thio-derivative yields the corresponding thymine.

1-Methylthymine, $\text{CO}\begin{array}{c} \nwarrow \text{NMe}\cdot\text{CO} \\ \nearrow \text{NH}-\text{CH} \end{array}\text{CMe}$, crystallises from water in stout prisms, m. p. 202—205° (decomp.), and the isomeric 3-methylthymine crystallises from the same solvent in prismatic needles or octahedral prisms, m. p. 280—282°. In the formation of the latter compound, a certain amount of 6-oxy-2-thio-3:5-dimethylpyrimidine,



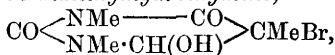
is also formed; it is less soluble in water than the methylthymine, and crystallises in needles, m. p. 229—230°.

Bromine water converts 1-methylthymine into 5-bromo-4-hydroxy-1-methylhydrothymine, $\text{CO}\begin{array}{c} \nwarrow \text{NMe}-\text{CO} \\ \nearrow \text{NH}\cdot\text{CH}(\text{OH}) \end{array}\text{CMeBr}$, which crystallises in stout prisms, m. p. 123—125°, when heated slowly. The corresponding 5-nitro-derivative, $\text{C}_8\text{H}_9\text{O}_5\text{N}_3$, obtained by the action of nitric acid on the base, forms well-developed prisms, m. p. 135—136° (decomp.).

The isomeric 5-nitro-4-hydroxy-3-methylhydrothymine, obtained by the action of nitric acid on 3-methylthymine, crystallises in large prisms, which decompose at 178—181°.

The *monopotassium* derivative of thymine, $C_5H_5O_2N_2K$, crystallises from alcohol in long needles.

1:3-Dimethylthymine (Steudel, Abstr., 1901, i, 108) is most readily obtained by methylating thymine, and with bromine water yields 5-bromo-4-hydroxy-1:3-dimethylhydrothymine,



in the form of prisms, m. p. 132—133°.

Monopotassiumuracil, obtained by digesting uracil with the theoretical amount of alcoholic potassium hydroxide, has the composition $C_4H_3O_2N_2K, H_2O$, and loses its water of hydration at 120°. When uracil is methylated in the presence of potassium hydroxide,

1:3-dimethyluracil, $CO \begin{array}{c} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{array} \text{CH}$, which crystallises from a mixture of ether and alcohol in long, slender prisms, m. p. 121—122°, is obtained. With bromine water this base yields 5-dibromo-4-hydroxy-

1:3-dimethylhydrouracil, $CO \begin{array}{c} \text{NMe} \text{---} \text{CO} \\ \text{NMe} \cdot \text{CH}(\text{OH}) \end{array} \text{CBr}_2$, m. p. 135—136°, which is transformed into 5-bromo-1:3-dimethyluracil when digested with alcohol.

3-Methylcytosine, $CO \begin{array}{c} \text{N}=\text{C}(\text{NH}_2) \\ \text{NMe} \text{---} \text{CH} \end{array} \text{CH}$, obtained by methylating cytosine, crystallises from methyl alcohol in prisms, decomp. 278—279°. The *platinichloride*, $(C_5H_7ON_3)_2H_2PtCl_6, 2H_2O$, crystallises in slender prisms, and the *picrate* in long prisms, which decompose at 280° when heated slowly. 5-Bromo-3-methyluracil, $C_5H_5O_2N_2Br$, obtained by treating 3-methylcytosine with bromine and water and digesting the product with ethyl alcohol, crystallises from water in slender needles, which decompose at 255—260°.

2-Oxy-6-phenylmethylaminopyrimidine, $CO \begin{array}{c} \text{N}:\text{C}(\text{NPhMe}) \\ \text{NH} \text{---} \text{CH} \end{array} \text{CH}$, obtained by the action of methylaniline on 6-chloro-2-ethylthiolpyrimidine and digesting the product with hydrobromic acid, crystallises from alcohol in hexagonal plates, which do not decompose below 285°. When this base is methylated, it yields 2-oxy-6-phenylmethylamino-3-methylpyrimidine, $CO \begin{array}{c} \text{N}:\text{C}(\text{NPhMe}) \\ \text{NMe} \text{---} \text{CH} \end{array} \text{CH}$, which crystallises in striated prisms, m. p. 186—187°.

3:5-Dimethylcytosine, $CO \begin{array}{c} \text{N}:\text{C}(\text{NH}_2) \\ \text{NMe} \text{---} \text{CH} \end{array} \text{CMe}$, obtained by methylating 5-methylcytosine (Abstr., 1904, i, 624), crystallises from methyl alcohol in prisms, which decompose at 300—310°.

The formation of the 3-methylthymine by dissolving 3:5-dimethylcytosine in concentrated bromine water, evaporating to dryness, and digesting the product with absolute alcohol, establishes the positions of the methyl groups in 3:5-dimethylcytosine.

[With N. A. MARTIN.]—Electrical conductivity measurements have

been made with thymine and its *N*-methyl derivatives. The conductivities tend to increase with the length of time the solutions are kept, especially in the case of 1- and 3-methylthymines. J. J. S.

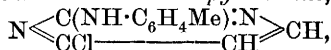
Pyrimidines. XXXV. Action of Potassium Thiocyanate on Some Imide Chlorides. TREAT B. JOHNSON and WALTER F. STOREY (*Amer. Chem. J.*, 1908, 40, 131—147).—Wheeler and Bristol (*Abstr.*, 1905, i, 483) have shown that 6-chloro-2-ethylthiopyrimidine, 6-chloro-2-ethylthiol-5-methylpyrimidine, and 6-chloro-5-bromo-2-ethylthiopyrimidine give thiocarbimido-derivatives when treated with potassium thiocyanate, but the intermediate formation of thiocyanates was not observed. Johnson and McCollum, however (*Abstr.*, 1906, i, 768), found that 6-chloro-5-ethoxy-2-ethylthiopyrimidine yields the 6-thiocyano-derivative, which can be transformed into the corresponding 6-thiocarbimido-derivative. The present authors have now examined the behaviour of potassium thiocyanate towards 6-chloro-2-*p*-toluidinopyrimidine, 6-chloro-2-*o*-toluidinopyrimidine, and 6-chloro-2-*p*-tolyl-4-methylpyrimidine; the two forms do not react with potassium thiocyanate, but the latter gives the corresponding thiocyno-derivative, which can be transformed into the isomeric thiocarbimido compound. Moreover, the substances examined by Wheeler and Bristol yield thiocyno-derivatives, readily transformed into the thiocarbimido-isomerides when the time of the reaction is limited to twenty to sixty minutes, instead of three to fifteen hours, as employed by these authors.

[With ELMER V. MCCOLLUM.]—6-Thiocyano-2-ethylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C(SeT)} = \text{N} \\ \text{C(SCN)} \cdot \text{CH} \end{smallmatrix} \text{CH}$, prepared by warming 6-chloro-2-ethylthiopyrimidine with potassium thiocyanate in acetone or 95% alcoholic solution, crystallises from alcohol in aggregates of rectangular prisms, *m. p.* 82°. On heating at 80—90° for four to five hours, it is transformed into the thiocarbimido-derivative. This is obtained as a yellow oil, *b. p.* 200—205°/45—50 mm., which, after some time, deposits a yellow, crystalline compound, *m. p.* 175—177°. This does not react with ammonia, and is regarded as a polymeric form of 2-ethylthiol-6-thiocarbimidopyrimidine (compare Wheeler and Bristol, *loc. cit.*).

6-Thiocyano-2-ethylthiol-5-methylpyrimidine, $\text{N} \begin{smallmatrix} \text{C(SeT)} = \text{N} \\ \text{C(SCN)} \cdot \text{CMe} \end{smallmatrix} \text{CH}$, crystallises from alcohol in prisms, *m. p.* 95°. It dissolves in thioacetic acid, forming prismatic crystals, *m. p.* 179—180°, which probably consist of 6-thio-2-ethylthiol-5-methylpyrimidine. 5-Bromo-6-thiocyano-2-ethylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C(SeT)} = \text{N} \\ \text{C(SCN)} \cdot \text{CBr} \end{smallmatrix} \text{CH}$, crystallises from alcohol in prisms, *m. p.* 81—82°. With thioacetic or thiobenzoic acid, it yields 5-bromo-6-thio-2-ethylthiopyrimidine, and, when heated for two hours at 150—160°, it is transformed into the thiocarbimido-isomeride.

6-Oxy-2-*o*-toluidinopyrimidine, $\text{NH} \begin{smallmatrix} \text{C(NH} \cdot \text{C}_6\text{H}_4\text{Me)} : \text{N} \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CH}$, prepared by heating a mixture of 6-oxy-2-ethylthiopyrimidine and *o*-toluidine for three days on the steam-bath, separates from alcohol or

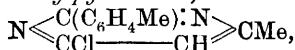
acetic acid in prismatic crystals, m. p. 219—220°. With phosphoryl chloride, it yields 6-chloro-2-o-toluidinopyrimidine,



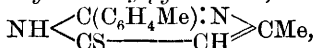
separating from alcohol in crystals, m. p. 78°, which, when heated with alcoholic ammonia, furnishes 6-amino-2-o-toluidinopyrimidine, crystallising from alcohol in small prisms, m. p. 124°, and when boiled with a benzene solution of aniline gives 6-anilino-2-o-toluidinopyrimidine, crystallising from alcohol in hexagonal plates, m. p. 128°; the hydrochloride forms slender needles, m. p. 126°.

6-Oxy-2-p-toluidinopyrimidine, prepared from 6-oxy-2-ethylthiopyrimidine and p-toluidine, crystallises from acetic acid in needles, m. p. 270—271°. With phosphoryl chloride, it gives 6-chloro-2-p-toluidinopyrimidine, separating from alcohol in prisms, m. p. 112—113°. This reacts with aniline, yielding 6-anilino-2-p-toluidinopyrimidine, which crystallises from alcohol in needles, m. p. 135°; the hydrochloride forms prisms, decomposing at 134°. 6-Oxy-2-β-naphthylaminopyrimidine, prepared from β-naphthylamine and 6-oxy-2-ethylthiopyrimidine, crystallises from alcohol in needles, m. p. 270°.

6-Chloro-2-p-tolyl-4-methylpyrimidine,



prepared by heating a mixture of 6-oxy-2-p-tolyl-4-methylpyrimidine, phosphorus pentachloride, and phosphoryl chloride, crystallises from alcohol in prisms, m. p. 107°. With potassium thiocyanate, this gives 6-thiocyano-2-p-tolyl-4-methylpyrimidine, separating from alcohol in fern-like crystals, m. p. 123°, which, when warmed with thiobenzoic acid, yields 6-thio-2-p-tolyl-4-methylpyrimidine,



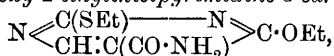
crystallising from alcohol in slender prisms, m. p. 114°. When the thiocyno-compound is heated for two and a-half hours at 130—135°, it undergoes re-arrangement, yielding prisms, m. p. 207—208°, which probably consist of a polymeric form of the thiocarbimido-derivative. With ammonia this gives 6-thiocarbamido-2-p-tolyl-4-methylpyrimidine, $\text{N} \begin{array}{c} \text{C}(\text{C}_6\text{H}_4\text{Me}) \text{---} \text{N} \\ \text{C}(\text{NH} \cdot \text{CS} \cdot \text{NH}_2) \text{---} \text{CH} \end{array} \text{CMe}$, crystallising from alcohol in prisms, m. p. 145—146°. When 6-chloro-2-p-tolyl-4-methylpyrimidine is heated with ammonia at 180—190° for two hours, it yields 6-amino-2-p-tolyl-4-methylpyrimidine, separating from alcohol in hexagonal tablets, m. p. 178—179°, and, when warmed with a benzene solution of aniline, 6-anilino-2-p-tolyl-4-methylpyrimidine, crystallising from alcohol in needles, m. p. 120—121°, is obtained; the hydrochloride separates from alcohol in clusters of needles, m. p. 269—270° (decomp.).

J. C. C.

Pyrimidines. XXXVI. Synthesis of Cytosine-5-carboxylamide. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1908, 40, 233—251. Compare Abstr., 1907, i, 559, 1083).—The authors have previously shown that ethyl-ψ-thiocarbamide and ethyl ethoxymethylenemalonate condense to form ethyl 2-ethylthiol-6-oxy-

pyrimidine-5-carboxylate, and that the corresponding acid is readily obtained from this. They have now succeeded in greatly increasing the yield of pyrimidine in this condensation, and have made it the starting point for further syntheses.

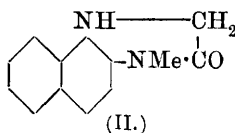
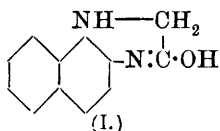
The acid chloride of 6-chloro-2-ethylthiopyrimidine-5-carboxylic acid, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CH:C}(\text{COCl}) \end{smallmatrix} \text{CCl}$, prepared by boiling the dry oxy-acid with phosphoryl chloride, separates from light petroleum in radiating clusters of colourless prisms, m. p. 38—40°. With cold aqueous ammonia, the corresponding amide, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CH:C}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{CCl}$, is formed, which separates from benzene in long, hair-like crystals, m. p. 134°, and with sodium ethoxide yields 6-ethoxy-2-ethylthiopyrimidine-5-carboxylamide,



m. p. 134°. When the acid chloride of 6-chloro-2-ethylthiopyrimidine-5-carboxylic acid is warmed with aqueous ammonia, 6-amino-2-ethylthiopyrimidine-5-carboxylamide, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CH:C}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{C}\cdot\text{NH}_2$, stout prisms, m. p. 218—219°, is produced; with bromine, it yields a dibromo-additive compound. When the latter is heated until the loss corresponds with the weight of one molecular proportion of hydrogen bromide, the resulting material dissolved in dilute potassium hydroxide, and the solution acidified with acetic acid, cytosine-5-carboxylamide, $\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}_2)\cdot\text{C}(\text{CO}\cdot\text{NH}_2) \end{smallmatrix} \text{CH}$, is obtained. This is also formed, together with the acid, by the action of hydrochloric acid on 6-amino-2-ethylthiopyrimidine-5-carboxylamide; it does not melt at 310°. The substance previously regarded as having this constitution (*loc. cit.*, 1083) was probably impure or partly hydrated cytosine. On hydrolysis with hydrochloric acid, it yields cytosine-5-carboxylic acid, and it forms the following salts: *hydrochloride*, colourless, stout, pointed prisms; *nitrate*, truncated octahedrons or tufts of short hairs; *sulphate*, pearly scales; and *picrate*.
J. C. C.

Preparation of 2-Hydroxydihydro- and 1-Alkyl-2-ketodihydro-quinoxalines. MARTIN LANGE (D.R.-P. 196563).—The *o*-nitrosophenols interact with aldehydes and primary amines or with Schiff's bases to form quinoxaline derivatives.

2-Hydroxydihydro-1':2'-naphthaquinoxaline (I), a yellow, sandy



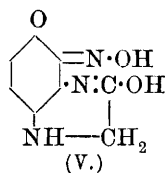
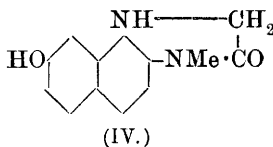
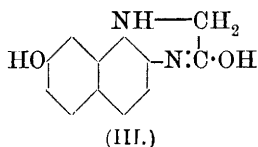
powder, m. p. 240°, is produced by adding acetaldehyde and ammonium chloride to an alkaline solution of 1-nitroso-β-naphthol.

2-Keto-1-methyldihydro-1':2'-naphthaquinoxaline (II), m. p. 155·5°, is obtained by substituting methylamine hydrochloride for ammonium

chloride in the foregoing reaction. The corresponding 2-keto-1-ethylidihydro-1':2'-naphthaquinoxaline, m. p. 164°, is produced by condensing 1-nitroso- β -naphthol with 30% ethylamine and acetaldehyde.

The patent contains a description of several other quinoxalines derived from 1-nitroso- β -naphthol, 2-nitroso- α -naphthol, and their carboxylic and sulphonic acids, and, in addition, two obtained from nitroso-2:7-dihydroxynaphthalene and one from dinitrosoresorcinol.

These compounds have the formulæ:



(III) and (IV) are obtained from 2:7-dihydroxynaphthalene, acetaldehyde, and ammonia, or methylamine, respectively.

(V), which is produced from dinitrosoresorcinol, acetaldehyde, and ammonia, separates in orange crystals. G. T. M.

Ethyl Pyromucylacetate [Furfuroylacetate]. II. 3-Furyl-5-pyrazolone. HENRY A. TORREY and JOAQUIN E. ZANETTI (*J. Amer. Chem. Soc.*, 1908, 30, 1241—1244).—When ethyl furfuroylacetate is treated with phenylhydrazine, it is converted into 1-phenyl-3-furyl-5-pyrazolone. This compound and some of its derivatives have been described previously (Abstr., 1907, i, 146).

By the action of hydrazine on ethyl furfuroylacetate, 3-furyl-5-pyrazolone, $\begin{matrix} \text{CH-O} \\ \text{CH-CH} \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{C} \begin{matrix} \diagdown \\ \diagup \end{matrix} \text{C} \begin{matrix} \diagup \\ \diagdown \end{matrix} \begin{matrix} \text{CH}_2\cdot\text{CO} \\ \text{N-NH} \end{matrix}$, m. p. 223° (decomp.), is obtained, and forms small, rectangular plates. The *picrate* decomposes at 192°. The *acetyl* derivative, m. p. 153—154°, and the *diacetyl* derivative, m. p. 102°, crystallise in long, white needles. The *benzylidene* derivative forms a light brown, amorphous powder, and does not melt at 300°. When the pyrazolone is treated with phenylcarbimide, a compound, probably 3-furyl-5-pyrazolonephenylcarbimide,

$\begin{matrix} \text{H}_2\text{C}\cdot\text{CO} \\ \text{C}_4\text{H}_3\text{O}\cdot\text{C} \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{N} \cdot \text{CO} \cdot \text{NHPh}$, m. p. 192°, is obtained in the form of small, white needles. E. G.

Trihydroxymethyldihydrouracil. ROBERT BEHREND and KARL BEER (*Annalen*, 1908, 362, 115—122. Compare Behrend and Grünewald, Abstr., 1902, i, 834).—A further account of the properties of α - and β -trihydroxymethyldihydrouracils (compare Behrend and Osten, Abstr., 1906, i, 309). Both of these compounds crystallise with 1H₂O. The compound obtained by the interaction of the β -compound and phenylhydrazine is a *phenylhydrazide*, C₁₁H₁₄O₄N₄, since it liberates phenylhydrazine when treated with alkali. Both α - and β -trihydroxymethyldihydrouracils are oxidised by potassium permanganate in the presence of potassium hydrogen carbonate, yielding *potassium acetoxalurate*, C₅H₅O₅N₂K·2H₂O, crystallising in needles

decomposing at 214—216°. An *acid* salt, $C_5H_5O_5N_2K \cdot C_5H_6O_5N_2$, m. p. 201°, separates when a solution of the neutral salt is acidified with hydrochloric acid.

The α -uracil when heated at 105—110° loses $2H_2O$, yielding a yellow powder which decomposes at 140—145°. The β -uracil also loses $2H_2O$ at 105—110°, yielding a syrupy acetylallanturic acid. The same acid is also formed when a neutral or slightly alkaline aqueous solution of either the α - or β -uracil is warmed. A *phenylhydrazone*, $C_{11}H_{12}O_3N_4$, forming yellow crystals decomposing at 219—220°, was prepared.

Acetylallanturic acid is oxidised by potassium permanganate in the presence of potassium hydrogen carbonate to oxaluric acid and acetic acid; in no case was either acetoxaluric acid or acetylcarbamide formed.

W. H. G.

Dimethylglycoluril and β -Methylhydantoin. EMIL WEITZNER (*Annalen*, 1908, 362, 125—131).—An account of attempts to obtain a fruitful and simple method for preparing β -methylhydantoin.

Methylcarbamide, or, better, its acetyl derivative, reacts with glyoxal in aqueous solution in the presence of hydrochloric acid, yielding dimethylglycoluril (compare Franchimont and Klobbie, *Abstr.*, 1888, 1179). The product so formed is shown to be a mixture of the two isomerides: $CO \begin{matrix} \text{NMe} \cdot \text{CH} \cdot \text{NMe} \\ | \qquad | \\ \text{NH} - \text{CH} - \text{NH} \end{matrix} CO$ and $CO \begin{matrix} \text{NMe} \cdot \text{CH} - \text{NH} \\ | \qquad | \\ \text{NH} - \text{CH} \cdot \text{NMe} \end{matrix} CO$.

Both these compounds when decomposed with hydrochloric acid yield the same product, namely, a mixture of α - and β -methylhydantoin, which is separated only with great difficulty. The best method for obtaining β -methylhydantoin is by acting on sarcosine hydrochloride with potassium cyanate in aqueous solution, and heating the resulting solution with hydrochloric acid.

The mixture of isomeric *dimethylglycolurils* prepared from glyoxal and acetylmethylcarbamide may be separated by fractional crystallisation from water. Both isomerides crystallise in long, colourless needles, and melt at 285—287° and 230—232° respectively.

W. H. G.

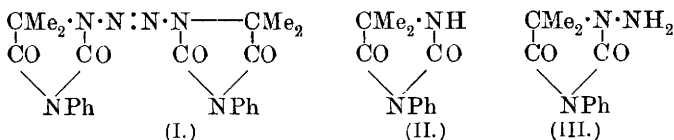
Preparation of Azoxy-derivatives. O. DIEFFENBACH (*D.R.-P.* 197714).—Azoxy-compounds may be conveniently obtained free from amines by digesting a mixture of a nitro-compound and hydrazo-derivative until they have interacted to furnish a mixture of azo- and azoxy-derivatives.

A mixture of azo- and azoxy-*o*-toluene is thus produced by maintaining a mixture of *o*-nitrotoluene, hydrazo-*o*-toluene, toluene, and aqueous sodium hydroxide (10%) at 90° for eight hours. Under similar conditions a mixture of *o*-nitrobenzoic acid and hydrazobenzene yields sodium *o*-azoxybenzoate and azobenzene, which are readily separated. This reaction may be combined advantageously with the electrolytic production of hydrazo-derivatives.

The azoxy-compound is reduced electrolytically to a hydrazo-compound and then more nitro-compound is added, which is then reduced to the azoxy-compound by the hydrazo-derivative present, so that the nitro-

compound is being continuously reduced chemically whilst the electrolytic reduction is effected on the azoxy-derivative. G. T. M.

Hydantointetrazones. J. R. BAILEY (*J. Amer. Chem. Soc.*, 1908, 30, 1412—1418. Compare Abstr., 1904, i, 826).—The author adduces further evidence in favour of the constitution of the azo-hydantoins (*loc. cit.*) by showing the relation of azophenyldimethylhydantoin (I) to phenyldimethylhydantoin (II) and to aminophenyldimethylhydantoin (III).



1-Azo-3-phenyl-5:5-dimethylhydantoin after purification by crystallisation from ethyl acetoacetate decomposes at 285° (corr.), instead of 270° as given previously. When heated at 60° with sulphuric acid or boiled with alcoholic potash, it loses nitrogen and yields 3-phenyl-5:5-dimethylhydantoin, crystallising from water in prisms, m. p. 171° (corr.), which is also obtained by condensing phenylcarbimide with aminoisobutyronitrile and hydrolysing the product.

[With BARNEY BROOKS.]—1-Amino-3-phenyl-5:5-dimethylhydantoin, m. p. 154.5° (corr.), is prepared by the action of dilute sulphuric acid on 1-carboxyisopropylamino-3-phenyl-5:5-dimethylhydantoin. It is oxidised with bromine water to 1-azo-3-phenyl-5:5-dimethylhydantoin. 1-Benzylideneamino-3-phenyl-5:5-dimethylhydantoin, prepared by heating aminophenyldimethylhydantoin with benzaldehyde or by heating phenylcarbimide with the benzylidenehydrazone of hydrazinoisobutyric acid, crystallises from alcohol in long, slender, pale yellow needles, m. p. 154° (corr.). J. C. C.

[Preparation of Diazo-derivatives of 1-Amino- β -naphthol-sulphonic Acids.] KALLE & Co. (D.R.-P. 195228 and 195322).—On adding aqueous sodium nitrite to a mixture of 1-amino- β -naphthol-4-sulphonic acid, zinc sulphate, and zinc hydroxide, diazotisation sets in, and is completed by heating at 40 — 55° for one or two hours. The diazo-derivative may be precipitated by the addition of acetic acid and sodium chloride. Other sulphonic acids of 1-amino- β -naphthol or 2-amino- α -naphthol may be diazotised in a similar manner.

The zinc salt may be replaced by the salts of magnesium, cobalt, nickel, and manganese, and, in general, by metallic salts of neutral reaction which are highly dissociated in aqueous solution. G. T. M.

The Extractives of Muscular Tissue. Relationship of Oblitine to Carnitine. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1908, 56, 417—424. Compare this vol., ii, 609).—When carnitine is evaporated several times with 96% alcohol and a little hydrochloric acid, a product is formed from which oblitine can be isolated in the form of its hydrochloride. Oblitine would thus appear to be the diethyl ester

of dicarnitine. The platinichloride has the formula $C_{18}H_{38}O_5N_2Cl_6Pt$, and not $C_{18}H_{40}O_5N_2Cl_6Pt$ (Kutscher). Since Kutscher in the isolation of oblitine used methods which would transform carnitine into oblitine, it is questionable whether this latter exists in muscle extract.

J. J. S.

Blood-pigment. IX. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1908, 56, 316—320. Compare this vol., i, 232).—A further investigation of the action of diazobenzene chloride on hæmopyrrole has shown that at least four, and probably five, products are formed. (a) A product, the hydrochloride of which crystallises in brown, monoclinic or triclinic needles, m. p. 233°. (b) Rhombic crystals, with a ruby-red colour and coppery lustre, m. p. 268°. (c) Green needles of a hydrochloride, m. p. above 300°. (d) Brown needles with a green shimmer of a hydrochloride, m. p. 185—186°. The chief product is usually (a); product (d) appears to be formed when the conditions are somewhat altered.

It is shown that treatment of hæmopyrrole with acid affects it in such a manner that the yield of product (a) is diminished, and is ultimately nil.

J. J. S.

Part Played by Alkali in the Hydrolysis of Proteins by Trypsin. T. BRAILSFORD ROBERTSON and C. L. A. SCHMIDT (*J. Biol. Chem.*, 1908, 5, 31—48).—The change in alkalinity during tryptic fermentation has been followed by means of the gas chain. It is found that when the total hydroxyl-ion concentration is greater than 10^{-6} , the changes in concentration can be expressed by a unimolecular formula, but that with lower concentrations the change can be represented by a bimolecular formula. These facts appear to be inconsistent with the view that the hydroxyl ions act as an accessory catalyst, but are in harmony with the view that the real catalyst is a hydrolysable compound of trypsin with sodium hydroxide or other base present in the system.

It is suggested that the equilibrium, as regards change in OH concentrations, which is attained after some time is a "false" equilibrium depending on the sum of the relations between the protein, trypsin, and alkali. The proteins used were casein and protamine.

J. J. S.

Hydrolysis of Legumin from the Vetch. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 22, 423—432).—The general properties of vetch legumin are similar to those of the pea legumin described previously (Abstr., 1907, i, 806). On hydrolysis, the various amino-acids are found in somewhat different proportions; these differences are most marked in the case of valine, aspartic acid, and lysine, but some hesitation is felt in drawing conclusions that these are sufficient in the present state of our technique to warrant the assertion that the two proteins are different.

W. D. H.

Photomethæmoglobin. OTTO LEERS (*Biochem. Zeitsch.*, 1908, 12, 252—258).—When methæmoglobin solutions are exposed to sunlight,

the brown colour is, as Bock has shown, converted into a red colour, and the modification of the blood-pigment, termed photomethæmoglobin, is formed. Its spectrum shows great similarity with that of cyanohæmoglobin. Methæmoglobin was prepared by a variety of methods, and this was converted into photomethæmoglobin by treatment with potassium ferricyanide and exposure to sunlight. The same effect was also produced by sodium ferro- and ferri-cyanides and other cyano-compounds. The solutions thus obtained exhibit on concentration the characteristic hydrocyanic acid odour, and give also the Prussian-blue and other characteristic hydrocyanic acid tests. Other evidence was also adduced to indicate the formation of hydrocyanic acid in the methæmoglobin solutions when treated with potassium ferricyanide; the facts indicate that photomethæmoglobin and cyano-(met)hæmoglobin are identical modifications of the blood-pigment.

S. B. S.

Coaguloses. III. D. LAWROFF (*Zeitsch. physiol. Chem.*, 1908, 56, 343—362. Compare Abstr., 1907, i, 995).—The present experiments were performed with crystallised egg-albumin, and confirm those previously recorded with hæmoglobin and caseinogen. In the various fractions the same two types of coagulose-yielding substances were detected after relatively short peptic digestion.

W. D. H.

Organic Chemistry.

Syntheses of Methane by means of Calcium Hydride. M. MAYER and V. ALTMAYER (*Ber.*, 1908, **41**, 3074—3080. Compare Abstr., 1907, i, 457).—Methane can be synthesised by the action of carbon, its monoxide, or dioxide on freshly-prepared calcium hydride. With carbon monoxide the reaction begins at 400°, and is rapid at 500°; thus when the gas is passed at the rate of 0·5 c.c. per minute the issuing mixture contains 42·75% methane and 51·86% hydrogen, and when the rate is 1 c.c. per minute the product contains over 60% of methane. At higher temperatures the amount of methane tends to decrease. The reaction can probably be represented by the equations: $3\text{CaH}_2 + 3\text{CO} = \text{CH}_4 + 3\text{CaO} + 2\text{C} + \text{H}_2$ and $\text{CaH}_2 + 2\text{C} = \text{CaC}_2 + \text{H}_2$.

Calcium carbide, calcium oxide, and carbon have been found in the residue. Carbon dioxide behaves in much the same manner as the monoxide.

With carbon (lamp-black) and calcium hydride, hydrogen is produced at 270°, and the formation of methane can only be recognised at higher temperatures. At 500° the gaseous mixture contains about 40% of methane. J. J. S.

Studies in the Hexene and Heptene Series. NICOLAI D. ZELINSKY and E. S. PRISCHEVALSKY (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1105—1123).—The action of quinoline or of aqueous or alcoholic potassium hydroxide on *n*-hexyl iodide yields as main fraction a hydrocarbon, C_6H_{12} , b. p. 64—64·5°, D_4^{15} 0·6789, D_4^{20} 0·6750, $n_D^{18.5}$ 1·3896, which gives only valeric acid on oxidation; the authors regard it as *n*-hexylene.

β -Methylhexyl iodide, $\text{C}_4\text{H}_9\cdot\text{CHMe}\cdot\text{CH}_2\text{I}$, prepared from the corresponding alcohol by the action of iodine and phosphorus, has b. p. 78—79°/19 mm., D_4^{17} 1·3707, D_4^{21} 1·3663, n_D^{21} 1·4891.

Methylpropylcyclopropane, $\text{CH}_2\begin{smallmatrix} \text{CHMe} \\ | \\ \text{CHPr} \end{smallmatrix}$, obtained by the action of alcoholic potassium hydroxide on β -methylhexyl iodide, b. p. 92—92·5°/753 mm., D_4^{15} 0·7077, D_4^{20} 0·7033, n_D^{18} 1·4044, gives, on oxidation with permanganate, (1) methyl *n*-butyl ketone; (2) butyric acid; (3) valeric acid; (4) heptic or *is*oheptic acid; (5) a glycol, $\text{C}_7\text{H}_{16}\text{O}_2$, possibly $\text{CH}_2\text{Pr}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which, on further oxidation, gives butyric, valeric (?), and heptic or *is*oheptic acid. On adding hydrogen iodide to methylpropylcyclopropane and treating the resulting iodo-compound with dilute aqueous potassium hydroxide in a sealed tube at 100—105°, $\Delta\gamma$ -heptylene, $\text{CHEt}\cdot\text{CHPr}$, b. p. 94·5—95·5°/757 mm., D_4^{15} 0·7124, D_4^{20} 0·7083, $n_D^{21.5}$ 1·4077, is obtained; on oxidation with permanganate, this hydrocarbon yields butyric and propionic acids, together with traces of acetone and valeric acid.

T. H. P.

Ozonides of the Simple Olefines. CARL D. HARRIES and KARL HAEFFNER (*Ber.*, 1908, 41, 3098—3102).—Although amylene and hexylene ignite when brought into contact with ozone, nevertheless it has been found possible to prepare their ozonides by using the method of Harries and Tank (this vol., i, 517), namely, treating a very dilute solution of the substance in an indifferent solvent with ozone. The ozonides of these olefines are very stable substances, and may be distilled in a vacuum. It is probable, from the observed values of the molecular refraction and dispersion of these ozonides, that the molecule contains one carbonyl oxygen atom and two ether oxygen atoms.

Amylene ozonide (trimethylethylene ozonide), $C_5H_{10}O_3$, is prepared by passing ozone into a dilute solution of the olefine in hexane, and heating at 60° in a vacuum the crude ozonide obtained after distilling off the solvent; it is a limpid, colourless liquid. The ozonide obtained by treating the crude ozonide with an aqueous solution of sodium hydrogen carbonate, when analysed, gives values which lie between those required for $C_5H_{10}O_3$ and $C_5H_{10}O_4$; it is far more explosive than the normal ozonide.

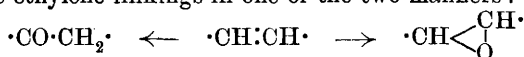
Hexylene ozonide, $C_6H_{12}O_3$, is prepared in the same way as the amylene ozonide. The crude ozonide first obtained is viscid, but yields the normal ozonide, a limpid liquid, when distilled at 60° under 12 mm. pressure. The amylene and hexylene ozonides are not readily decomposed by water.

Propylene ozonide is obtained by passing ozone into a dilute solution of propylene in ethyl chloride cooled in a carbon dioxide-ether freezing mixture. It is a limpid liquid with a pungent odour, b. p. $29-30^\circ/19.5$ mm., becomes solid at low temperatures, explodes with great violence when heated in a test-tube, and is rapidly decomposed by water.

W. H. G.

Absorption of Oxygen by Electro-condensation Products. SIMA M. LOSANITSCH (*Monatsh.*, 1908, 29, 753—762).—Chiefly an account of work already published (*Abstr.*, 1897, i, 179; this vol., ii, 32), and a criticism of Jovitschitsch's work (this vol., i, 118).

Since the compound $(C_{12}H_{22}O)_2$, formed by absorption of oxygen by the electro-condensation product of ethylene, distils unchanged, the oxygen must be in chemical combination. The addition may take place at the ethylene linkings in one of the two manners:



The solid condensation product of acetylene, when treated with ozonised oxygen, forms a compound, $(C_6H_8O_2)_n$; the liquid condensation product, on the other hand, absorbs oxygen only slowly, and, after several months, contains less oxygen than required for the formula $(C_6H_{10}O)_2$. Both condensation products of acetylene with ethylene absorb oxygen, but without forming definite compounds. The oxygenated compound derived from acetylene and carbon monoxide absorbs more oxygen than previously stated, but still without reaching the composition $(C_3H_3 \cdot CO \cdot O_2)_n$.

G. Y.

Action of Organo-magnesium Compounds on Crotonaldehyde and the Optical Behaviour of the Products. JOHANN REIF (*Ber.*, 1908, 41, 2739—2746).—The paper is a continuation of Grignard's research on the action of magnesium methyl iodide or magnesium *isoamyl* bromide on crotonaldehyde (*Abstr.*, 1901, i, 679). Employing the same method, the author has examined the action of magnesium ethyl, propyl, *isopropyl*, and *isobutyl* bromides. The resulting unsaturated alcohols, $\text{CHMe}:\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{R}$, described below are colourless, mobile liquids, which exhibit a normal molecular refraction, are oxidised by 1% potassium permanganate to the corresponding glycerols, and by distillation with potassium hydrogen sulphate yield diolefines of the type $\text{CHMe}:\text{CH}:\text{CH}:\text{CHR}$, which, in agreement with Brühl's observations on substances containing the group $>\text{C}:\text{CH}:\text{CH}:\text{C}<$, exhibit a marked exaltation of the molecular refraction.

The following new compounds are mentioned:

Δ^{β} -Pentene- δ -ol yields a *chloride*, $\text{CHMe}:\text{CH}\cdot\text{CHMeCl}$, b. p. 103—106° (decomp.), and a *glycerol*, $\text{C}_5\text{H}_{12}\text{O}_3$, b. p. 244—246°, of which the *triacetate* has m. p. 121° and b. p. 241—243°. Δ^{β} -Hexene- δ -ol, $\text{CHMe}:\text{CH}\cdot\text{CHEt}\cdot\text{OH}$, b. p. 133—135° or 85—87°/118 mm., D_4^{25} 0.8409, n_D^{25} 1.4312; the *acetate* has b. p. 153—155°; the *chloride* has b. p. 122—126° (decomp.) or 65—70°/110 mm., and is converted by methyl-alcoholic potassium hydroxide into δ -methoxy- Δ^{β} -hexene, $\text{CHMe}:\text{CH}\cdot\text{CHEt}\cdot\text{OMe}$, b. p. 110—113° (compare Vaubel, *Abstr.*, 1891, 996); the *glycerol*, $\beta\gamma\delta$ -hexantriol, has b. p. 256—257°, and yields a solid *triacetate*, b. p. 254—256°. Δ^{β} -Heptene- δ -ol,

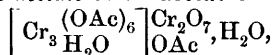


b. p. 152—154° or 104—105°/106 mm., D_4^{20} 0.8445, n_D^{20} 1.4373, forms an *acetate*, b. p. 168—170°, and a *chloride*, b. p. 140—144° or 86—90°/104 mm. ζ -Methyl- Δ^{β} -hexene- δ -ol, $\text{CHMe}:\text{CH}\cdot\text{CHPr}^{\beta}\cdot\text{OH}$, has b. p. 139—140° or 92—94°/105 mm., D_4^{20} 0.8426, n_D^{20} 1.438; the *acetate* has b. p. 108—110°/100 mm. ζ -Methyl- Δ^{β} -heptene- δ -ol,



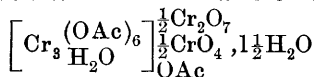
D_4^{19} 0.8389, n_D^{19} 1.4395, forms an *acetate*, b. p. 123—126°/108 mm. $\Delta^{\beta\delta}$ -Pentadiene, C_5H_8 , b. p. 40—41°, D_4^{25} 0.6794, n_D^{25} 1.4206. $\Delta^{\beta\delta}$ -Hexadiene, C_6H_{10} , b. p. 80—82°, D_4^{21} 0.7177, n_D^{21} 1.4463, yields a *dihydrobromide*, b. p. 199—201° or 98—102°/30 mm., and a *tetrabromide*, m. p. 180°. $\Delta^{\beta\delta}$ -Heptadiene, C_7H_{12} , b. p. 104—106°, $D_4^{21.5}$ 0.7327, $n_D^{21.5}$ 1.4486. ϵ -Methyl- $\Delta^{\beta\delta}$ -hexadiene, C_7H_{12} , b. p. 97—99°, $D_4^{24.5}$ 0.7192, $n_D^{24.5}$ 1.4266. ζ -Methyl- $\Delta^{\beta\delta}$ -heptadiene, C_8H_{14} , b. p. 114—116°, D_4^{25} 0.7401, n_D^{25} 1.4397. η -Methyl- $\Delta^{\beta\delta}$ -octadiene, C_9H_{16} , b. p. 149°, D_4^{18} 0.7521, n_D^{18} 1.4543, yields a *dihydrobromide*, b. p. 124—126°/16 mm., and a *tetrabromide*, b. p. 184°/18 mm. C. S.

Salts of an Acetatochromo-base. RUDOLF F. WEINLAND (*Ber.*, 1908, 41, 3236—3245).—When chromic acid (1 part) is warmed at 100° with glacial acetic acid (2 parts) until no more carbon dioxide is evolved, the *dichromate acetate* of an acetatochromo-base,



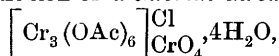
is obtained in brownish-black, microscopic prisms. If this salt is

treated with a little water, it first dissolves, and afterwards olive-green plates of a *chromate acetate* with 1.5 mols. of chromic acid,



are precipitated. On the other hand, if the dichromate acetate is recrystallised from a larger quantity of water, dark green crystals of a simpler *chromate acetate*, $\left[\text{Cr}_3 \begin{smallmatrix} (\text{OAc})_6 \\ \text{H}_2\text{O} \end{smallmatrix} \right] \begin{smallmatrix} \text{CrO}_4, 3\frac{1}{2} \text{H}_2\text{O} \\ \text{OAc} \end{smallmatrix}$, are produced. This compound is also formed directly from the two acids.

Addition of hydrochloric acid to a solution of the dichromate acetate causes the separation of a *chloride chromate*,

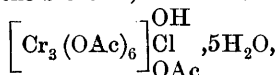


as dark green crystals.

The *platinichloride*, $\left[\text{Cr}_3 (\text{OAc})_6 \right] \begin{smallmatrix} (\text{OH})_3 \\ \frac{1}{2} \text{PtCl}_6 \end{smallmatrix}, 5\text{H}_2\text{O}$, is obtained from all the above salts of the base.

A basic *chromate acetate*, $\left[\text{Cr}_3 (\text{OAc})_6 \right] \begin{smallmatrix} \text{OH} \\ \frac{1}{2} \text{CrO}_4, 5\text{H}_2\text{O} \\ \text{OAc} \end{smallmatrix}$, is obtained when

lead acetate is added to the dichromate acetate until only $\frac{1}{4}$ mol. of chromic acid is left in the solution, and a basic *chloride*,



and basic *nitrate*, $\left[\text{Cr}_3 (\text{OAc})_6 \right] \begin{smallmatrix} \text{OH} \\ \text{NO}_3, 2\frac{1}{2} \text{H}_2\text{O} \\ \text{OAc} \end{smallmatrix}$, can be obtained by similar

means. The *diacetate*, $\left[\text{Cr}_3 (\text{OAc})_6 \right] \begin{smallmatrix} \text{OH} \\ (\text{OAc})_2 \end{smallmatrix}, 5\text{H}_2\text{O}$, is obtained from the solution of the chromate acetate, after treatment with lead acetate, as a light green, crystalline powder. Silver nitrate precipitates silver acetate from its concentrated solution, proving the presence of acetic acid ions, but the nitrate acetate solution gives no such precipitate. The method of preparation of these compounds shows that the positive complex contains three atoms of chromium and six acetic residues. The water remaining after drying to constant weight in a vacuum over sulphuric acid is held to be joined to the cation.

The free acetatochromo-base prepared from the chloride acetate and excess of silver oxide is dark green in solution. The alkaline liquid is unstable, and gradually becomes acid.

The corresponding *iron base*, $\left[\text{Fe}_3 (\text{OAc})_6 \right] \begin{smallmatrix} \text{Cr}_2\text{O}_7, \text{H}_2\text{O} \\ \text{OAc} \end{smallmatrix}$, and *propionato-bases* have been prepared. W. R.

Stereochemical Nature of the Addition of Chlorine to Crotonic Acid. ARTHUR MICHAEL and O. D. E. BUNGE (*Ber.*, 1908, 41, 2907—2913).—Ordinary fumaroid crotonic acid absorbs chlorine both in the dark and in sunlight, forming $\alpha\beta$ -dichlorobutyric acid, m. p. 63°, and the same compound is obtained under similar conditions

from *allocrotonic acid*. A stereoisomeric dichlorobutyric acid, m. p. 78° , is produced by the addition of hydrogen chloride to α -chloro-crotonic acid, and is regarded as the maleoid derivative. That this is not the case is shown by the fact that the more fusible dichlorobutyric acid has a greater electrical conductivity than the isomeride, and it must therefore be regarded as the maleoid derivative (crotonic acid *allodichloride*). The fumaroid acid yields, primarily, maleoid additive products, and the further isomeric change takes place much less readily in the case of the crotonic acids than with the cinnamic acids. Actinic rays are unable to effect it, and it requires prolonged heating with concentrated hydrochloric acid to bring about the conversion of crotonic acid *allodichloride* into the less fusible isomeride.

Of the two dichlorosuccinic acids melting at 175° and 215° , the more fusible isomeride is the stronger acid. E. F. A.

Action of Ozone on Compounds containing Double and Treble Linkings. ETTORE MOLINARI (*Ber.*, 1908, 41, 2782—2785).—The author replies to Harries' criticisms (this vol., i, 387), and re-states his right to work on ozonides. C. S.

Triolein Ozonide and its Decomposition Products. ETTORE MOLINARI and P. FENAROLI (*Ber.*, 1908, 41, 2789—2794).—When triolein is ozonised in hexane solution, an insoluble, gelatinous, yellow mass, probably a polymerised ozonide, is obtained, which is converted by thirty minutes' heating with 1% potassium hydroxide on the water-bath into *triolein ozonide*, $C_{57}H_{104}O_{15}$, a viscous, colourless oil, which decomposes at 136° . This ozonide, not the polymerised form, is obtained by the ozonisation of olive oil. It is decomposed by 30% alcoholic potassium hydroxide on the water-bath, yielding glycerol, azelaic and nonoic acids, a white hydroxy-acid, $C_{18}H_{36}O_3$ (compare Molinari and Soncini, *Abstr.*, 1906, i, 792), and an oily acid, $C_{18}H_{32}O_6$, which is oxidised quantitatively to azelaic acid by potassium permanganate. Hydrogen peroxide is not formed, and aldehydes only in small amount.

Arnold and Mentzel's benzidine reaction is the best test for hydrogen peroxide in the presence of aldehydes; some of the higher aldehydes give with potassium ferrieyanide and ferric chloride, or with titanium sulphate, the same reactions as hydrogen peroxide.

The authors hope that the saponification value of ozonides will form a new constant in the analysis of oils and fats. C. S.

Products of the Decomposition of Oleic Acid Ozonide. ETTORE MOLINARI and C. BAROSI (*Ber.*, 1908, 41, 2794—2799).—According to Harries, the primary products of the decomposition of oleic acid ozonide by hot water are exclusively hydrogen peroxide, nonaldehyde, and the semialdehyde of azelaic acid (*Abstr.*, 1906, i, 793; 1907, i, 11); Molinari and Soncini (*Abstr.*, 1906, i, 792; compare also preceding abstract) obtained no hydrogen peroxide, but aldehydes in small amount, and mainly azelaic, nonoic, and two other acids, $C_{18}H_{32}O_6$ and $C_{18}H_{36}O_3$. To ascertain whether these four acids are

secondary oxidation products, the authors have investigated the decomposition of oleic acid ozonide, $D^{18} 1.0218$, by hot saturated potassium hydrogen sulphite. The reaction is very complicated, and several of the products have not yet been investigated. The main results are: (a) primarily formed acids are azelaic, nonoic, and the acids $C_{18}H_{32}O_6$ and $C_{18}H_{36}O_3$. The acid $C_{18}H_{36}O_3$ (calcium salt insoluble) has m. p. 41° (compare Molinari and Soncini, *loc. cit.*), and is a hydroxystearic acid, $CH_3 \cdot [CH_2]_7 \cdot CH(OH) \cdot [CH_2]_8 \cdot CO_2H$, produced by the aldol condensation of nonaldehyde and nonoic acid. The acid $C_{18}H_{32}O_6$ (calcium salt soluble) is probably produced by the condensation of 2 mols. of the semialdehyde of azelaic acid; (b) the aldehydes liberated from their bisulphite compounds undergo polymerisation; *paranonaldehyde*, $(C_9H_{18}O)_3$, a white, crystalline mass, m. p. 28° , has been isolated, and also another substance, b. p. 190° , which forms a *semicarbazone*, $C_{10}H_{30}O_3N_3$, m. p. 54° , and probably is formed by the aldol condensation of 2 mols. of nonaldehyde; (c) the semialdehydes are isolated in the form of a viscous, brown oil, which no longer shows the properties of aldehydes, and consists probably of condensation or oxidation products of the semialdehyde of azelaic acid. By prolonged boiling with water, azelaic acid is extracted, and the residue contains the acid $C_{18}H_{32}O_6$ and other unexamined substances. C. S.

Constitution of the So-called Elæomargaric Acid. TOKUHEI KAMETAKA (*J. Coll. Sci. Tôkyô*, 1908, 25, iii, 1—8. Compare *Trans.*, 1903, 83, 1042).—Elæomargaric acid cannot be a homologue of sorbic acid, as stated by Cloez (this *Journ.*, 1877, i, 454), since it does not yield tartaric acid when oxidised with potassium permanganate (compare Doebner, *Abstr.*, 1890, 1274). Cloez also states that it is a homologue of stearolic acid, but this is improbable, since it does not give a definite product with concentrated sulphuric acid. As stated by Maquenne (*Abstr.*, 1903, i, 62), elæomargaric acid when oxidised yields azelaic acid, but the presence of valeric acid could not be established. It is therefore highly probable that one of the two ethylene linkings in elæomargaric acid is in the middle of the chain of eighteen carbon atoms. The other ethylene linking is probably situated on that side of the middle ethylene linking which is further removed from the carboxyl group. This view is supported by the behaviour of the acid towards aniline; it yields an *anilide*, $C_{18}H_{31}O \cdot NPh$, which crystallises in lustrous scales, m. p. about 80° , but does not form an aniline additive product; consequently, an ethylene linking is not near the carboxyl group (compare Autenrieth and Pretzell, *Abstr.*, 1903, i, 474). The anilide combines with bromine, forming a *substance*, m. p. about 95° .

The *ethyl* ester of elæomargaric acid is a yellow liquid, b. p. 230 — $240^\circ/25$ mm; the *methyl* ester decomposes when warmed.

W. H. G.

Japanese Vegetable Oils. TOKUHEI KAMETAKA (*J. Coll. Sci. Tôkyô*, 1908, 25, iv, 1—7).—*Japanese Wood Oil (Kiri-abura)*.—The iodine number of the fresh, cold-drawn oil was found by Hübl's method to be 161.3; after storing in a stoppered bottle in the dark for eleven

months, the value obtained by the same method was 150.0. The iodine number after three months, determined by Wys' method, was 156.3, and after eleven months, 153.2. The low iodine number of Japanese wood oil cannot, therefore, be ascribed to previous oxidation, as stated by some chemists (compare Ingle, *J. Soc. Chem. Ind.*, 1902, 21, 187), although the value does decrease on oxidation. Using the number 161.3, it is found by calculation that the oil consists of about 86% of elæomargarin and 14% of olein. The following constants were determined: acid number, 3.81; D_{25}^{20} 0.9307; saponification number, 196.0. An enzyme, capable of hydrolysing the oil and also ethyl acetate, was obtained from the seeds of *Elæococca vernicia*. Since this enzyme is present in small quantities in the oil itself, it possibly plays some part in the rapid drying of this oil.

Camellia Oil or Oil of *Thea japonica* (*Tsubaki-abura*) has D_4^{15} 0.9138 and iodine number (Hübl's method) 79.47. The principal acid in the oil is oleic acid.

Oil of *Terrya nucifera* (*Kayana-abura*) has the iodine number (Hübl's method) 137.3. It contains linolic acid or its isomerides, together with stearic acid.

Soja-bean Oil or Oil of *Glycine hispida* (*Daidzu-abura*).—The unsaturated acids in this oil are chiefly oleic acid and linolic acid or its isomerides.

Oil of *Perilla* (*Eno-abura*) appears to contain linolenic acid or its isomeride.

W. H. G.

Compounds of Bismuth with Aliphatic Hydroxy-acids.

HANS TELLE (*Arch. Pharm.*, 1908, 246, 484—503).—Compounds of bismuth with lactic, malic, tartaric, and citric acids have been prepared, and a new method of preparing such salts, depending on the decomposition of the soluble hydrated acid lactate with the appropriate acid, is described.

Freshly-precipitated bismuth hydroxide dissolves slowly in lactic acid slightly diluted with water, and the solution gradually deposits bunches of glancing needles of the *hydrated* salt, $\text{BiC}_6\text{H}_9\text{O}_6 \cdot 7\text{H}_2\text{O}$. This is readily soluble in water, and at 105° furnishes the anhydrous salt, $\text{BiC}_6\text{H}_9\text{O}_6$, which is scarcely soluble in water, and can be obtained in rhombic tablets by digesting bismuth hydroxide with lactic acid at 100°. The anhydrous salt decomposes slightly when boiled for some time with water (compare Engelhardt, this Journ., 1848, 1, 400, and Brunig, *Annalen*, 1857, 104, 195).

Bismuth malate, $\text{BiC}_4\text{H}_3\text{O}_5 \cdot \text{H}_2\text{O}$, colourless needles, can be prepared either by heating bismuth hydroxide with just enough malic acid dissolved in a little water for a few minutes, or by adding a solution of malic acid to one of the hydrated lactate referred to above and boiling the mixture. It is nearly insoluble in water.

Attempts to prepare bismuthotartaric acid by Baudran's method (*Abstr.*, 1900, i, 375) resulted in the formation of minute needles of the *hydrated* salt, $\text{BiC}_8\text{H}_9\text{O}_{12} \cdot 3\text{H}_2\text{O}$, instead of the compound, $\text{C}_4\text{H}_5(\text{BiO})\text{O}_6 \cdot \text{H}_2\text{O}$, described by Baudran (compare Rosenheim and Vogelsang, *Abstr.*, 1906, i, 231). This can also be obtained by adding a solution of tartaric acid to one of the hydrated lactate and boiling

the liquid. It is nearly insoluble in water, but dissolves in solutions of alkali hydroxides or carbonates, yielding syrups from which no crystalline product could be obtained.

Rother's bismuth citrate, $\text{BiC}_6\text{H}_5\text{O}_7$ (this Journ., 1876, ii, 173), can be prepared in a well-crystallised condition, either by dissolving bismuth hydroxide in a solution of citric acid, or from the hydrated lactate by the general method. T. A. H.

Dehydrocamphenylic Acid. GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1908, 41, 2747—2750).—By the oxidation of camphene by dilute nitric acid, Jagelki obtained an unsaturated acid, $\text{C}_{10}\text{H}_{14}\text{O}_2$, which he claimed to be identical with Wagner's dehydrocamphenylic acid (*Abstr.*, 1899, i, 627, 629). Since the latter is saturated, the authors have re-examined Jagelki's compound, and find that it is saturated and identical with dehydrocamphenylic acid and with an acid obtained by Konowaloff (*Abstr.*, 1907, i, 279). The *silver*, *lead*, and *calcium* salts are mentioned. The *ethyl* ester, $\text{C}_{12}\text{H}_{18}\text{O}_2$, b. p. 100—101°/10 mm., D_4^{20} 1.0143, n_D^{20} 1.47299, shows the molecular refraction of a saturated, tricyclic ester. The *amide*, m. p. 114.5°, and *anilide*, $\text{C}_9\text{H}_{13}\cdot\text{CO}\cdot\text{NHPh}$, m. p. 102—103°, have been prepared. C. S.

Active Pinonic and Pinic Acids. PHILLIPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1908, 147, 597—600).—Previous authors, using pinene of low rotatory power, have only succeeded in obtaining racemic pinonic acid by oxidation of this terpene. When *l*-pinene (b. p. 155—157°, $[\alpha]_D - 37.2^\circ$) is oxidised by potassium permanganate in the cold, a mixture of racemic pinonic acid and *l*-pinonic acid is produced. *l*-Pinonic acid, $\text{C}_{10}\text{H}_{16}\text{O}_3$, forms large crystals, m. p. 67—69°, $[\alpha]_D^{25} - 90.5^\circ$ (in chloroform), and gives a mixture of two *oximes*, the γ crystallising in dextrorotatory micro-crystals, m. p. 189—191°, difficultly soluble in ether, and the β crystallising in large, levorotatory tablets, m. p. 128°, readily soluble in ether. On oxidation by sodium hypochlorite or hypobromite, the acid gives *d*-pinic acid, having m. p. 135—136°, $[\alpha]_D^{25} + 7.1^\circ$. A *d*-pinene, having D_0 0.8745, D_{14}^4 0.8635, n_D 1.46977, $[\alpha]_D + 39.4^\circ$, b. p. 155—158°, on oxidation in a similar manner, gives a mixture of *d*-pinonic acid and the racemic acid. *d*-Pinonic acid has m. p. 67—68°, $[\alpha]_D^{25} + 89.0^\circ$, and, when fused with an equal weight of the *l*-acid, gives immediately the racemic acid, m. p. 104°. The *d*-acid gives the β and γ oximes identical with those described by Baeyer. The conclusion is drawn that Tiemann's acid, having m. p. 98—99°, and giving an oxime, m. p. 147°, is not the true *l*-pinonic acid derived from *l*-pinene; the two acids are possibly the *cis*- and *cis-trans*-isomerides predicted by theory. E. H.

Equilibrium in the System: Potassium Oxalate, Oxalic Acid, Water. IWAN KOPPEL and M. CAHN (*Zeitsch. anorg. Chem.*, 1908, 60, 53—112).—The equilibrium relations in the system $\text{K}_2\text{O}-\text{CrO}_3-\text{H}_2\text{O}$ have been determined over a wide range of temperature, and the results are illustrated by numerous curves and are summarised on projected space diagrams. The three potassium oxalates already known, $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$, KHC_2O_4 , and $\text{KHC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$,

exist in equilibrium with solution within certain limits of concentration at all the temperatures at which measurements have been made. Further, an acid salt of the formula $2K_2C_2O_4, H_2C_2O_4, 2H_2O$ (the salt *M*), not previously known, is stable between its cryohydric point and its transition point in the neighbourhood of 84° .

In the course of the investigation, the complete isothermals have been determined at 0° , 30° , and 60° by solubility observations in the usual way, and the ice lines and boiling-point lines have also been determined. The *M*-salt is decomposed by water under all conditions, with separation of potassium hydrogen oxalate, and this salt is decomposed by water from its cryohydric point up to about 50° . Oxalic acid itself is partly decomposed when heated in aqueous solution above 100° , even in the presence of acid oxalates.

The transition temperature of the *M*-salt, represented by the equation: $2K_2C_2O_4, H_2C_2O_4, 2H_2O \rightleftharpoons K_2C_2O_4, H_2O + 2KHC_2O_4 + H_2O$, was determined both by solubility and dilatometer experiments, the mean value being about 84° , as mentioned above.

In preparing pure potassium hydrogen oxalate, rather more than the theoretical amount of alkali should be employed, otherwise the salt which separates from solution is contaminated with tetroxalate. Observations have been made which support Wyruboff's statement, that the acid oxalate exists in two forms: an anhydrous modification in monoclinic crystals, stable above 15° , and a monohydrate in orthorhombic crystals, which separates from solution below 15° . G. S.

Decomposition of Lead Oxalate by Saline Solutions. H. CANTONI and L. MAURI (*Bull. Soc. chim.*, 1908, [iv], 3, 929—935).—An extension of the investigation previously described (Abstr., 1906, i, 557) on the action of alkali sulphates on oxalates of the alkaline earths to the case of lead oxalate reacting with solutions of alkali chlorides or sulphates. Tables of the numerical results obtained are given in detail in the original. These show that alkali sulphates in solution decompose lead oxalate, and that the extent of this decomposition increases (1) with rise of temperature, (2) time of action, and (3) concentration of the solution. Of the three sulphates tried, namely, potassium, sodium, and ammonium, the first is the most active and the third least, but the potassium salt is relatively much more active than either of the other two. The alkali chlorides attack the oxalate far less readily than do the sulphates, and there is little to choose between the three chlorides tried in this respect. In the cold, neither alkali sulphates nor chlorides exert any considerable action on lead oxalate. T. A. H.

Complex Ferrimalonates. MOTOOKI MATSUI (*J. Coll. Sci. Tōkyō*, 1908, 25, ii, 1—5).—Complex ferrimalonates having the composition $(CO_2M \cdot CH_2 \cdot CO_2)_3Fe$, where M represents either sodium, potassium, or ammonium, have been prepared by adding ferric chloride to an aqueous solution of the malonate so long as the mixed solution did not give a red coloration with potassium thiocyanate. These salts are decomposed by acids and alkalis; in aqueous solution, they dissociate into the complex ion, $[Fe(CO_2 \cdot CH_2 \cdot CO_2)_3]^{3-}$, and the ion of the alkali

metal. The aqueous solution is unstable, the green colour soon changing into brown; it is probable that the decomposition is due to hydrolysis, since the addition of sodium malonate renders the solution stable. The acid corresponding with these salts has not yet been isolated, but it is obtained in aqueous solution by dissolving moist ferric hydroxide in a warm solution of malonic acid.

Sodium ferrimalonate, $\text{Fe}(\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Na})_3$, forms green, sandy crystals and decomposes at about 200° . *Potassium ferrimalonate*, $\text{Fe}(\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{K})_3\cdot 4\text{H}_2\text{O}$, crystallises in green prisms. *Ammonium ferrimalonate*, $\text{Fe}(\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{NH}_4)_3\cdot 4\text{H}_2\text{O}$, forms green, prismatic crystals. The *barium* and *calcium* salts were prepared, but not analysed.

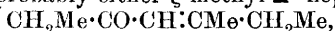
Ferrous iron also forms complex malonates, which are precipitated as yellow crystals by adding alcohol to an aqueous solution of a malonate and ferrous sulphate. They are very unstable, and immediately change in the air to the corresponding ferric compounds.

W. H. G.

Formation of Compounds in Solutions of Tartaric Acid and Sodium Molybdate. HERMANN GROSSMANN (*Zeitsch. anorg. Chem.*, 1908, 60, 50—52).—Remarks on a recent paper by Quinet (this vol., i, 713). Priority is claimed for certain results described in Quinet's paper (Rosenheim and Itzig, *Abstr.*, 1900, i, 135, 272; Grossmann and Pötter, 1906, i, 799). Further, it is pointed out that the mixture of tartaric acid and sodium molybdate of maximum rotatory power contains the components in the ratio $1\text{C}_4\text{H}_6\text{O}_6 : 1\text{Na}_2\text{MoO}_4$, and not 1:2 as given by Quinet, and that the other characteristic point corresponds with the composition $\text{C}_4\text{H}_6\text{O}_6 : \frac{1}{2}\text{Na}_2\text{MoO}_4$. G. S.

Some Citrates. E. I. VAN ITALLIE (*Pharm. Weekblad*, 1908, 45, 1201—1210).—The action of ammonia on aqueous solutions of citric acid at 30° only yields known hydrates; that of calcium hydroxide at the same temperature produces the hydrates $(\text{C}_6\text{H}_7\text{O}_7)_2\text{Ca}\cdot 3\text{H}_2\text{O}$ and $\text{C}_6\text{H}_6\text{O}_7\text{Ca}\cdot 4\text{H}_2\text{O}$. A. J. W.

Action of Calcium Carbide on Some Ketones. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1908, [iv], 3, 829—833).—Acetone prepared from its sodium hydrogen sulphite compound reacts energetically with powdered calcium carbide, evolving acetylene and forming mesityl oxide and more complex substances boiling between 170° and 350° . Whatever the conditions, the proportion of mesityl oxide only varies from 8% to 12%; the yield of the higher boiling products, on the other hand, depends on the length of time the acetone is in contact with the carbide. Commercial acetone, the vapour of which acts on fragments of calcium carbide, has no action on the latter when powdered. Pure butanone also acts on calcium carbide, although more slowly, giving, besides higher boiling products, an agreeably smelling ketone, $\text{C}_8\text{H}_{14}\text{O}$, b. p. $164\text{—}166^\circ/760$ mm. and $66\text{—}68^\circ/20$ mm., $D_{25}^{20} 0.853$. This is probably either ζ -methyl- Δ^8 -heptene- γ -one,



or $\gamma\delta$ -dimethyl- $\Delta\gamma$ -hexene- β -one, $\text{CH}_2\text{Me}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CMe}$, or a mixture

of the two. If commercial butanone, dried over potassium carbonate and rectified, is used, the new ketone apparently contains a liquid richer in oxygen.

Boiling δ -pentanone and acetophenone have no action on calcium carbide. The vapour of the latter ketone at ordinary, but not at reduced, pressure acts on the carbide, giving a gummy mass.

The author finds that certain esters retard or altogether prevent the action of acetone, and draws the conclusion that the inactivity of commercial acetone is due to its containing an impurity of this nature.

E. H.

Reduction of $\alpha\beta$ -Unsaturated Ketones. ALADAR SKITA, A. ARDAN, and M. KRAUSS (*Ber.*, 1908, 41, 2938—2946).—The paper deals with the comparative study of the reduction of aliphatic and alicyclic $\alpha\beta$ -unsaturated ketones by Sabatier and Senderens' method.

Mesityl oxide, reduced at 185° for seven hours, yields methyl isobutyl ketone in 60% yield and a small quantity of methylisobutylcarbinol; reduced for eight hours at 210° in a more rapid current of hydrogen (220 c.c. per minute), mesityl oxide yields β -methylpentane (compare Darzens, *Abstr.*, 1905, i, 66, 172). Phorone, reduced at 225° for five hours (velocity of hydrogen = 100 c.c. per minute), gives a 65% yield of valerone, whilst at 235° and with a velocity of 280 c.c. of hydrogen per minute, the products are valerone and an unidentified, unsaturated hydrocarbon, diisobutylcarbinol, and $\beta\zeta$ -dimethylheptane.

1:3-Dimethyl- Δ^3 -cyclohexen-5-one, reduced for six hours at 235° (velocity of hydrogen = 100 c.c. per minute), yields 1:3-dimethylcyclohexane, b. p. $119-120^\circ$, D_{20}^{20} 0.7822. Ethyl 1-methyl- Δ^6 -cyclohexen-5-one-2-carboxylate (Hagemann, *Abstr.*, 1893, i, 393), reduced for four hours at $280-285^\circ$ with an equally rapid current of hydrogen, yields ethyl 1-methyl- $\Delta^{4 \text{ (or } 5)}$ -cyclohexene-2-carboxylate, of which the acid has b. p. $114-130^\circ/9$ mm., and forms a crystalline dibromide, $C_8H_{12}O_2Br_2$.
C. S.

Density of Sucrose. G. FOUQUET (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 26, 176—177).—The author finds that different methods of crystallising sucrose produce crystals of varying density; one specimen of crystals examined had D 1.550 to 1.575, whilst another had D 1.580 to 1.610. The actual cause which produces the variation in the density has not yet been ascertained.
W. P. S.

Aqueous Solutions and their Densities: Sucrose Solutions. G. FOUQUET (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 26, 160—176).—The curve of contractions occurring when sucrose is dissolved in water, calculated on the value 1.590 for D_{15}^{15} of sucrose, exhibits a maximum for 40% by weight of sucrose, whilst for a saturated solution (66—67% of sucrose) the contraction is zero. The above value for the density of sucrose is calculated from the value D_4^{15} 1.5881. For concentrations up to 15%, the contraction is sensibly proportional to the concentration, whilst for concentrations (p) up to 40%, the contraction is represented by the formula: $\delta = 0.000225p(80 - p)$. When p increases from 5% to 75%, the density of the sugar in solution diminishes continuously, and the same is probably the case for increase of p from 0% to 5%,

although here the increase is only slight. For concentrations up to 5%, the values of D_4^{15} for sucrose solutions are represented by the expression: $162.91956/(163.05 - 0.6313 p)$. These considerations are extended to impure sucrose solutions. T. H. P.

Inversion of Sucrose. YUKICHI OSAKA (*J. Coll. Sci. Tōkyō*, 1908, 25, i, 1—8).—It is shown that, whereas in moderately dilute solutions the hydrolysis of sucrose by an acid may be regarded as practically complete, in strong solutions (80 grams of sugar in 100 c.c. of solution) the hydrolysis is incomplete. It is therefore probable that the inversion of sucrose by an acid is a reversible reaction. This view is supported by the result of the following experiment. A solution of about 20 grams of sucrose in 50 c.c. of solution was hydrolysed completely by hydrochloric acid; 5.7507 grams of this solution, treated with sodium acetate and diluted to 25 c.c., gave a rotation of -3.83° . The same weight of the inverted solution (5.7507 grams) was then concentrated to about one-half by passing dry air over the surface of the solution; it was then treated with sodium acetate and made up to 25 c.c. as before; this solution had a rotation of -3.30° . The reversion product could not be maltose or isomaltose, since the author finds that no reversion takes place in concentrated solutions of dextrose under the influence of an acid at 25° during a period of two months. W. H. G.

Inversion of Sucrose by Invertase. II. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, 30, 1564—1583).—A continuation of the work previously recorded (this vol., i, 605). The results completely confirm O'Sullivan and Tompson's conclusions (*Trans.*, 1890, 51, 834).

The velocities of the mutarotation of dextrose and lævulose at 30° in water and in aqueous solutions of hydrochloric acid and invertase have been determined. The velocities are not affected by invertase, but are greatly accelerated by acids. This difference between the action of invertase and acids on the products of the inversion of sucrose causes the action of invertase to appear irregular, owing to the influence of the mutarotation of the invert-sugar on the polarimetric reading. On correcting for this, the inversion of sucrose by invertase proves to be a catalytic reaction of the first order.

The acceleration of the mutarotation of dextrose at 30° by hydrochloric acid is such that the rate is a linear function of the hydrogen-ion concentration. In the case of lævulose, a minimum rate occurs in dilute acid solutions similar to the less pronounced minimum which has been found in the case of dextrose at 25° (*Abstr.*, 1907, ii, 942).

The action of invertase is greatly accelerated by minute traces of acid, but the addition of further small quantities of acid does not increase the effect. The inversion of sucrose, in both dilute and concentrated solutions, by invertase is proportional to the concentration of the invertase.

A method is given for calculating the amounts of fresh dextrose and lævulose that are present at any instant in the solution undergoing inversion. This method is also applicable to the determination of the forms

in which the various hexoses are liberated from glucosides and di- and tri-saccharides by the action of enzymes. It is shown that the dextrose formed from sucrose by the action of invertase has $[\alpha]_D$ 100—125°, and is therefore in the form of α -dextrose ($[\alpha]_D = 106^\circ$). E. G.

Action of Cold Aqueous Sodium Hydroxide on Cellulose.

II. WALTHER VIEWEG (*Ber.*, 1908, 41, 3269—3275. Compare Abstr., 1907, i, 893).—From 11% to 24% sodium hydroxide solutions, cellulose takes up an amount of the alkali sufficient to form the compound $C_{12}H_{19}O_{10}Na$, and, if the results are plotted, the curve obtained is discontinuous, the point of discontinuity corresponding with the formation of this compound. The curve up to this point is abnormal, but afterwards it is a horizontal straight line pointing to a chemical reaction. It is also shown that the higher the degree of mercerisation the greater the capacity for absorption of sodium hydroxide, and more is taken up at lower than at higher temperatures. Contrary to the statement of Miller (this vol., i, 78), the addition of sodium chloride to the sodium hydroxide increases the absorption, and the conclusion is drawn that the reaction is physical as well as chemical. W. R.

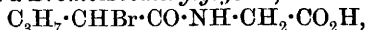
Walden's Inversion. III. EMIL FISCHER and HELMUTH SCHEIBLER (*Ber.*, 1908, 41, 2891—2902. Compare Abstr., 1907, i, 192; this vol., i, 324).—The optical properties of valine (α -aminoisovaleric acid) are not altered by the double transformation into bromofatty acid and back to amino-compound. There are some reasons for thinking that this is due rather to a double Walden inversion than to its absence.

d-Valine forms *l*- α -bromoisovaleric acid, which, when coupled with valine and treated with ammonia, yields *l*-valyl-*d*-valine. This dipeptide yields racemic valine on hydrolysis, and forms also *trans*-valine anhydride. *l*-Valine, when treated with nitrosyl bromide, forms *d*- α -bromoisovaleric acid, from which *d*-valylglycine is obtained on treatment with ammonia and *d*-valine on subsequent hydrolysis. Thus *d*-bromoisovaleric acid yields *l*-valine, and *d*-bromoisovalerylglycine yields *d*-valine. The ester of *d*-bromoisovaleric acid likewise appears to yield *d*-valine.

Both silver oxide and potassium hydroxide, acting on *d*-bromoisovaleric acid, give rise to the same hydroxyisovaleric acid, which is dextrorotatory in alkaline solution. *d*-Bromoisovalerylglycine, treated with silver oxide in a similar manner, yields a highly optically active hydroxy-compound, which, on hydrolysis, gives rise to the same dextrorotatory hydroxyisovaleric acid. This acid is also formed from *l*-valine by the action of nitrous acid, which in this case produces inversion, an observation quite contrary to what has been observed for alanine or aspartic acid.

The α -hydroxyisovaleric acid, prepared by means of silver oxide, has in normal sodium hydroxide, $[\alpha]_D^{20} + 11.8^\circ$; prepared using potassium hydroxide, it has $[\alpha]_D^{20} + 12.0^\circ$; nitrous acid yields the same compound, $[\alpha]_D^{20} + 12.2^\circ$.

d-*a*-Bromoisovalerylchloride, $C_3H_7 \cdot CHBr \cdot COCl$, has b. p. $54-55^\circ/13$ mm. (corr.). *d*-*a*-Bromoisovalerylglycine,

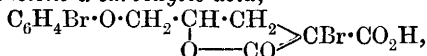


forms large, well-formed, radiating prisms, m. p. $119-120^\circ$ (corr.) to a colourless liquid after sintering at 115° (corr.). It has $[\alpha]_D^{20} + 47.5^\circ$. The *a*-hydroxyisovaleric acid obtained from this by means of silver oxide has $[\alpha]_D^{20} + 11.8^\circ$.

The zinc salt of active *a*-hydroxyisovalerylglycine crystallises in silvery, four-cornered prisms, $[\alpha]_D^{20} + 48.7^\circ$ in water and $+36.1^\circ$ in *N*-hydrochloric acid. E. F. A.

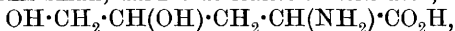
Preparation of α -Amino- γ -dihydroxy-*n*-valeric Acid. EMIL FISCHER and ADOLF KRÄMER (*Ber.*, 1908, 41, 2728—2739).—In view of the general occurrence of serine in the scission products of proteins, and the formation of hydroxyproline in the hydrolysis of gelatin, it is probable that other aliphatic aminohydroxy-acids are formed by the decomposition of proteins. Among these are to be expected derivatives of *n*-valeric and *n*-hexoic acids, owing to their relation to ornithine and lysine. α -Amino- δ -hydroxy-*n*-valeric acid has already been synthesised by Sørensen (*Abstr.*, 1905, i, 749), and converted into *r*-proline by hydrochloric acid. The authors have now made experiments on the synthesis of an aminodihydroxy-acid, which should stand in a similar relation to hydroxyproline, and to this end have employed the method used by Fischer and Blumenthal (*Abstr.*, 1907, i, 191) for the synthesis of α -amino- γ -hydroxybutyric acid.

γ -Chloro- β -hydroxy- α -phenoxypropane, $OPh \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$, prepared by heating epichlorohydrin with phenol under pressure, is a colourless, viscous oil, b. p. $152-153^\circ/12$ mm., with a rancid odour and a bitter taste; when treated with ethyl sodiomalonate and the product hydrolysed, it yields δ -phenoxy- γ -valerolactone- α -carboxylic acid, $OPh \cdot CH_2 \cdot \underset{\text{O}-CO}{\underset{|}{CH}} \cdot CH_2 > CH \cdot CO_2H$, in slender needles, sintering at $93-96^\circ$ (corr.) and evolving gas at a higher temperature. A chloroform solution of this gives with bromine, α -bromo- δ -bromophenoxy- γ -valerolactone- α -carboxylic acid,



forming slender needles, m. p. 157° (corr.), losing carbon dioxide when heated, with the production of α -bromo- δ -bromophenoxy- γ -valerolactone, which crystallises in slender, microscopic needles or rods and sometimes prisms, m. p. 128° (corr.). By the action of ammonia, this is converted into α -amino- δ -bromophenoxy- γ -valerolactone, which forms microscopic, slender, colourless leaflets, m. p. 230° (corr., decomp.); the hydrochloride has m. p. 229° (corr., decomp.), and the hydrobromide has m. p. 235° (corr., decomp.). The aminolactone dissolves in alkalis, forming salts of α -amino- γ -hydroxy- δ -bromophenoxyvaleric acid, of which the silver salt was analysed. When the aminolactone is heated under pressure with concentrated hydrobromic acid and the product hydrolysed (to remove combined

bromine), a mixture of amino-acids is obtained, which can be separated by means of the copper salts. The sparingly soluble product is the copper salt of (*a*)- γ -hydroxyproline (Leuchs, Abstr., 1905, i, 545), and the readily soluble one is probably *copper α -amino- γ -dihydroxy-n-valerate*; it forms small, dark blue leaflets. The acid,



prepared from the copper salt by treatment with hydrogen sulphide, forms bushy needles, m. p. 160—165°. J. C. C.

Action of Certain Oxidising Agents on Thiocyanic Acid.

C. BONGIOVANNI (*Gazzetta*, 1908, 38, ii, 299—301).—The author has shown previously (Abstr., 1907, i, 833; this vol., i, 770) that the product of the reaction between a ferric salt and a thiocyanate is a salt of the composition $\text{Fe}(\text{CNS})_3$, and not a peroxygenated salt, as Tarugi (Abstr., 1905, i, 176) supposes. Further experimental evidence in support of this view is now adduced.

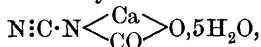
When freshly-prepared nickel or cobalt hydroxide is treated for some days with a 3% thiocyanic acid solution, it is converted into the nickelous or cobaltous salt of the acid without any formation of red hyper-acid occurring. Further, the addition of acid produces no red coloration, as it should do if the reaction resulted in the formation of a colourless salt of the type $\text{Na}_3\text{C}_3\text{N}_3\text{S}_3\text{O}_3$. It is found that the thiocyanic acid is not decomposed, owing to the strong oxidising action of the nickel or cobalt hydroxide, and that the salt formed has no oxidising properties. Molybdenum thiocyanate has a red colour, but is only formed in presence of a reducing agent, which cannot, of course, determine the formation of a hyper-acid. T. H. P.

Supposed Ammoniacal Fermentation of Cyanamide.

CELSEO ULPIANI (*Gazzetta*, 1908, 38, ii, 358—417).—The experiments of Löhnis (Abstr., 1905, ii, 412) and of Löhnis and Sabaschnikoff (this vol., ii, 220) on the formation of ammonia from calcium cyanamide by the action of bacteria led to erroneous conclusions, because (1) "Kalkstickstoff" gradually undergoes change, and only when freshly prepared does it contain one single nitrogenous compound, calcium cyanamide; (2) after sterilisation by heating, solutions of calcium cyanamide contain no trace of the latter, and (3) many amidic substances, besides ammonium salts, yield ammonia when their solutions are distilled with magnesia at the ordinary pressure. From the fact that "Kalkstickstoff" solutions which have not been sterilised by heating do not undergo bacterial decomposition, Löhnis assumes that the action of heat results in the conversion of the asymmetric form of cyanamide, $\text{N}:\text{C}\cdot\text{NH}_2$, into the symmetrical form, $\text{NH}:\text{C}:\text{NH}$, which alone is attackable by bacteria; this assumption the author shows to be superfluous.

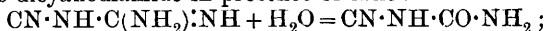
The preparation of pure cyanamide from calcium cyanamide, which is complicated by the tendency of the cyanamide to polymerise into dicyanodiamide, may be affected as follows. One part of "Kalkstickstoff" is thoroughly mixed with four parts of cold water, and

through the filtered solution, cooled with ice, a current of carbon dioxide is passed. The calcium cyanamidocarboxylate,



thus precipitated may be converted into (1) dicyanodiamide by drying at the ordinary temperature or in an oven, $2(\text{C}_2\text{O}_2\text{N}_2\text{Ca}, 5\text{H}_2\text{O}) = 8\text{H}_2\text{O} + 2\text{CaCO}_3 + (\text{CN}_2\text{H}_2)_2$, or (2) cyanamide by triturating with water and subjecting the mass to the prolonged action of carbon dioxide; $\text{C}_2\text{O}_2\text{N}_2\text{Ca} + \text{H}_2\text{O} = \text{CaCO}_3 + \text{CH}_2\text{N}_2$.

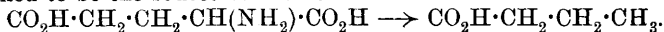
The decomposition of pure cyanamide takes place far more slowly than that of cyanamide accompanied by the secondary products also present in "Kalkstickstoff," and proceeds as well in the presence as in the absence of chloroform, all possibility of bacterial action being thus excluded. The factors which determine the decomposition of cyanamide are calcium, soil, and the secondary products of "Kalkstickstoff," which are capable, in presence of bacteria and of a suitable nutritive medium, of yielding ammonia. These secondary products are found to be: (1) Carbamide, formed by hydrolysis of the cyanamide. (2) Dicyanodiamide, formed by polymerisation. (3) Aminodicyanic acid, $\text{CN}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, separated in the form of its copper salt, $\text{Cu}(\text{C}_2\text{H}_2\text{ON}_3)_2, 4\text{H}_2\text{O}$, which, when treated with hydrogen sulphide, gives, not the free acid, but thiobiuret, $\text{CN}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{H}_2\text{S} = \text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$. Aminodicyanic acid is formed by the hydrolysis of the dicyanodiamide in presence of lime:



if the hydrolysis is effected by means of acid, dicyanodiamidine is formed: $\text{CN}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH} + \text{H}_2\text{O} = \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH}$. (4) Ammeline, formed by the hydrolysis of melamine, $\text{C}_3\text{H}_6\text{N}_6 + \text{H}_2\text{O} = \text{C}_3\text{H}_5\text{ON}_5 + \text{NH}_3$, itself produced by polymerisation of the cyanamide. When free from acids and bases, a solution of cyanamide remains unchanged at the ordinary temperature.

A list of papers previously published on this subject is given, and the results given therein discussed. T. H. P.

The Biochemical Conversion of Glutamic into *n*-Butyric Acid. WALTHER BRASCH and CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 13, 299—304).—*n*-Butyric acid was shown by Neuberg and Rosenberg to account for about one-third of the volatile fatty acids obtained from the putrefaction of caseinogen. As aminobutyric acid has not been definitely proved to be a product of hydrolysis, glutamic acid was assumed to be the source of the volatile acid:



By actual putrefaction experiments with glutamic acid, butyric acid was obtained to the amount of about 58·6% of the theoretically possible quantity. The other acids formed were formic and succinic acids. Glutaric acid was not obtained, nor did the latter acid yield *n*-butyric acid when treated with putrefying organisms. S. B. S.

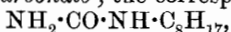
α -Camphoramic Acids. MLLÉ. G. FREYDON (*Ann. Chim. Phys.*, 1908, [viii], 15, 278—288).—The author has shown (this vol., i, 827) that α -aminoethylbenzene condenses with camphoric anhydride to form

two ethylbenzene- α -camphoramic acids, which are enantiomorphously related to one another; in the present paper, the substituted α -camphoramic acids obtained similarly from diethylamine, β -amino-butane, and γ -amino-octane are described, but, although each of the last two bases contains an asymmetric carbon atom, they do not furnish stereoisomeric α -camphoramic acids.

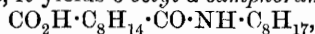
Diethyl- α -camphoramic acid, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NEt}_2$, crystallises in needles, m. p. 169—170°, and has $[\alpha]_D^{20} + 19\cdot29^\circ$ in alcoholic solution.

β -Butyl- α -camphoramic acid, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_4\text{H}_9$, has m. p. 206—208°, and $[\alpha]_D^{20} + 28\cdot80^\circ$ in alcoholic solution.

δ -Amino-octane, $\text{C}_8\text{H}_{17}\cdot\text{CH}(\text{NH}_2)\cdot\text{C}_4\text{H}_9$, prepared by reducing the *oxime*, $\text{C}_8\text{H}_7\cdot\text{C}(\text{NOH})\cdot\text{C}_4\text{H}_9$, b. p. 116—117°/20 mm., by means of sodium and alcohol, has b. p. 64—65°/18 mm., and forms a *hydrochloride*, m. p. 194—195°, and a *carbonate*; the corresponding *carbamide*,



has m. p. 166—168°. When heated for six hours at 120° with camphoric anhydride, it yields *δ -octyl- α -camphoramic acid*,



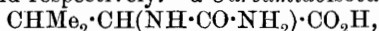
which has m. p. 177—178°, and $[\alpha]_D^{20} + 24\cdot45^\circ$.

M. A. W.

Carbamido-acids. II. and III. FRITZ LIPPICH (*Ber.*, 1908, 41, 2953—2974, 2974—2983. Compare Abstr., 1906, i, 813).—II.—The author finds that the Baumann and Hoppe-Seyler reaction for the preparation of hydantoic acid (this Journ., 1874, 466) is a general reaction of amino-acids, and presents a simple method for the preparation of carbamido-acids. The present communication deals with the α -amino-acids of the glycine series, aspartic and glutamic acids, taurine, and tyrosine. The reaction takes place by heating the amino-acid for six to ten hours with two to three times its weight of carbamide and 200—500 c.c. of baryta water, and is represented by the equation: $\text{NH}_2\cdot\text{R}\cdot\text{CO}_2\text{H} + \text{CO}(\text{NH}_2)_2 = \text{CO}_2\text{H}\cdot\text{R}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{NH}_3$.

The carbamido-acids so obtained give flocculent precipitates with mercuric nitrate in the absence of chlorides or free acid, crystalline compounds with alcoholic mercuric chloride or silver nitrate, do not respond to the biuret test, yield hydantoins, $\text{R}\begin{matrix} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}-\text{NH} \end{matrix}$, by treatment with cold concentrated or with warm dilute mineral acids, and are hydrolysed by hot alkalis or hot concentrated hydrochloric acid, regenerating the amino-acid.

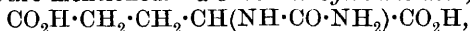
Hydantoic acid (carbamidoacetic acid) has m. p. 163° in a sealed capillary tube (compare Weidel and Roitner, Abstr., 1906, i, 470); the *barium*, *copper*, *lead*, *mercury*, and *silver* salts are described. α -Carbamidopropionic acid and α -carbamidoisobutyric acid are known in the literature as lacturamic acid (Urech, this Journ., 1873, 380) and acetonyluramic acid respectively. α -Carbamidoisovaleric acid,



m. p. 176°, separates from water in tufts of long needles; the *barium*, *mercury*, and *silver* salts are described. α -Carbamidoisohexoic acid (*isobutylhydantoic acid*: compare Pinner and Spilker, Abstr., 1889, 704) yields crystalline *barium*, *lead*, *copper*, *mercury*, and *silver* salts. The

acids prepared from leucine, obtained from different sources, show slight differences in solubility, m. p., and per cent. of nitrogen; these are explained by specific differences in the original leucines.

α -Carbamidosuccinic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$, m. p. 162° , prepared from aspartic acid, separates from dilute alcohol in rhombic plates or prisms; the copper, lead, mercury, silver, and silver hydrogen salts are mentioned. α -Carbamidoglutaric acid,



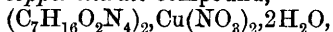
m. p. 150° , crystallises in needles. Taurocarbamic acid, obtained by Salkowsky (this Journ., 1874, 148), and later by Gabriel, is prepared very readily by the author's method. α -Carbamido- β -*p*-hydroxyphenylpropionic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$, m. p. 218° (decomp.), is identical with Jaffe's tyrosinehydantoic acid (*Zeitsch. physiol. Chem.*, 1882, 7, 306). The anhydride, tyrosinehydantoin, has m. p. 242 — 245° (decomp.).

III.—The Baumann and Hoppe-Seyler reaction has been successfully applied to anthranilic, metanilic, sulphanilic, and β -aminobutyric acids and to β -phenylalanine.

Other general methods for the preparation of carbamido-acids are : (a) an amino-acid and a urethane are boiled with aqueous barium hydroxide. Applied to leucine and isoamyl carbamate, a 40% yield of α -carbamidoisohexoic acid is obtained. (b) An amino-acid is boiled with an excess of a concentrated aqueous solution of carbamide. The reaction really occurs between the amino-acid and ammonium cyanate; the continuous removal of the latter destroys the equilibrium of the system carbamide \rightleftharpoons ammonium cyanate (compare Walker and Hambly, *Trans.*, 1895, 67, 746). The method is advantageously used in the case of optically active amino-acids, since the reaction occurs in the absence of acid or alkali. Applied to leucine from different sources, the method yields α -carbamido- α -isohexoic acids, which again show slight differences in physical properties. Similarly, glycine gives ammonium hydantoate, $\text{C}_3\text{H}_5\text{O}_3\text{N}_2(\text{NH}_4)\cdot\text{H}_2\text{O}$; aspartic acid is converted into α -carbamidosuccinic acid, which is isolated as the hydantoin, $\text{C}_5\text{H}_6\text{O}_4\text{N}_2$, m. p. 208° (decomp.), whilst tyrosine very readily yields the ammonium salt of the corresponding carbamido-acid. Leucine and potassium cyanate in boiling aqueous solution give an 83% yield of the carbamido-acid. (c) Prolonged boiling of an aqueous solution of an amino-acid and guanidine carbonate. The method has been used successfully with leucine and with tyrosine. C. S.

Synthesis of α - ω -Aminoguanidinehexoic Acid. FRITZ HECKEL (*Monatsh.*, 1908, 29, 779—785).—Lysine, which was the starting point of this synthesis, was prepared from the sparingly soluble phosphotungstates obtained by fractional precipitation with phosphotungstic acid of the acid-hydrolytic products of casein; the precipitate is dissolved in aqueous ammonia, treated with barium hydroxide, and the mixture of amino-acids separated by means of the picrates, that of arginine being more soluble than lysine picrate. The latter is then converted into the dihydrochloride. This is treated in aqueous solution with silver cyanamide; after separating unchanged

lysine by means of silver nitrate, an uncrystallisable syrup of the *base* was obtained. The *copper nitrate* compound,



forms dark blue, crystalline platelets; the anhydrous salt has m. p. 210° (decomp.). The compound of the nitrate with silver nitrate, $\text{C}_7\text{H}_{16}\text{O}_2\text{N}_4 \cdot \text{AgNO}_3 \cdot \text{HNO}_3$, forms white needles, blackening at 60° , m. p. 125° (decomp.). The nitrate has $[\alpha]_D + 5.37^\circ$. J. C. C.

Reduction of Nitriles in Neutral Solutions. HEINRICH BRUNNER and A. RAPIN (*Chem. Zentr.*, 1908, ii, 676—677; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 455—457).—Reduction is effected most rapidly by using a magnesium-copper couple, the reaction only taking place with Devarda's alloy when warmed. In both cases the action is identical, but the yield is better when Devarda's alloy is used. Hydrogen cyanide gives, on reduction, formaldehyde and ammonia. Acetonitrile gives acetaldehyde, ethylamine, and ammonia. Propionitrile gives propaldehyde, ethylamine, methylethylamine, methylpropylamine, and ammonia. *n*-Butyronitrile yields butaldehyde, butylamine, dibutylamine, and ammonia. Benzonitrile gives benzaldehyde,

benzylamine, dibenzylamine, *diphenylethylenimide*, $\begin{matrix} \text{CHPh} \\ | \\ \text{CHPh} \end{matrix} > \text{NH}$, and

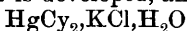
ammonia. *o*-Toluenitrile gives *o*-xylylamine. *m*-Toluenitrile gives *m*-tolualdehyde, *m*-xylylamine, *m*-dixylylamine, and ammonia. *p*-Toluenitrile yields *p*-tolualdehyde, *p*-xylylamine, *p*-dixylylamine, *ditolylethylenimide*, $\begin{matrix} \text{CHMePh} \\ | \\ \text{CHMePh} \end{matrix} > \text{NH}$, and ammonia. *o*-Cyanodiphenylmethane gives

o-aminodiphenylmethane, $\text{CH}_2\text{Ph} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH}_2$. *m*- and *p*-Cyanodiphenylmethane give *m*- and *p*-aminodiphenylmethanes. *Diphenylethylenimide* forms a very sparingly soluble nitrite and nitrate; the hydrochloride is more soluble, and the sulphate very soluble in water.

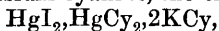
Salts of *ditolylethylenimide* are more readily soluble.

Catalytic Action of Ethylamine.—It is mentioned that a few drops of this substance hastens the reaction between methyl iodide or ethyl iodide and sodium; the behaviour of acetonitrile in this respect (*Abstr.*, 1901, i, 457) is probably due to ethylamine formed by its reduction. J. V. E.

Preparation of Mercuric Cyanide. ERWIN RUPP and S. GOY (*Chem. Zentr.*, 1908, ii, 773; from *Apoth. Zeit.*, 1908, 23, 373—374).—When mercuric chloride and potassium cyanide are brought together in water, considerable heat is developed, and the compound



crystallises on cooling. The same product is obtained from mercuric cyanide and potassium chloride. In a similar manner, the analogous compound is prepared from mercuric cyanide and potassium bromide, but with mercuric cyanide and potassium iodide, as also from mercuric iodide and potassium cyanide, the triple salt,



crystallises in large needles. The preparation of pure mercuric cyanide is effected by treating sodium cyanide with mercuric sulphate

in the presence of water ; the solution becomes very warm, and, on cooling, practically pure mercuric cyanide separates out. J. V. E.

Saturated Compounds of the *cyclo*Hexane Group. NICOLAI D. ZELINSKY (*Ber.*, 1908, 41, 2676—2680).—*cyclo*Hexylpropionic acid is prepared by the following series of reactions. ω -Iodomethylcyclohexane (b. p. 82—83°/10 mm., D_4^{20} 1.5310) is condensed with ethyl sodiomalonate, and the *ethyl hexahydrobenzylmalonate* formed, b. p. 145—155°/12 mm., hydrolysed to *hexahydrobenzylmalonic acid*, m. p. 106.5°. On heating the latter at 170°, it loses carbon dioxide and yields *cyclohexylpropionic acid*, b. p. 143.5°/11 mm., D_4^{20} 0.9966, n_D^{20} 1.4364 ; the *amide* forms thin, soft needles, m. p. 120° (corr.).

[With D. SCHWEDOFF.]—*cyclo*Hexylglycollic acid, prepared by treating the hydrogen sulphite compound of hexahydrobenzaldehyde with potassium cyanide and hydrolysis of the resulting nitrile, crystallises from acetone in silvery scales, m. p. 166°. ω -Nitromethylcyclohexane, prepared by the interaction of ω -iodomethylcyclohexane and silver nitrite, has b. p. 98°/10 mm., D_4^{20} 1.0473, n_D^{20} 1.4688. From its salts, acids precipitate the labile *aci*-form as a heavy, golden-yellow oil, which slowly resumes the stable form.

2-Chloro-1-methylcyclohexane, prepared by the action of fuming hydrochloric acid on 1-methylcyclohexan-2-ol, is stereoisomeric with the compound obtained by the action of phosphorus pentachloride. It has b. p. 91—92°/100 mm., D_4^{20} 0.9699, n_D^{20} 1.4575, and with magnesium and carbon dioxide furnishes *cis*-1-methylcyclohexane-2-carboxylic acid, b. p. 122—123°/10 mm., of which the *amide* forms slender needles, m. p. 151—153°. [The author has overlooked the fact that this *cis*-acid has already been described by Freer and Perkin, jun. (*Trans.*, 1888, 53, 208), and Goodwin and Perkin, jun. (*Trans.*, 1895, 67, 125).]

J. C. C.

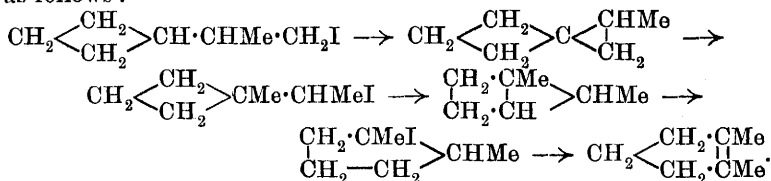
Isomeric Changes in the Transformations of *cyclo*Butyldimethylcarbinol. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 994—1015. Compare this vol., i, 530).—The transformations of *cyclobutyldimethylcarbinol* as yet studied are all abnormal changes, and the preparation from this carbinol of a hydrocarbon of the tetramethylene series has not yet been effected, all the methods employed for this purpose yielding products of isomeric change. This isomeric change of the carbon skeleton of *cyclobutyldimethylcarbinol* either leads exclusively to the formation of *cyclopentane* derivatives or is complicated by the formation of *cyclohexane* derivatives, according to the conditions under which it takes place.

The formation of derivatives of 1:1-dimethylcyclopentane from *cyclobutyldimethylcarbinol* by the action of hydriodic (or hydrobromic) acid

is probably effected by way of the stages : $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe}_2\text{I} \rightarrow$

$\begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix} \text{CMe}_2 \rightarrow \begin{smallmatrix} \text{CH}_2 \cdot \text{CHI} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CMe}_2$; both the bromide and iodide formed, when treated with alcoholic potassium hydroxide, yield 1:1-dimethyl- Δ^2 -cyclopentene, the structure of which is demonstrated

by the formation of $\alpha\alpha$ -dimethylglutaric acid on oxidation. The formation of 1:2-dimethyl- Δ^1 -cyclopentene by the action of hydriodic or hydrobromic acid on cyclobutyldimethylcarbinol probably proceeds as follows:



The structure of this hydrocarbon, which is regarded as identical with Rénard's heptinene and with that obtained by Maquenne from perseitol (see this vol., i, 530), is deduced from the fact that it yields γ -acetobutyric acid on oxidation.

The action of hydrobromic acid on cyclobutyldimethylcarbinol yields: (1) 2-bromo-1:1-dimethylcyclopentane, $\text{C}_7\text{H}_{13}\text{Br}$, b. p. $167^\circ/764$ mm., D_0^{20} 1.2523, n_D^{20} 1.4797, which gives 1:1-dimethyl- Δ^2 -cyclopentene (*vide infra*) on treatment with alcoholic potassium hydroxide; (2) an unstable bromo-derivative, which yields 1:2-dimethyl- Δ^1 -cyclopentene when distilled in a current of steam.

1:1-Dimethyl- Δ^2 -cyclopentene, $\begin{array}{c} \text{CH}=\text{CH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CMe}$, b. p. $78-78.5^\circ/754$ mm., D_0^{20} 0.7580, n_D^{20} 1.4190, has an odour resembling that of naphthalene, gives an intense green coloration when it is heated with concentrated sulphuric acid and alcohol added to the mixture, and yields $\alpha\alpha$ -dimethylglutaric acid when oxidised with nitric acid.

The action of hydriodic acid on cyclobutyldimethylcarbinol also yields two products: (1) 2-iodo-1:1-dimethylcyclopentane, $\text{C}_7\text{H}_{13}\text{I}$, b. p. $98-99^\circ/40$ mm., D_0^{20} 1.5020, n_D^{20} 1.5240, which gives 1:1-dimethyl- Δ^2 -cyclopentene when treated with alcoholic potassium hydroxide; (2) an unstable iodo-derivative, which gives 1:2-dimethyl- Δ^1 -cyclopentene when distilled in a current of steam.

The reduction of 1:1-dimethyl- Δ^2 -cyclopentene by Sabatier's method, and the reduction of 2-iodo-1:1-dimethylcyclopentane by means of a zinc-copper couple, both yield 1:1-dimethylcyclopentane (compare Abstr., 1905, i, 772).

The reduction of 1:1-dimethyl- Δ^2 -cyclopentene by means of sulphuric acid yields 1:2-dimethylcyclopentane, which is also obtained, together with methylcyclohexane, when the reduction is effected by means of hydriodic acid. The reduction of 2-bromo-1:1-dimethylcyclopentane by hydriodic acid also yields a mixture of 1:2-dimethylcyclopentane and methylcyclohexane.

The oxidation of 1:2-dimethyl- Δ^1 -cyclopentene by means of nitric acid gives, as main products, acids such as oxalic and succinic, which are accompanied by a small proportion of a compound, $\text{C}_7\text{H}_{12}\text{O}_4\text{N}_2$, m. p. 202° (decomp.), the nature of which was not determined.

1:2-Dimethylcyclopentane, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CHMe}$, prepared by the reduction of 1:2-dimethyl- Δ^2 -cyclopentene by Sabatier's method, is a liquid, b. p. $92.7-93^\circ/762$ mm., D_0^{20} 0.7534, n_D^{20} 1.4126, which is

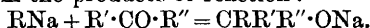
completely dissolved when heated with nitric acid (D 1.52), giving products which are under investigation. T. H. P.

Electro-Syntheses. III. SIMA M. LOSANITSCH (*Ber.*, 1908, 41, 2683—2688. Compare this vol., ii, 32).—In the apparatus previously described, benzene vapour alone, or mixed with other gases, is submitted to the silent electric discharge. Benzene alone gives a solid, insoluble in benzene; a liquid, soluble in ether or benzene; a solid, soluble in benzene, insoluble in ether. All three have the formula $C_{24}H_{25}$, and absorb oxygen. In presence of air, the resulting product is a dark, viscous substance containing nitrogen; with hydrogen, a yellow oil, $C_{28}H_{34}$, is obtained; with methane, a viscous, yellowish-red liquid, $C_{28}H_{36}$; with ethylene, a viscous, brownish-red liquid, $C_{28}H_{34}$; with acetylene, a yellowish-brown mass containing two substances, one soluble, the other insoluble, in benzene. Both have the composition $C_{48}H_{46}$, and absorb oxygen. The product with carbon monoxide is a dark viscous liquid, containing one substance soluble in ether, and a second, insoluble, which absorbs oxygen, yielding substances of the composition $C_{22}H_{22}O_2$ and $C_{20}H_{20}O_3$ respectively, and with carbon disulphide a dark solid, $C_8H_{10}, 6CS_2$.

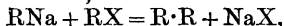
The behaviour of ammonia, mixed with other gases, under the influence of the silent discharge has been examined. With an equal volume of ethylene, it yields a yellow basic oil, $C_{10}H_{21}N_3$, which absorbs oxygen; with acetylene, a dark red basic liquid, $C_{18}H_{30}N_4$, is formed, which absorbs oxygen; with benzene, a reddish-brown oily liquid, $C_{16}H_{24}N_2$, is formed, which absorbs oxygen.

In his answer to Loeb's criticisms (this vol., i, 117), the author states that the analyses of the preceding substances give concordant results only after the preparations have been saturated with oxygen by exposure to the air for about a month. C. S.

Syntheses by means of Sodium and Alkyl Halides. PAUL SCHORIGIN (*Ber.*, 1908, 41, 2711—2717).—In continuation of his former work (*Abstr.*, 1907, i, 753), the author has investigated the action of sodium and alkyl halides on ketones. Here, as before, it is probable that the sodium alkyl is formed as an intermediate product, for the corresponding tertiary alcohols (or their dehydration products) can be isolated from the products of reaction:



In addition to this, several other reactions take place, for example, the formation of hydrocarbons, thus:



and the formation of compounds of sodium with the ketones. The production of compounds of high b. p. also occurs, so that the yield of tertiary alcohols is low, varying from 5% to 10%.

The nature of the blue substances which are formed in the Fittig and Wurtz syntheses is discussed, and the author suggests that they may consist of a blue modification of sodium iodide or possibly salts of sodium quadratoxide.

aa-Diphenyl-δ-methyl-Δ^a-amylene, $CPh_2 \cdot CH \cdot CH_2 \cdot CHMe_2$, prepared by the action of sodium on a mixture of benzophenone and *isoamyl*

bromide in ethereal solution, is a colourless liquid, b. p. $178^{\circ}/16$ mm., D_4^{20} 0.9907, D_4^{25} 0.9725, $n_D^{17.5}$ 1.57463. It is not formed by the action of magnesium *isoamyl* bromide on benzophenone. When ethyl iodide is substituted for *isoamyl* iodide in the above reaction, diphenylethyl-carbinol is produced. The interaction of sodium, acetophenone, and *isoamyl* iodide leads to the formation of *phenylmethylisoamylcarbinol*, a colourless liquid, b. p. $135-137^{\circ}/15$ mm., D_4^{20} 0.9608, D_4^{25} 0.9450, n_D^{19} 1.50596.

When a stream of carbon dioxide is led through a mixture of sodium, benzene, and *isoamyl* bromide, a blue substance (referred to above) is produced, which is indifferent towards carbon dioxide, and, in addition, a small amount of benzoic acid is formed.

By the action of carbon dioxide on a mixture of sodium and *isobutyl* bromide in ethereal solution, a very small quantity of *isovaleric* acid is obtained.

J. C. C.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid. GUSTAV HELLER (*Ber.*, 1908, 41, 2689—2692).—The discovery of a new step in the reduction of *o*-nitromandelonitrile by zinc dust and 33% acetic acid at a low temperature, whereby a double compound of a dihydroxylamino- and a hydroxylamino-derivative is produced (*Abstr.*, 1906, i, 585; Heller and Sourlis, this vol., i, 208), has led the author to submit a number of other *o*-nitro-compounds to this process of reduction. It is remarkable that the presence of an ortho-substituent appears to favour the reduction, for, whilst *o*-nitromandelonitrile is readily reduced at 0° , nitrobenzene, even at the ordinary temperature, is scarcely attacked, yielding only a small amount of phenylhydroxylamine.

o-Nitrobenzaldehyde gives a solution containing *o*-aminobenzaldehyde and anthranil.

[With JULIUS SÖLLING.]—*o*-Nitrobenzoic acid, when reduced with zinc dust and 50% acetic acid in presence of sodium acetate at $35-40^{\circ}$, yields a mixture of benzidine-2 : 2'-dicarboxylic acid and azoxybenzoic acid; the latter is also produced when the reduction is carried on in ammoniacal solution.

J. C. C.

Products of the Nitration of *o*-Chloronitrobenzene. IWAN OSTROMISLENSKY (*J. pr. Chem.*, 1908, [ii], 78, 260—262).—According to Jungfleisch (*Ann. Chim. Phys.*, 1868, [iv], 15, 239), 1-chloro-2 : 4-dinitrobenzene, formed by nitration of chlorobenzene or of *o*-chloronitrobenzene, is obtained in a labile modification, m. p. 43° , and a stable modification, m. p. 50° . As the reduction products of these two modifications were found not to be identical, Beilstein considered (*Handbuch*, 3rd ed., II, 84) the labile form to be 1-chloro-2 : 6-dinitrobenzene, and states that this undergoes intramolecular change into the 1 : 2 : 4-isomeride when brought into contact with a crystal of the latter. As no other such transformation of a benzene derivative is known, the present author undertook a fresh study of the nitration of *o*-chloronitrobenzene, and has found that, whilst the main product is 1-chloro-2 : 4-dinitrobenzene, there is formed also 1-chloro-

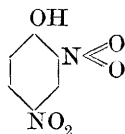
2:6-dinitrobenzene, $C_6H_3Cl(NO_2)_2$, which crystallises in needles, m. p. 38° , yields 2:6-dinitrophenol on treatment with warm concentrated potassium hydroxide, and is not identical with Jungfleisch's labile modification. G. Y.

Structure of Benzene. I. Polymorphic Modifications of Aromatic Compounds. II. Homogeneity of the ortho- and of the meta-Derivatives of Benzene. III. The Two Chemically Isomeric 2:4-Dinitrophenols. IWAN OSTROMISLENSKY (*J. pr. Chem.*, 1908, [ii], 78, 263—279. Compare Abstr., 1907, i, 120, 596; preceding abstract).—It is found that both modifications of 1-chloro-2:4-dinitrobenzene, (1) on reduction with tin and hydrochloric acid or with stannous chloride (Claus and Stiebel, Abstr., 1887, 810), yield two chloronitroanilines, m. p. 117.8° and $101\text{--}102^\circ$; (2) when treated with aniline, form 2:4:2':4'-tetranitrodiphenylamine, m. p. $155\text{--}156^\circ$, and (3) on treatment with cold concentrated potassium hydroxide, are converted into 2:4-dinitrophenol, m. p. 113.2° . The two modifications are, therefore, chemically identical. Attempts to prepare two modifications of either of the chloronitroanilines were unsuccessful. It is suggested that Jungfleisch's chloronitroaniline, m. p. 89° , may be 2-chloro-3-nitroaniline, derived from 1-chloro-2:6-dinitrobenzene.

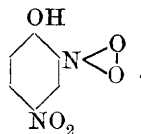
The existence of the liquid modification of 1-chloro-3:4-dinitrobenzene (Laubenheimer, this Journ., 1876, ii, 294) is confirmed. A mixture of the liquid and solid modifications is obtained when the solid modification is recrystallised from ether. The action of ammonia on the ethereal solution of this mixture leads to the formation of a chloronitroaniline, $C_6H_5O_3N_2Cl$, which crystallises in yellow prisms, melts when handled, has a blue fluorescence, is not identical with either of the known 3-chloro-6-nitro- and 4-chloro-6-nitro-anilines, and is probably a derivative of the liquid modification of 1-chloro-3:4-dinitrobenzene. It is considered that these cases of isomerism may depend on a difference in the structure of a nitro-group.

With the object of proving the homogeneity of the ortho- and of the meta-derivatives of benzene, *o*-chloronitro-, *m*-chloronitro-, *o*-dinitro-, 1-chloro-3:4-dinitro-, and 1-chloro-2:4-dinitro-benzene were subjected to fractional separation in the manner employed by Groos for the separation of the rare earths. The number of fractions obtained varied between 60 and 125. All the fractions of each substance were identical as to the m. p. and the crystalline constants.

The two modifications of 2:4-dinitrophenol are discussed, and it is suggested that here, also, the isomerism arises from a difference in the structure of a nitro-group, the two modifications having the constitutions:



and



G. Y.

Transformation of Phenylnitromethane [ω -Nitrotoluene] into Phenyldinitromethane [Di- ω -nitrotoluene]. GIACOMO PONZIO (*Gazzetta*, 1908, 38, ii, 417—420).—*Phenyldibromonitromethane* [*Di- ω -bromo- ω -nitrotoluene*], $\text{CPhBr}_2 \cdot \text{NO}_2$, prepared by the action of an alkaline solution of bromine on the sodium derivative of phenyl-nitromethane, is a colourless oil heavier than water, and has a pungent odour. On treatment with potassium hydroxide and potassium nitrite in alcoholic solution, it is converted into the potassium derivative of phenyldinitromethane; the reaction is possibly expressed by the equation:

$$\text{CPhBr}_2 \cdot \text{NO}_2 + \text{KNO}_2 + 2\text{KOH} = \text{CPhK}(\text{NO}_2)_2 + 2\text{KBr} + \text{H}_2\text{O} + \text{O},$$
 the oxygen oxidising part of the alcohol (compare ter Meer, *Abstr.*, 1876, 30, 185). Phenyldinitromethane is obtained from its potassium derivative by the action of dilute sulphuric acid. T. H. P.

Partial Electrolytic Reaction of Polynitro-compounds in the Presence of Vanadium Compounds. HANS HOFER and FRITZ JAKOB (*Ber.*, 1908, 41, 3187—3199).—The use in electrolytic reactions of inorganic compounds which are themselves reduced at the cathode, modifies the reduction of nitro-compounds. Vanadium, occurring as it does in so many forms of oxidation, gives a potential scale extending from the low oxidation potential of vanadic acid to the high reduction potential of bivalent vanadium salts. It should therefore be suitable for the partial reduction of polynitro-compounds, as it gives the necessary high potential (compare Brand and Zöller, *Abstr.*, 1906, i, 80; 1907, i, 755).

The preliminary work consisted in measuring the potential of the various vanadium compounds, with the result: vanadic acid -1.17 , vanadyl sulphate -0.76 , vanadic sulphate -0.23 volt (e_h for mercurous sulphate electrode -0.69 volt). From the Peters-Nernst formula, the "equilibrium potential" for mixtures of salts can be calculated, and the reduction tension determined.

The cathode was contained in a narrow beaker containing the vanadyl sulphate, sulphuric acid, alcohol, and the polynitro-compound; the lead anode was placed in a porous cell containing normal sulphuric acid at $50-60^\circ$.

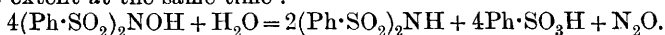
2:4-Dinitrotoluene, with a platinum cathode and potential 0.03 volt, gave chiefly *p*-nitrotoluidine with tolylenediamine and 2:2'-dinitro-4:4'-azoxytoluene. With a potential of $0.10-0.15$ volt, more of the azoxy-compound was produced. Lead and zinc are very much less suitable as cathodes; with copper, no azoxy-derivative was obtained, but some dinitrotoluene was recovered unchanged.

Platinum was used as electrode in the remaining experiments. 2:6-Dinitrotoluene gave 2:2'-dinitro-6:6'-azoxytoluene, 2-nitro-6-toluidine, and a little of the corresponding diamine. With 2:4:6-trinitrotoluene, only 2:6-dinitro-4-aminotoluene was obtained. It sinters at 108° , m. p. 127° , to a viscous liquid, which becomes mobile at 150° (Beilstein gives m. p. 168° : *Abstr.*, 1880, 636); its constitution was determined by preparing 2:6-dinitrotoluene by digesting the diazo-compound with alcohol.

m-Dinitrobenzene gave *m*-nitroaniline, *m*-phenylenediamine, and the

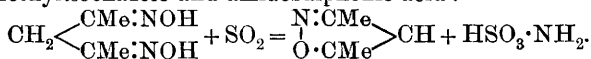
dinitroazoxybenzene; 2:4-dinitrophenol yielded *o*-nitro-*p*-amino-phenol, and picric acid, picramic acid. W. R.

Simple Method of Preparing the Imides of the Aromatic Sulphonic Acids. TAMEMASA HAGA (*J. Coll. Sci. Tōkyō*, 1908, 25, xiii, 1—30).—Very little work has been done hitherto on the aromatic sulphonimides (compare Farbwerke vorm. Meister, Lucius & Brüning, Abstr., 1902, i, 364). It is found that these compounds can be readily obtained by reducing aromatic sulphonylhydroxylamines, preferably with sulphur dioxide, thus: $(\text{Ph}\cdot\text{SO}_2)_2\text{NOH} + \text{SO}_2 + \text{H}_2\text{O} = (\text{Ph}\cdot\text{SO}_2)_2\text{NH} + \text{H}_2\text{SO}_4$. The following reaction also takes place to some extent at the same time:



This reaction proceeds in the absence of sulphur dioxide, for it is found that dibenzenesulphonylhydroxylamine in aqueous alcoholic solutions decomposes mainly according to the last equation, a small quantity of tribenzenesulphonylhydroxylamine also being formed. It is probable that the sulphonate, $(\text{Ph}\cdot\text{SO}_2)_2\text{N}\cdot\text{SO}_3\text{H}$, is formed as an intermediate product during the reduction of dibenzenesulphonylhydroxylamine with sulphur dioxide, but its existence could not be established. Dibenzenesulphonylhydroxylamine, when reduced with sodium amalgam, yields a quantity of benzenesulphinic acid, with liberation of ammonia; the yield of dibenzenesulphonimide is very small.

Krafft and Bourgois (Abstr., 1892, 700) have shown that an oximino-nitrogen atom attached to carbon alone becomes sulphonated when treated with sulphur dioxide, and is at the same time detached from the carbon. When, however, a compound containing two oximino-radicles united to two separate carbon atoms in the molecule is reduced with sulphur dioxide, only one of the nitrogen atoms is separated in the form of amidosulphonic acid; the other nitrogen atom remains united to carbon. For example, when acetylacetonedioxime in aqueous solution is treated with sulphur dioxide, it is converted into 3:5-dimethylisooxazole and amidosulphonic acid:



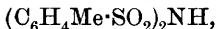
The non-removal of one of the nitrogen atoms is not due to the tendency of forming a ring compound, since acetonylacetonedioxime, when similarly treated, yields amidosulphonic acid and an oily substance, which still contains a nitrogen atom combined with carbon in a form capable of yielding hydroxylamine on hydrolysis.

Diphenylsulphonylhydroxylamine (dibenzenesulphohydroxamic acid) crystallises with $1\text{Et}\cdot\text{OH}$ and sometimes with $2\text{H}_2\text{O}$; the anhydrous substance has m. p. 132° ; Angeli, Angelico, and Scurti give m. p. 126° (Abstr., 1902 i, 765). *Dibenzenesulphonimide*, $(\text{Ph}\cdot\text{SO}_2)_2\text{NH}$, probably crystallises with $1\frac{1}{2}\text{H}_2\text{O}$; it forms thick prisms, and when anhydrous has m. p. 157° ; the barium, $\text{C}_{24}\text{H}_{20}\text{O}_8\text{S}_4\text{N}_2\text{Ba}\cdot 2\text{H}_2\text{O}$, mercuric, $\text{C}_{24}\text{H}_{20}\text{O}_8\text{S}_4\text{N}_2\text{Hg}$,

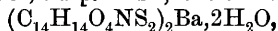
potassium, $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2\text{NK}$, mercurous, silver, sodium, and ammonium salts are described.

Di-o-tolylsulphonylhydroxylamine, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2)_2\text{NOH}$, prepared by

the action of nitrous acid on *o*-toluenesulphinic acid, crystallises with $1\text{H}_2\text{O}$ in small prisms, m. p. $106-107^\circ$; it is converted by an excess of nitrous fumes evolved from arsenious oxide and nitric acid (D 132) into *tri-o-tolylsulphonylhydroxylamine*, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2)_3\text{NO}$, crystallising in small needles, m. p. 129.5° . *Di-o-toluenesulphonimide*,



crystallises with H_2O in thick plates or short prisms; the anhydrous substance sinters at 178° , m. p. 184° ; the *barium* salt,



forms minute needles.

Di-p-toluenesulphonimide, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2)_2\text{NH}$, forms crystals, m. p. $168-170^\circ$. W. H. G.

Oximes and Imides of Benzenedisulphonic Acids. TSUNEO SUZUKI (*J. Coll. Sci. Tōkyō*, 1908, 25, xiv, 1—21).—Mol.-wt. determinations show that the substance described by Autenrieth and Hennings as *m*-benzenedisulphonylhydroxamic acid, $\text{C}_6\text{H}_4\cdot(\text{SO}_2)_2\cdot\text{NOH}$ (compare Abstr., 1902, i, 389), is bimolecular, and probably has the formula $\text{OH}\cdot\text{N} < \begin{smallmatrix} \text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2 \\ \text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2 \end{smallmatrix} > \text{N}\cdot\text{OH}$. It crystallises with alcohol, $[\text{C}_6\text{H}_4(\text{SO}_2)_2\text{NOH}]_2\cdot 1\frac{1}{2}\text{EtOH}$, and with acetone, $[\text{C}_6\text{H}_4(\text{SO}_2)_2\text{NOH}]_2\cdot \frac{2}{3}\text{COMe}_2$.

When reduced by sulphur dioxide, it yields *m*-benzenedisulphonimide, $\text{NH}(\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_2\text{NH}$, crystallising in prisms with $2\text{H}_2\text{O}$; the *potassium* ($1\frac{1}{2}\text{H}_2\text{O}$), *sodium* ($6\text{H}_2\text{O}$), *silver*, and *potassium silver* salts are described.

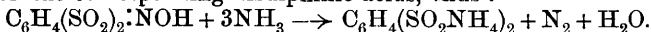
p-Benzenedisulphonehydroxamic acid (*p*-benzenedisulphonylhydroxylamine), $\text{NOH}(\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_2\text{NOH}$, prepared by the action of nitrous acid on *p*-benzenedisulphinic acid, crystallises with $1\frac{1}{2}\text{COMe}_2$ in thin plates, and decomposes suddenly at 210° .

p-Benzenedisulphonimide, $\text{NH}(\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_2\text{NH}$, crystallises with $2\text{H}_2\text{O}$ in colourless prisms; the *sodium*, *potassium*, *silver*, and *mercurous* salts are described.

p-Bromo-*o*-benzenedisulphonylhydroxamic acid, $\text{C}_6\text{H}_3\text{Br}(\text{SO}_2)_2\cdot\text{NOH}$, crystallises in prisms, and decomposes at 82° ; it is reduced by sulphur dioxide to the corresponding *sulphonimide*.

o-Benzenedisulphonylhydroxamic acid crystallises in colourless prisms, and decomposes at 45° ; when reduced, it yields a *sulphonimide*.

The benzenedisulphonehydroxamic acids described above are converted by cold fuming nitric acid into the corresponding sulphonimides, and are decomposed by aqueous ammonia, yielding ammonium salts of the corresponding disulphinic acids, thus:



Ammonium m-benzenedisulphinate, $\text{C}_6\text{H}_4(\text{SO}_2\text{NH}_4)_2\cdot\text{H}_2\text{O}$, crystallises in star-like clusters of elongated tetrahedra, m. p. $113-115^\circ$; the *silver* salt, $\text{C}_6\text{H}_4(\text{SO}_2\text{Ag})_2$, is crystalline. *Ammonium p*-benzenedisulphinate, $\text{C}_6\text{H}_4(\text{SO}_2\text{NH}_4)_2\cdot\text{H}_2\text{O}$, crystallises in slender needles, and decomposes at about 200° ; the *silver* salt is amorphous. W. H. G.

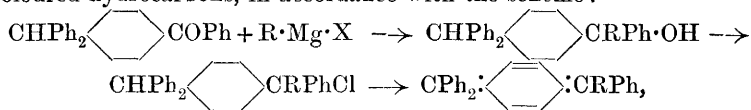
[Coloured and Colourless Triphenylmethyl.] BERNHARD FLÜRSCHHEIM (*Ber.*, 1908, 41, 2746—2747).—Schmidlin's equilibrium

formula, $\text{CPh}_3 \cdot \text{CPh}_3 \rightleftharpoons \text{CPh}_3$, for triphenylmethyl (this vol, i, 623) has been already suggested by the author (Abstr., 1905, i, 614).

C. S.

Preparation of Hydrocarbons of the Quinodimethane Series and their Derivatives. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1908, 41, 2770—2778. Compare Thiele and Balhorn, Abstr., 1904, i, 491; Staudinger, this vol., i, 410, 411).—The tendency of *p*-benzhydryltriphenylmethyl chloride or bromide to acquire an orange colour (this vol., i, 624) is due to the ready elimination of hydrogen halide with the formation of tetraphenylquinodimethane, $\text{CPh}_2 \cdot \langle \text{C}_6\text{H}_4 \rangle : \text{CPh}_2$.

This reaction leads to a convenient method for the preparation of such coloured hydrocarbons, in accordance with the scheme:



where $\text{R} = p\text{-C}_7\text{H}_7$, $\alpha\text{-C}_{10}\text{H}_7$, or $p\text{-C}_6\text{H}_4\text{Br}$.

The elimination of the halogen acid occurs slightly at the ordinary temperature, but is best effected by quinoline in hot xylene in an atmosphere of carbon dioxide.

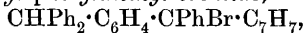
The converse operation, the addition of the halogen acid to the quinodimethane hydrocarbon, proceeds readily, resulting in the formation of the original halide, $\text{CHPh}_2 \langle \text{C}_6\text{H}_4 \rangle \text{CPh}_2\text{Cl}$, in the case of tetraphenylquinodimethane, whilst with unsymmetrical hydrocarbons the addition takes place in two directions, yielding the original halide, $\text{CHPh}_2 \langle \text{C}_6\text{H}_4 \rangle \text{CRPhCl}$, or the isomeride, $\text{CPh}_2\text{Cl} \langle \text{C}_6\text{H}_4 \rangle \text{CHRPh}$; when $\text{R} = \alpha\text{-C}_{10}\text{H}_7$, both additive products are obtained.

Tetraphenylquinodimethane has the properties described by Thiele and Balhorn and by Staudinger (*loc. cit.*). The m. p. in a sealed capillary tube filled with carbon dioxide is 268° (partial decomp.). The addition of hydrogen chloride or bromide is effected by treating a solution of the hydrocarbon in hot benzene with the hydrogen halide, dissolved in glacial acetic acid, in an atmosphere of carbon dioxide. *p*-Benzhydryltriphenylmethyl bromide does not melt at 140° as given (Tschitschibabin, *loc. cit.*), but decomposes gradually above 200° .

The reaction between magnesium α -naphthyl bromide and *p*-benzoyltriphenylmethane in ether leads, after the usual operations, to the formation of a viscous oil, which is converted by hydrogen chloride in glacial acetic acid into *p*-benzhydryldiphenyl- α -naphthylmethyl chloride, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhCl} \cdot \text{C}_{10}\text{H}_7$, m. p. $129\text{--}130^\circ$, from which triphenyl- α -naphthylquinodimethane, $\text{CPh}_2 \cdot \text{C}_6\text{H}_4 : \text{CPh} \cdot \text{C}_{10}\text{H}_7$, is obtained. The hydrocarbon has m. p. $240\text{--}241^\circ$ (in carbon dioxide), forms intensely orange-red crystals, and, like the chloride, dissolves in concentrated sulphuric acid with a green or violet-red colour, according to the concentration of the solution. The dry hydrocarbon is stable in air, but oxidises readily in solution. The addition of hydrogen chloride results mainly in the formation of *p*-phenyl- α -naphthylmethyltri-

phenylmethyl chloride, $\text{CPh}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{C}_{10}\text{H}_7$, m. p. 174—175° (decomp.).

p-Benzhydryldiphenyl-p-tolylmethyl bromide,



m. p. 156—164° (decomp.), is a yellow powder. *Triphenyl-p-tolylquinodimethane*, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_7\text{H}_7$, m. p. 197° (in carbon dioxide), forms orange-red crystals, develops an orange colour in sulphuric acid, and is very sensitive to oxygen or light when incompletely dried. *p-Bromotetraphenylquinodimethane*, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. 257—259° (decomp.) in carbon dioxide, is a brownish-red, crystalline powder; it dissolves in sulphuric acid to an orange-red solution.

C. S.

Sodium Derivative of Fluorene. RUDOLF WEISSGERBER (*Ber.*, 1908, 41, 2913—2916).—The reaction between fluorene and sodium or sodamide occurs at much lower temperatures than with potassium hydroxide (*Abstr.*, 1901, i, 521). When fluorene is heated with the calculated amount of sodamide at 120°, and finally at 150°, or with sodium at 180—200°, the *sodium* derivative, $\text{C}_6\text{H}_4\text{CHNa}$, is obtained as a hard, yellowish-brown, crystalline mass, which is decomposed by water, yielding fluorene and sodium hydroxide; bis-diphenylene-ethane is formed as a by-product. The same reaction occurs when dry ammonia is passed into fused sodium and fluorene at 150°, but in this case the by-products are very small.

C. S.

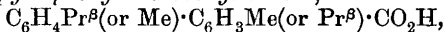
Structure of Retene. PAUL LUX (*Monatsh.*, 1908, 29, 763—777).—It has been stated by Fortner (*Abstr.*, 1904, i, 729) that retene is either 2-methyl-8-propyl- or 8-methyl-2-propyl-phenanthrene. This conclusion is confirmed by the present author, who finds that when retene ketone or retenequinone is fused with potassium hydroxide, a methylisopropylidiphenyl-2-carboxylic acid is formed; the position of the carboxyl group is decided by the fact that the acid cannot be esterified; hence one of the side-chains in retene is in the ortho-position to the $\text{CH}:\text{CH}$ group. At the same time a small amount of an isopropylidiphenyldicarboxylic acid is produced; as this readily yields a neutral ester, it is probably either 4-isopropylidiphenyl-2:3'- or 3-isopropylidiphenyl-2':4'-dicarboxylic acid.

Dimethyl fluorenonedicarboxylate, m. p. 188—189° (corr.) (Bamberger and Hooker, *Abstr.*, 1885, 906, give m. p. 184°), when partly hydrolysed, furnishes an *acid* ester, m. p. 260—261° (corr.), and by partly esterifying the dicarboxylic acid a second *acid* ester, m. p. 275—277° (corr.), is obtained. The *silver* salt of the first ester, on distillation in a vacuum, gives methyl fluorenone-2-carboxylate, m. p. 186—187° (corr.) (Fortner gives 181°), and the *silver* salt of the second ester yields the same compound, so that apparently an interchange of silver and methyl takes place; hence the constitution of the two acid esters cannot be decided from these data, and the intended preparation of fluorenone-1- and -2-carboxylic acids could not be effected.

Retenelycollic acid is produced when retenequinone is boiled with

10% methyl-alcoholic potash; the *methyl* ester has m. p. 112—113° (corr.).

Methylisopropylidiphenyl-2-carboxylic acid,



prepared by fusing a mixture of retenequinone (or retene ketone) and lead peroxide with potassium hydroxide, crystallises in octahedra, m. p. 132—134° (corr.); the *silver* salt was analysed. By treating the acid with thionyl chloride, or by distilling it with lime or its barium salt with sodium methoxide, retene ketone is produced. On distilling the silver salt in a current of hydrogen, the acid passes over.

4-isoPropylidiphenyl-2 : 3'-dicarboxylic acid (or 3-isopropylidiphenyl-2' : 4'-dicarboxylic acid) has m. p. 247—249° (corr.); the *methyl* ester is a white, microcrystalline powder, m. p. 93—95° (corr.); the *silver* salt was analysed. J. C. C.

Nitration of Aniline and its Derivatives. OTTO N. WITT and ERHARD WITTE (*Ber.*, 1908, 41, 3090—3097).—In continuation of the investigation of Witt and Utermann (compare Abstr., 1907, i, 27), the effect produced by using a very large excess of strong mineral acids during the nitration of aniline has been studied. Both *o*- and *p*-nitroaniline, dissolved in concentrated sulphuric acid (monohydrate), are converted by a mixture of concentrated sulphuric and nitric acids (prepared by adding dry potassium nitrate to the sulphuric acid), at temperatures below 5°, into picramide, the yield being between 58% and 67% of the theoretical, and trinitrophenylnitramic acid. Picramide may also be prepared in a similar manner from acetanilide, the yield being 67% of the theoretical.

m-Nitroaniline is converted by the nitric-sulphuric acid mixture into tarry products, but *m*-nitroacetanilide under the same treatment yields 3 : 4-dinitroacetanilide; if the action is allowed to proceed for several days, this substance undergoes further nitration, forming 3 : 4 : 6-trinitroaniline.

The conclusion drawn by Martinsen (Abstr., 1905, ii, 149), that only 67% of the *p*-nitroaniline is converted into picramide because of a simultaneous sulphonation of the *p*-nitroaniline, is thus shown to be incorrect, since the remainder is converted into trinitrophenylnitramic acid; further, picramide is not best prepared by the nitration of aniline in the presence of sulphuric acid, as stated by this author, since the *m*-nitroaniline formed together with the ortho- and para-isomerides would not be converted into picramide.

Picramide acetate, $\text{C}_8\text{H}_4\text{O}_7\text{N}_4$, prepared by adding one drop of concentrated sulphuric acid to a solution of picramide in acetic anhydride, forms colourless needles, which commence to decompose at 207°, m. p. about 230°.

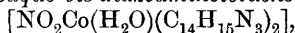
The following additive compounds of picramide (compare Mertens, Abstr., 1878, 725) are prepared by boiling equivalent quantities of the constituents dissolved in acetic acid. *Picramide α -naphthylamine*, $\text{C}_6\text{H}_4\text{O}_6\text{N}_4\cdot\text{C}_{10}\text{H}_9\text{N}$, crystallises in dark red needles, having a metallic lustre; the *β -naphthylamine additive* compound forms red crystals.

Picramide α -naphthol, $\text{C}_6\text{H}_4\text{O}_6\text{N}_4\cdot\text{C}_{10}\text{H}_8\text{O}$, crystallises in scarlet needles; the *β -naphthol isomeride* crystallises in red needles.

reactive, the formation of substances was to be expected, which would ordinarily be produced so rapidly as intermediate products when free nitrous acid is employed as to render their isolation impossible.

p-Toluidine reacts with sodium cobaltinitrite in aqueous-alcoholic solution containing acetic acid, yielding diazoaminotoluene and *p*-toluidine tetranitrito-bis-*p*-toluidinocobaltiate, $[\text{N}_4\text{O}_8\text{Co}(\text{C}_7\text{H}_9\text{N})_2]\text{H}, \text{C}_7\text{H}_9\text{N}$, crystallising in brownish-red, pointed, compact prisms. It is converted by alcoholic ammonia into ammonium cobaltinitrite, with elimination of *p*-toluidine. It is stable at the ordinary temperature, but decomposes when its aqueous solution is boiled, yielding nitroresol with evolution of nitrogen.

In the absence of acetic acid, *p*-toluidine reacts with sodium cobaltinitrite, forming *nitritoquo-bis-diazoaminotoluene cobalt*,



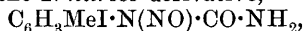
which crystallises in glistening, black, thick, rhombic plates or pyramids. It is very stable towards acids and alkalis, being attacked by these only at high temperatures.

Hydrazine unites with sodium cobaltinitrite in solutions containing small quantities of acetic acid, yielding *sodium diammonium cobaltinitrite*, $[\text{Co}(\text{NO}_2)_6]\text{NaN}_2\text{H}_6$, which forms yellow, rectangular crystals. It decomposes with evolution of two atoms of nitrogen when its aqueous solution is heated, and does not explode when heated alone. It loses $2\text{H}_2\text{O}$ when kept for some time over concentrated sulphuric acid, yielding *sodium nitrosohydrazine cobaltinitrite* (*sodium nitrosohydrazinetetranitritocobaltiate*), $[\text{N}_4\text{O}_5\text{Co}(\text{NO}\cdot\text{NH})_2]\text{Na}$, obtained as glistening, dark purplish-violet crystals.

Hydroxodinitritohydrazine cobalt, $[\text{HO}(\text{N}_2\text{O}_4)\text{Co}(\text{N}_2\text{H}_4)\text{NH}_2]_2$, is formed by the action of an alkaline solution of hydrazine on sodium cobaltinitrite. It forms aggregates of dark purplish-red needles, decomposes violently when heated, and liberates nitrogen when boiled with water.

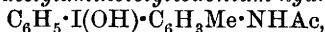
W. H. G.

Derivatives of 2-Iodo-*p*-toluidine and 2-Iodo-4-nitrobenzoic Acid containing Uni- and Ter-valent Iodine. CONRAD WILLGERODT and RUDOLF GARTNER (*Ber.*, 1908, 41, 2813—2826).—I. 2-Iodo-*p*-toluidine and its Derivatives.—2-Iodo-*p*-toluidine, $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NH}_2$, prepared by reducing 2-iodo-*p*-nitrotoluene with ferrous sulphate in ammoniacal solution, crystallises in large, white needles, m. p. 37° ; the *hydrochloride*, long, rather dark needles, the *sulphate*, shining leaflets, the *nitrate*, well-formed rhombs, and the *oxalate*, small rhombs, are described. 2-Iodoaceto-*p*-toluidide, $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NHAc}$, prepared from the base and acetic anhydride, forms white needles, m. p. 130° . 2-Iodo-*p*-tolylcarbamide, $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, forms well-defined rhombs, m. p. 194° ; the *N*-nitroso-derivative,



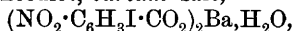
crystallises in yellow, shining needles, which soon turn brown and decompose in the air, m. p. 99° (decomp). Aceto-*p*-toluidide *o*-iodochloride, $\text{C}_6\text{H}_3\text{Me}(\text{ICl}_2)\cdot\text{NHAc}$, prepared by passing chlorine into a glacial acetic acid solution of 2-iodoaceto-*p*-toluidide to which chloroform is added, forms yellow needles, decomposing at 100° . It was not found possible to prepare 2-iodoso- or 2-iodoxy-aceto-*p*-toluidide. An aqueous

solution of *phenyl-p-acetylaminotolyliodonium hydroxide*,

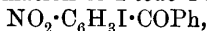


is obtained by the interaction of the iodochloride and mercury diphenyl; the *iodide*, pale yellow needles, m. p. 145°, the *bromide*, white prisms, m. p. 159·5—160°, the *dichromate*, yellow needles, becoming reddish-brown when dry and decomposing at 80°, and the *platinichloride*, small, yellow crystals, m. p. 125° (decomp.), are described.

II. *2-Iodo-4-nitrobenzoic acid and its Derivatives*.—*2-Iodo-4-nitrobenzoic acid*, prepared by oxidising 2-iodo-*p*-nitrotoluene with nitric acid under pressure, forms long, pale yellow needles, m. p. 142°; the *silver* salt, white needles, *barium* salt,

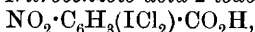


methyl ester, long needles, m. p. 89°, and *ethyl* ester, large, shining prisms, m. p. 44°, are described. *2-Iodo-4-nitrobenzoyl chloride* forms yellow needles, b. p. 196°/18 mm.; the *amide* forms yellow, rhombic crystals, m. p. 205°. The interaction of 2-iodo-4-nitrobenzoyl chloride, benzene, and aluminium chloride in presence of a small quantity of light petroleum leads to the formation of *2-iodo-4-nitrobenzophenone*,



which forms aggregates of small needles, m. p. 90—91°; on heating with hydroxylamine hydrochloride and a little alcohol under pressure, there is formed the *oxime* in small prisms, m. p. 161—161·5°. This, when boiled with 50% aqueous sodium hydroxide, is condensed to

5-nitrophenylindoxazen, $\text{NO}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{CPh} \\ \text{O} \end{smallmatrix}\rangle\text{N}$, which forms small rhombs, m. p. 135°. *4-Nitrobenzoic acid 2-iodochloride*,



prepared by the action of chlorine on a chloroform solution of 2-iodo-4-nitrobenzoic acid, forms yellow needles; on warming with 10% aqueous sodium hydroxide, it is converted into *2-iodoso-4-nitrobenzoic acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{IO})\cdot\text{CO}_2\text{H}$ or $\text{NO}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{CO} \\ \text{I}(\text{OH}) \end{smallmatrix}\rangle\text{O}$, which is also

formed in small amount by treating 2-iodo-4-nitrobenzoic acid with fuming nitric acid. This acid crystallises in white needles, the m. p. of which varies with different preparations; the m. p.'s 190°, 196°, and 201° were observed. It can be crystallised unchanged from formic acid, and, when boiled with aqueous sodium hydroxide and alcohol, is decomposed with formation of iodic, 2-iodo-4-nitrobenzoic, and 4-nitrobenzoic acids. The *sodium* salt, brown leaflets, *silver* salt, small needles, *barium* salt, yellow needles, *copper* salt, bright green, amorphous precipitate, and *lead* salt, yellow powder, are described. *Methyl 2-iodo-4-nitrobenzoate*, when treated with chlorine in chloroform solution, yields *methyl-4-nitrobenzoate-2-iodochloride* as a pale yellow, crystalline precipitate, which, under the action of sodium hydroxide or carbonate, gives 2-iodoso-4-nitrobenzoic acid. The *methyl* ester of 2-iodoso-4-nitrosobenzoic acid was finally prepared by the action of hydrogen chloride on a methyl-alcoholic solution of 2-iodoxy-4-nitrobenzoic acid (see below); it crystallises in small needles, m. p. 180—181°.

2-Iodoxy-4-nitrobenzoic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{IO}_2)\cdot\text{CO}_2\text{H}$, prepared by

oxidising the iodoso-acid with potassium permanganate in sulphuric acid solution, or, better, with sodium hypochlorite, forms white needles, m. p. 205° (mild explosion); the *silver* salt, small needles, which explode on heating, and the *lead* salt, bright yellow powder, are described.

III. *Preparation of 2-Iodo-4-aminobenzoic Acid.*—2-Iodo-4-acetylaminobenzoic acid, prepared by oxidising 2-iodoaceto-*p*-toluidide with potassium permanganate with the addition of magnesium sulphate, forms needles, m. p. 213—214°. On hydrolysis with concentrated hydrochloric acid, it yields 2-iodo-4-aminobenzoic acid, crystallising in needles, m. p. 180° (decomp.), which can also be obtained by reducing 2-iodo-4-nitrobenzoic acid with stannous chloride and hydrochloric acid; the *hydrochloride*, well-formed prisms, the *silver* salt, small, white needles, and the *methyl* ester, needles, m. p. 112°, are described.

J. C. C.

Quaternary Phenacylammonium Salts. EDGAR WEDEKIND (*Ber.*, 1908, 41, 2802—2805).—Quaternary phenacylammonium salts are obtained when one molecule of a tertiary base is allowed to act on one molecule of ω -bromoacetophenone at the ordinary temperature, care being taken that when the bromide is dissolved in the tertiary base the temperature does not exceed 30—40°.

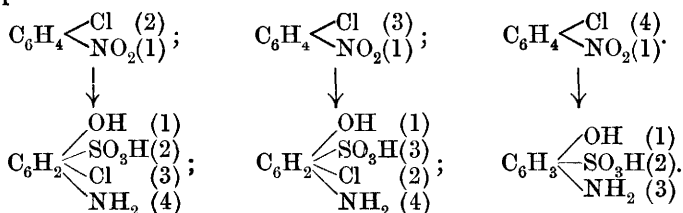
Phenacylphenyldimethylammonium bromide (Abstr., 1902, i, 278) sinters between 100° and 110°, and decomposes between 115° and 125°. By shaking with moist silver oxide, it yields the corresponding *base*, from which the *platinichloride*, small, yellow prisms, and the *aurichloride* were prepared. Phenacylphenylbenzylmethylammonium bromide crystallises in fine, colourless needles, which decompose at 149—150°. Phenacylphenylmethylethylammonium bromide forms crystals, decomposing at 145°; the *d*-bromocamphorsulphonate is not suitable for experiments on resolving the substance, and no resolution could be effected by means of the *d*-camphorsulphonate. The latter forms small, colourless crystals, decomposing at 176°.

J. C. C.

Phenylcarbylamine from Pyrogallol and Nitrobenzene. HEINRICH BRUNNER and V. VUILLEUMIER (*Chem. Zentr.*, 1908, ii, 588; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 436).—When a few drops of nitrobenzene are heated with a small quantity of pyrogallol in an aqueous alkaline solution, the characteristic odour of phenylcarbylamine is strongly developed. In alcoholic solution, the reaction proceeds differently, ammonia being evolved and no formation of carbylamine taking place. If, however, the product is treated with ether and fractionated in a vacuum, carbylamine may be isolated. The use of catechol instead of pyrogallol, leads to the formation of only a trace, whilst with resorcinol, quinol, phloroglucinol, and hydroxyquinol, carbylamine is not produced. *o*-, *m*-, and *p*-Chloro- and bromonitrobenzenes and *o*- and *m*-nitrotoluenes give carbylamine, but nitromethane, nitroethane, nitropropane, dinitrobenzene, *o*- and *p*-nitrophenols, β -naphthol, and *p*-nitrotoluene liberate ammonia, and do not give carbylamine.

J. V. E.

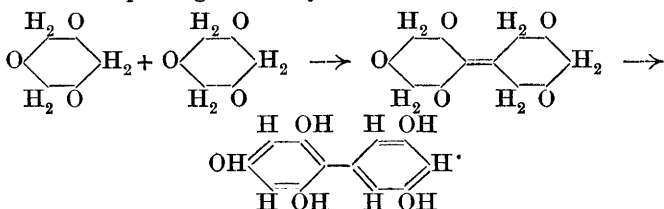
***p*-Aminophenolsulphonic Acid.** HEINRICH BRUNNER and V. VUILLEUMIER (*Chem. Zentr.*, 1908, ii, 587—588; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 434—436).—When nitrobenzene is heated alone with sulphuric acid at 225°, there is obtained a small quantity of *p*-aminophenolsulphonic acid. In a similar manner, when resorcinol, quinol, catechol, pyrogallol, glycerol, mannitol, or dextrose is heated with nitrobenzene and sulphuric acid, 4-aminophenol-2-sulphonic acid is produced. This may be explained by an oxygen atom of the nitrobenzene wandering to the para-position, and then reduction occurring by the sulphur dioxide produced from the sulphuric acid and phenol. This view is supported by the fact that nitrobenzene, when heated with carbon and sulphuric acid, yields *p*-aminophenolsulphonic acid. Wandering of oxygen appears to be a common property of the nitro-group, as is indicated by the following observed changes which take place:



The corresponding bromo-derivatives behave in a similar manner.
J. V. E.

Picrates. OTTO ANSELMINO (*Ber.*, 1908, 41, 2996).—When picric acid or yellow ammonium picrate is dissolved in 10% ammonium hydroxide at 80°, and crystallisation is induced at a higher temperature, a red modification of ammonium picrate, $\text{C}_6\text{H}_6\text{O}_7\text{N}_4$, is obtained, which appears to be stable when kept, but reverts to the yellow form on recrystallisation (compare Suida, this vol., i, 523). C. S.

Phloroglucide. JOSEPH HERZIG and RICHARD KOHN (*Monatsh.*, 1908, 29, 677—688).—The ease with which phloroglucide is formed from 2 mols. of phloroglucinol by loss of 1 mol. of water under the



influence of concentrated sulphuric acid suggests that the glucide is an anhydride of the glucinol. Herzig, however, found (*Abstr.*, 1899, i, 31) that phloroglucide forms a penta-acetyl derivative, and considered that the two phloroglucinol residues must be united by a carbon linking. A further study of phloroglucide has now confirmed the presence of the five hydroxyls, and it is suggested that the

formation of the glucide may take place according to the preceding scheme.

When treated with diazomethane in ethereal solution, or with methyl sulphate and potassium hydroxide, phloroglucide forms a *pentamethyl ether*, $C_{12}H_5(OMe)_5$, which separates from alcohol in white crystals, m. p. 117—120°. The *monomethyl ether*, $C_{12}H_9O_4 \cdot OMe$, prepared by the action of hydrogen chloride on the glucide in methyl-alcoholic solution, has m. p. 222—225°, yields the preceding pentamethyl ether on treatment with diazomethane, and, when boiled with acetic anhydride and sodium acetate, forms a *tetra-acetyl* derivative, $OMe \cdot C_{12}H_5(OAc)_4$, which is obtained in colourless crystals, m. p. 102—105°. The *monoethyl ether*, $C_{12}H_9O_4 \cdot OEt$, has m. p. 165—168°.

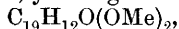
Pentabromophloroglucide, $C_{12}Br_5(OH)_5$, formed by treating phloroglucide with bromine in glacial acetic acid or dichloroethylene solution, separates from ethyl acetate in colourless crystals, m. p. 242—245°, yields with diazomethane a *pentamethyl ether*, $C_{12}Br_5(OMe)_5$, m. p. 200—202°, and, when boiled with acetic anhydride and sodium acetate, forms a *penta-acetyl* derivative, $C_{12}Br_5(OAc)_5$, m. p. 198—202°.

Bromination of pentamethylphloroglucide in dichloroethylene solution leads to the formation of a *tetrabromo-derivative*, $C_{12}HBr_4(OMe)_5$, which separates from ethyl acetate in colourless crystals, m. p. 228—229°.

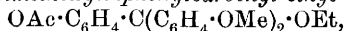
The tautomeric nature of phloroglucide appears in that, whilst the bromine of the pentabromophloroglucide is eliminated quantitatively by means of potassium hydroxide, the brominated ethers are stable under the same conditions. The results of a study of the hydrolysis of the tetra-acetyl derivative of monomethylphloroglucide by means of sulphuric acid show that with very dilute acid the four acetoxy groups are hydrolysed completely, but that with increasing concentration of the acid there appears a condensation in which one acetyl group takes part; this reaction is smoothest when the proportion of acid to water present is 3 : 1.

G. Y.

Aurin Dimethyl Ether. JOSEF HERZIG (*Monatsh.*, 1908, 29, 653—659. Compare Baeyer and Villiger, *Abstr.*, 1902, i, 769).—Aurin is readily methylated by diazomethane, although not by other common methylating agents, yielding *aurin dimethyl ether*,



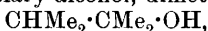
which crystallises in orange needles, m. p. 183—186°, is soluble in aqueous alkalis, and, when recrystallised from dilute hydrochloric acid, is converted into a *hydrate*, $C_{21}H_{18}O_3 \cdot H_2O$; this forms red crystals, m. p. 57—65°, and loses H_2O at 110°, forming again the dimethyl ether, m. p. 183—186°. Whilst aurin is readily acetylated, forming tri-acetylaurincarbinol, aurin dimethyl ether reacts only with difficulty with acetic anhydride alone or in presence of sodium acetate, but, on treatment with the anhydride and sulphuric acid, it yields a white *product*, which, on recrystallisation from alcohol, forms the *acetyl* derivative, *acetoxymethoxytriphenylcarbinyl ether*,



crystallising in white needles, m. p. 136—138°. The *acetyl* derivative of trimethoxytriphenylcarbinol, $C_{19}H_{12}(OMe)_3 \cdot OAc$, prepared by recrystallisation of the white product from methyl alcohol, forms

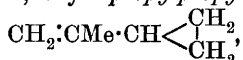
white crystals, m. p. 105—108°. Both acetyl derivatives readily undergo partial hydrolysis, becoming slightly yellow. It is considered that the immediate product of the acetylation is probably the diacetyl derivative, $C_{19}H_{12}(OMe)_2(OAc)_2$. G. Y.

Relative Stability of Cyclic Polycarbon Groups. LOUIS HENRY (*Compt. rend.*, 1908, 147, 557—561).—In an earlier paper (Abstr., 1907, i, 374), the author has shown that, under the action of suitable reagents, the tertiary alcohol, dimethylisopropylcarbinol,



loses H_2O , and the corresponding bromide loses HBr , to form the isomeric ethylenic hydrocarbons, $CMe_2 : CMe_2$ and $CHMe_2 \cdot CMe : CH_2$, in the proportions of 3 : 1. The investigation has been extended to cyclopropyldimethylcarbinol, $OH \cdot CMe_2 \cdot CH < \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}$, and the results

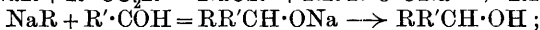
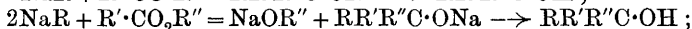
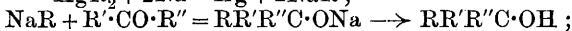
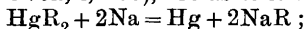
show that the cyclic group, $-CH < \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}$, is much more stable than the isopropyl group, $-CHMe_2$; thus, when cyclopropyldimethylcarbinol is treated with acetic anhydride, or its bromide is heated with potassium acetate, the acetate, $OAc \cdot CMe_2 \cdot CH < \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}$, b. p. 159—160°, is formed; the ethylenic hydrocarbon, α -cyclopropylpropylene, b. p. 77°,



is only formed when the alcohol is heated with phosphoric oxide, or the bromide heated at 170° with powdered potassium hydroxide.

M. A. W.

Sodium-alkyl Compounds and Syntheses made Therewith. PAUL SCHORIGIN (*Ber.*, 1908, 41, 2717—2723).—The author has investigated the action of a mixture of sodium and mercury dialkyls (which probably contains the corresponding sodium dialkyl; compare Buckton, *Annalen*, 1859, 112, 320) on carbon dioxide, ketones, aldehydes, and esters. The reactions, which confirm the author's assumption that sodium alkyls are formed in syntheses by means of sodium and alkyl halides (this vol., i, 866), are as follows:



When an ethereal solution of mercury diethyl and benzophenone is added to ether and sodium, a stream of nitrogen or hydrogen being led through the mixture, a vigorous reaction occurs, with the production of diphenylethylcarbinol in a 40% yield. The $\alpha\alpha$ -diphenylpropylene obtained from this has m. p. 48.5° (Masson, Abstr., 1903, i, 28, gives 51°; the author states that Masson gives 6°, but this is the m. p. ascribed by the latter to diphenylethylene. Klages, Abstr., 1902, i, 668, gives 52°, as do also Hell and Bauer, Abstr., 1904, i, 241). Sodium, mercury diethyl, and methyl benzoate give a 24% yield of

phenyldiethylcarbinol, D_4^0 0.9986, D_4^{19} 0.9836, b. p. $109^\circ/15$ mm. (Kling, Abstr., 1904, i, 2, gives $125-127^\circ/10$ mm.; Grignard, Abstr., 1904, i, 214, gives $101-102^\circ/11$ mm.; Klages, Abstr., 1904, i, 28, gives $107-109^\circ/14$ mm., and $223-224^\circ$ under atmospheric pressure).

By the interaction of sodium, mercury diethyl and benzaldehyde, phenylethylcarbinol is produced in a 15% yield, b. p. $108-109^\circ/17$ mm.; the density varies from D_4^0 1.017 to 1.020, probably owing to the presence of benzyl alcohol (Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 322, gives b. p. 212° , D_4^0 1.016; Errara, Abstr., 1887, 35, gives b. p. $215-217^\circ$). A specimen prepared from magnesium ethyl iodide and benzaldehyde had b. p. $108.5^\circ/17$ mm., and D_4^0 1.012—1.015. The identity of both preparations was proved by oxidising them to propiophenone, which yielded an identical semicarbazone, m. p. 175° (corr.) (Blaise, Abstr., 1902, i, 164, gives 182°).

By passing a current of carbon dioxide into a mixture of sodium and mercury diethyl in ethereal solution, propionic acid is formed; when mercury dimethyl is used, acetic acid is produced, and by employing mercury diisocamyl, isohexic acid results. J. C. C.

Lupeol. N. H. COHEN (*Arch. Pharm.*, 1908, 246, 520—522).—It is pointed out that the data recorded by Klobb (Abstr., 1903, i, 165) for antheasterol and its derivatives are in close agreement with those observed for lupeol and the corresponding derivatives of this (Likiernik, Abstr., 1891, i, 551, 1446; Romburgh, 1904, i, 905, and Cohen, 1907, i, 211), and that, consequently, antheasterol may be lupeol.

The same considerations applied to the phytosterol acetate obtained by Marino Zuco (Abstr., 1890, i, 757) from Dalmatian insect flowers, led to the supposition that this might be a mixture of acetates of amylin and lupeol, but experiments made by the author, whilst giving slightly higher melting points for the various derivatives than those recorded by Marino Zuco, show that the substance contains neither lupeol nor amylin. T. A. H.

Liquid Crystals of Ergosteryl Esters. PAUL GAUBERT (*Compt. Rend.*, 1908, 147, 498—500).—A series of esters prepared from Tanret's ergosterol and fongisterol (this vol., i, 637) has been examined with a view to ascertaining whether, like the esters of the closely-allied cholesterol, they yield liquid crystals (Lehmann, Abstr., 1906, i, 952, and Gaubert, 1907, ii, 939).

Ergosteryl esters present a liquid, anisotropic phase, but this is very difficult to observe in the cases of the acetate and propionate. The crystalline liquids are more viscous than those of the corresponding cholesterol esters. Ergosterol, cholesterol, and fongisterol, when fused with orcinol, each yield a new compound presenting a liquid, crystal phase. Both ergosterol and fongisterol, when allowed to solidify on a glass slip under a cover glass, do not form spherulites with helical scrolls; this serves to distinguish them from cholesterol and phytosterol. T. A. H.

Double Linkings in Phytosterol and Cholesterol. ETTORRE MOLINARI and P. FENAROLI (*Ber.*, 1908, 41, 2785—2788).—Windaus'

supposition, that phytosterol contains two double linkings and cholesterol one (Abstr., 1907, i, 921), is not supported by Willstätter and Mayer (this vol., i, 636) or Langheld (*ibid.*, i, 316), whose results indicate the presence of two double linkings in cholesterol. The authors have therefore examined the behaviour of phytosterol from Calabar beans and nut oil, of cholesterol, and of bombycesterol in chloroform towards ozonised air; in each case an ozonide, $C_{27}H_{46}O_7$, is obtained, the ozone number proving the presence of two double linkings. *Phytosterol ozonide* is a white, crystalline substance, which decomposes at about 100° . The ozone number of ozonides which do not decompose at 50 — 60° can be determined in two to three hours by saturating the unsaturated compound in a volatile solvent with ozonised air and evaporating the solution to constant weight in a vacuum at 60° on the water-bath.

The authors regard the ozone number as the best indication of the number of true double linkings in an organic compound.

C. S.

Phytosterol from Cotton-seed Oil. A. HEIDUSCHKA and H. W. GLOTH (*Pharm. Zentr.-h.*, 1908, 49, 836—837).—The phytosterol of cotton-seed oil, prepared by saponifying the latter and extracting a solution of the soap in water with ether, when acetylated and then brominated as described by Windaus and Hauth (Abstr., 1907, i, 129, 921) does not, like stigmasterol (*loc. cit.*), deposit a crystalline acetate tetrabromide, but only a small quantity of an amorphous *dibromo-acetate* (m. p. 127° , approx.). The substance remaining in solution in the mother liquor is also a *dibromo-derivative*, $C_{29}H_{48}O_2Br_2$, and can be crystallised from alcohol. On treatment with zinc dust and sodium amalgam, it yields the corresponding acetate, and this, on hydrolysis, gives an alcohol, having m. p. 136° , identical with that of the phytosterol started with, so that the latter may be regarded as a single substance.

T. A. H.

Phytosterols from Balata. N. H. COHEN (*Arch. Pharm.*, 1908, 246, 510—514).—A continuation of work on the crystalline constituents of the portion of balata soluble in alcohol (Abstr., 1907, i, 715; compare Tschirch and Schereschewski, Abstr., 1905, i, 713). After the removal of β -amyrin acetate, the residue by crystallisation from alcohol yields two impure products, which can be separated into the same two constituents by the use of (1) mechanical means, followed by (2) fractional crystallisation. The first substance, identical with the β -balalban of Tschirch and Schereschewski (*loc. cit.*), $C_{31}H_{50}O_2$ or $C_{32}H_{52}O_2$, m. p. 111 — 112° , $[\alpha]_D + 57^\circ$ in chloroform, crystallises in colourless leaflets, and, on hydrolysis, furnishes an acid, having the reactions of formic acid, and a crystalline alcohol, m. p. 115 — 116° . The latter yields an *acetate*, m. p. 107 — 107.5° (which does not depress the m. p. of the original ester, so that the latter may be the acetate, not the formate), and a *benzoate*, m. p. 120 — 122.5° , crystallising from alcohol in lustrous leaflets.

The third *constituent*, m. p. 208 — 210° , crystallises in lustrous leaflets, and, on hydrolysis, yields lupeol (compare Abstr., 1907, i,

211) and an acid, having the odour of butyric acid, but the silver salt of which contains silver equivalent to that of silver acetate. *Lupeol butyrate*, m. p. 194—195°, crystallises in small, glancing leaflets, and depresses the melting point of the original ester when mixed with it. Lupeol acetate, m. p. 215°, does not depress the melting point of the original ester when mixed with it, but as the synthetic ester crystallises in needles and the natural one in leaflets, it is suggested that the latter may be the acetate of an isomeride of lupeol, which is converted into lupeol in the process of hydrolysis, or again, the difference in crystalline form may be due to the presence of an impurity in the natural ester, as prepared from balata. T. A. H.

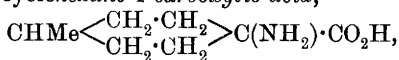
Phytosterols from South African "Rubber." N. H. COHEN (*Arch. Pharm.*, 1908, 246, 515—520).—The coagulated latex from a South African *Euphorbia*, which contained 70·0% of resin and only 5·5% of a caoutchouc-like substance, has been systematically examined with a view to the identification of the resin-alcohols it contains.

An extract of the product in boiling alcohol deposits, first, β -amyirin acetate, and eventually a second substance, $C_{30}H_{50}O$, m. p. 112—116°, $[\alpha]_D + 8\cdot75^\circ$ in chloroform, which crystallises from cold alcohol in thin, lustrous, colourless leaflets, and is not affected by boiling with potassium hydroxide in alcohol. With acetic anhydride, it furnishes an acetate, m. p. 117—122°, $[\alpha]_D + 25^\circ$ in chloroform, but when heated with benzoyl chloride it yields two crystalline products, m. p. 146—152° and m. p. 159—164°, and these, on hydrolysis, furnish substances of m. p. 110·5—111° and 115—117·5° respectively, indicating possibly that the parent alcohol, m. p. 110°, may have been a mixture of two substances.

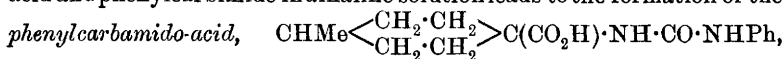
For the detection of lupeol (compare Abstr., 1907, i, 211), the portion of the coagulated latex soluble in alcohol was treated with potassium hydroxide in alcohol, and the neutral hydrolytic product benzoylated. No lupeol benzoate was found, but, in addition to amyirin benzoate, a second substance, $C_{31}H_{44}O$ or $C_{33}H_{48}O_2$, m. p. 193—195°, $[\alpha]_D + 75^\circ$ in chloroform, crystallising from acetone in glancing needles, was obtained. This, on hydrolysis by alkalis in alcohol, gave a product, $C_{24}H_{40}O, H_2O$ or $C_{26}H_{44}O, H_2O$, $[\alpha]_D + 58\cdot6^\circ$, which crystallises in needles from acetone diluted with water, and in some respects resembles Schulze's *ischolesterol* (Abstr., 1898, i, 463), but, whilst the latter, according to Schulze, gives an amorphous acetate, the phytosterol from this *Euphorbia* latex yields a crystalline acetate, $C_{26}H_{42}O_2$ or $C_{28}H_{46}O_2$, m. p. 134—135°. T. A. H.

Hydrocyclic α -Amino-acids. ALADAR SKITA and R. LEVI (*Ber.*, 1908, 41, 2925—2937).—The comparison of aliphatic and alicyclic α -amino-acids is not without interest, since recent researches (Zelinsky and Gutt, this vol., i, 638; Merling, *ibid.*, i, 653) have shown not unimportant differences in the behaviour of aliphatic and alicyclic carboxylic acids. Whilst the esters of *cis*-hydrocyclic δ -amino-acids yield unimolecular anhydrides by treatment with sodium ethoxide (Skita, Abstr., 1907, i, 1040), a similar behaviour of hydrocyclic α -amino-acids is impossible, since the amino- and the carboxyl groups,

being attached to the same carbon atom, must always have the *trans*-configuration. The esters of such amino-acids ought to yield bimolecular anhydrides, cyclic 2:5-diketopiperazines, which should hydrolyse to cyclic dipeptides. Such behaviour has been observed in the cases of 4-amino-1-methylcyclohexane-4-carboxylic acid,



and 2-amino-1-methylcyclohexane-2-carboxylic acid. The first acid is obtained by treating 1-methylcyclohexan-4-one (Wallach, Abstr., 1906, i, 514) with concentrated aqueous potassium cyanide and ammonium chloride, and hydrolysing the resulting amino-nitrile (*hydrochloride*, $\text{C}_8\text{H}_{14}\text{N}_2 \cdot \text{HCl}$, m. p. 191° , decomp.) by ten hours' boiling with concentrated hydrochloric acid; it has m. p. above 300° , forms a blue copper salt, $(\text{C}_8\text{H}_{14}\text{O}_2\text{N})_2\text{Cu} \cdot \text{H}_2\text{O}$, has a neutral reaction, and is tasteless. Nitrous acid converts it into the corresponding *hydroxy-acid*, $\text{C}_8\text{H}_{14}\text{O}_3$, m. p. 115° , whilst the reaction between equal molecular quantities of the acid and phenylcarbimide in alkaline solution leads to the formation of the



m. p. 190° , which, warmed with 25% hydrochloric acid, yields the corresponding cyclic *hydantoin*, $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$, m. p. 184° .

2-Amino-1-methylcyclohexane-2-carboxylic acid is best obtained by heating 1-methylcyclohexan-2-one, dissolved in light petroleum, for two hours at 60° with potassium cyanide, ammonium chloride, and a little water, and hydrolysing the resulting amino-nitrile (the *hydrochloride*, $\text{C}_8\text{H}_{14}\text{N}_2 \cdot \text{HCl}$, decomposes at 182°) by ten hours' heating with concentrated hydrochloric at 100° under pressure; 1-methylcyclohexan-2-one is obtained as a by-product. The acid has a sweet taste, and melts above 300° ; the *naphthylcarbamido-acid*, $\text{C}_{19}\text{H}_{22}\text{O}_3\text{N}_2$, has m. p. 180° (decomp.). In this acid, steric hindrance caused by the neighbouring methyl group (compare also Skita, *loc. cit.*) is observed, not only during the hydrolysis of the preceding amino-nitrile, but also in the esterification of the acid and in the hydrolysis of the resulting ester. Whilst 4-amino-1-methylcyclohexane-4-carboxylic acid is readily esterified by alcoholic hydrogen chloride, the isomeric acid must be saturated in alcoholic solution with hydrogen chloride and heated for ten hours at 100° under pressure. The esters are very reactive liquids, with a basic odour and an alkaline reaction.

Ethyl 4-amino-1-methylcyclohexane-4-carboxylate, $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}$, b. p. $103\text{--}105^\circ/11\text{ mm.}$, $D_{20}^{20} 0.928$, is easily hydrolysed by boiling water, produces local anaesthesia like the esters of δ -amino-acids, and forms a *picrate*, $\text{C}_{16}\text{H}_{22}\text{O}_5\text{N}_4$, m. p. 185° , and a *phenylthiocarbamide*, $\text{C}_{17}\text{H}_{24}\text{O}_2\text{N}_2\text{S}$, m. p. $205\text{--}206^\circ$. By treating the ester in chloroform with *D*-alanyl chloride and hydrolysing the resulting ester, a mixed aliphatic, alicyclic dipeptide is obtained, $\text{C}_{11}\text{H}_{20}\text{O}_3\text{N}_2$, which has m. p. above 300° , and $[\alpha]_D^{20} 22.33^\circ$ in 21% hydrochloric acid. *Ethyl 2-amino-1-methylcyclohexane-2-carboxylate*, b. p. $99\text{--}100^\circ/12\text{ mm.}$, forms a *phenylthiocarbamide*, m. p. $198\text{--}199^\circ$, and requires heating with sodium hydroxide for hydrolysis to occur.

The esters of both acids are converted by twenty to twenty-four hours' heating at 200° into cyclic derivatives of 2:5-diketopiperazine,

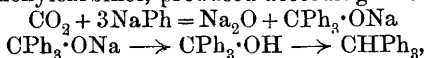
$C_7H_{12} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} C_7H_{12}$, which melt above 300° ; the one derived from 4-amino-1-methylcyclohexane-4-carboxylic acid can be partly hydrolysed by concentrated hydrobromic acid at 100° under pressure, yielding a cyclic *dipeptide*, $CO_2H \cdot C_7H_{12} \cdot NH \cdot CO \cdot C_7H_{12} \cdot NH_2$, which is isolated as the reddish-violet *copper* salt, $(C_{16}H_{27}O_3N_2)_2Cu$.

C. S.

New Synthesis of Aromatic Carboxylic Acids from the Hydrocarbons. PAUL SCHORIGIN (*Ber.*, 1908, 41, 2723—2728).—The author has shown that when carbon dioxide acts on a mixture of sodium and mercury alkyl in ethereal solution, the corresponding aliphatic acid is produced (this vol., i, 882). When dry benzene is used instead of ether in this reaction, in addition to the aliphatic acid, benzoic acid is formed in considerable amount. The reaction is due, as in the previous case, to the intermediate formation of sodium alkyl, for by the interaction of carbon dioxide, sodium, and benzene, or of carbon dioxide, mercury diethyl, and benzene, benzoic acid is not obtained. In this reaction the mercury diethyl can be replaced by zinc diethyl, but the yields are smaller: $C_6H_6 + C_2H_5Na = C_6H_5Na + C_2H_6$; $C_6H_5Na + CO_2 = C_6H_5 \cdot CO_2Na$.

The reaction proceeds also in the case of other aromatic hydrocarbons, but the carboxyl group enters the side-chain; thus toluene gives phenylacetic acid, *m*-xylene gives *m*-tolylacetic acid, and ethylbenzene yields α -phenylpropionic acid. When zinc diethyl is used instead of mercury diethyl, toluene gives *p*-toluic acid in addition to phenylacetic acid.

In addition to these acids, neutral by-products are sometimes formed; thus benzene yields a small amount of triphenylmethane mixed with triphenylcarbinol, produced according to the scheme:



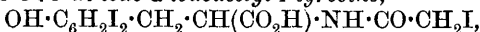
and ethylbenzene gives a *hydrocarbon*, $C_{16}H_{18}$, which is a colourless liquid with a weak, sweetish, aromatic odour, b. p. $161-163^\circ/13$ mm., D_4^{20} 0.9858, D_4^{25} 0.9685, and is very stable towards oxidising agents. Negative results were obtained on applying the reaction to *cyclohexane* and *diisomyl*.

J. C. C.

Derivatives of 3:5-Di-iodo-*l*-tyrosine. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Ber.*, 1908, 41, 2852—2857. Compare this vol., i, 420).—Acid chlorides containing iodine, when coupled with amino-acids, yield compounds which crystallise better than the corresponding bromine derivatives. Their use is attended, however, with the disadvantage that they cause racemisation; thus, *d*-bromopropionic acid and potassium iodide react to give optically inactive iodo-propionic acid.

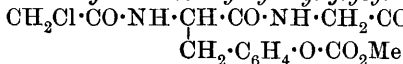
Iodoacetic acid is obtained in colourless plates, m. p. 83° , by the interaction of potassium iodide and monochloroacetic acid. *Iodoacetyl-chloride*, $CH_2I \cdot CO \cdot Cl$, prepared by warming the acid with thionyl-chloride, is a heavy oil, b. p. $49-52^\circ/15$ mm., D^{25} 2.25. At the same time, *iodoacetic anhydride* is formed in transparent, colourless crystals, m. p. 46° .

Ethyl iodoacetyltyrosine forms rhombic, colourless, crystalline plates, m. p. 120° (corr.). By the action of iodine and sodium hydroxide, it is converted into 3:5-di-iodo- α -iodoacetyl-*l*-tyrosine,



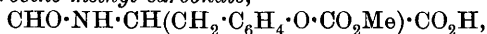
which crystallises in colourless, prismatic needles, becoming brown at 190° (corr.), and m. p. 209° (corr., decomp.). *dl*- α -Iodopropionic acid is conveniently prepared in colourless crystals, m. p. 45.5° (corr.), by the interaction of bromopropionic acid with potassium iodide. *dl*- α -Iodopropionyl chloride, $\text{CH}_3\cdot\text{CH}_2\text{I}\cdot\text{COCl}$, is a faintly-brown, pungent-smelling oil, b. p. 51—53°/13 mm., D_{25}^{25} 1.989. *Ethyl dl*- α -iodopropionyl-*l*-tyrosine crystallises in colourless plates, m. p. 126°, to a colourless oil. *dl*-3:5-Di-iodo- α -iodopropionyl-*l*-tyrosine crystallises in fine needles, m. p. 210.5° (corr., decomp.). *dl*-3:5-Di-iodoalanyl-*l*-tyrosine, obtained by the action of ammonia on the foregoing, has m. p. 217—219°, $[\alpha]_D^{20} + 47.23^\circ$. E. F. A.

The Synthesis of Polypeptides. XXV. Derivatives of Tyrosine and of Aminoacetal. EMIL FISCHER (*Ber.*, 1908, 41, 2860—2875).—In part already published (this vol., i, 544). A tetrapeptide containing tyrosine was obtained by the following method. The hydrochloride of glycyl-*d*-alanine methyl ester, prepared by the action of gaseous hydrogen chloride and dry methyl alcohol on the dipeptide, forms thin, colourless, silky, glistening prisms, m. p. 160—162° (corr.). This salt is decomposed by a little less than the calculated quantity of sodium methoxide, and is immediately used for further synthesis, as it easily passes over into glycine-*d*-alanine anhydride. Coupled with chloroacetyltyrosyl chloride methyl carbonate, it yields methyl chloroacetyl-tyrosyl-glycyl-*d*-alanine ester methyl carbonate,



This ester crystallises in concentrically-arranged, short prisms of a faint yellow colour, which sinter at 200°, m. p. 208° (corr.), to a yellow liquid. On hydrolysis, the tetrapeptide, glycyl-tyrosyl-glycyl-*d*-alanine, is formed. This is an amorphous, faintly yellow powder, which, quickly heated, colours at 180—190° and decomposes at 225° (corr.). It is precipitated like the albumoses by saturated ammonium sulphate in concentrated solution, but not in dilute solution. It is probably a mixture of stereoisomerides.

*Formyl-*l*-tyrosine methyl carbonate,*

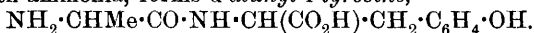


crystallises from water in glistening, large, thin plates, which sinter at 142°, m. p. 147° (corr.), $[\alpha]_D^{20} + 66.7^\circ$. *Formyl-*l*-tyrosine ethyl carbonate* forms centimetre-long, thin, silky, glistening needles, m. p. 177—179° (corr., decomp.), after sintering at 173°. E. F. A.

Synthesis of Polypeptides. XXVIII. Derivatives of Glycine, *d*-Alanine, *l*-Leucine, and *l*-Tyrosine. EMIL ABDERHALDEN and ALFRED HIRSZOWSKI (*Ber.*, 1908, 41, 2840—2851).—The presence of *l*-tyrosine in polypeptides may possibly give them properties similar to those of the albumoses, but, in addition, the position of the tyrosine

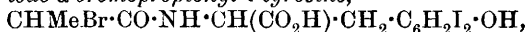
in the molecule must be defined. The polypeptide isolated by Fischer and Abderhalden (Abstr., 1907, i, 737, 990) from silk consists of two molecules of glycine, one of *d*-alanine, and one of *l*-tyrosine; on partial hydrolysis, it yields glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride. Of the eight possible stereoisomeric polypeptides of this composition, but one has been prepared synthetically; this, however, is not precipitated by ammonium sulphate. The polypeptides now described containing tyrosine are likewise not precipitated by ammonium sulphate.

Ethyl *l*-tyrosine and *d*- α -bromopropionyl chloride were coupled by Fischer's method to *ethyl d*- α -bromopropionyl-*l*-tyrosine, which crystallises in bunches of long plates, m. p. 133.5—134.5° (corr.). On hydrolysis, it is converted into *d*- α -bromopropionyl-*l*-tyrosine, which forms crystalline plates pointed at both ends, m. p. 165° (corr.), and, when treated with ammonia, forms *d*-alanyl-*l*-tyrosine,

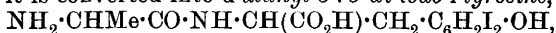


The dipeptide crystallises in large, hexagonal plates, m. p. (frothing) 202° (decomp. at 285°, corr.), and has $[\alpha]_D^{20} + 43.14^\circ$. It is rapidly hydrolysed by the pancreas extract of the dog.

d-3:5-Di-iodo- α -bromopropionyl-*l*-tyrosine,



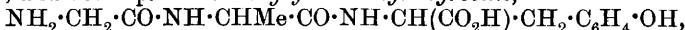
prepared by the action of iodine in chloroform on bromopropionyl-tyrosine ester dissolved in sodium hydroxide, crystallises in rosettes of long, thin needles, m. p. 217° (corr., decomp.). By the action of ammonia, it is converted into *d*-alanyl-3:5-di-iodo-*l*-tyrosine,



which, on heating, becomes yellow at 188°, brown at 205°, and has m. p. 231° (corr., decomp.).

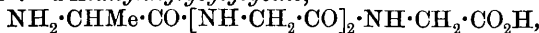
d- α -Bromoisohexoyl-*l*-tyrosine is obtained as an amorphous solid, m. p. 141.5° (corr.), by the interaction of ethyl tyrosine and *d*- α -bromoisohexoyl chloride. *l*-Leucyl-*l*-tyrosine, as prepared by the action of aqueous ammonia on the foregoing, is amorphous. It has m. p. 269° (corr., decomp.), $[\alpha]_D^{20} + 10.37^\circ$, and is hydrolysed by pancreas extract.

Chloroacetyl-d-alanyl-*l*-tyrosine, prepared by coupling chloroacetyl chloride with *d*-alanyl-*l*-tyrosine, is amorphous, sinters at 97°, m. p. 108°, and decomp. 236°. *Glycyl-d*-alanyl-*l*-tyrosine,



is also amorphous; it becomes yellow at 193°, m. p. 208° (corr., decomp.), and has $[\alpha]_D^{20} - 4.83^\circ$. It gives an amorphous precipitate with phosphotungstic acid, but only a slight clouding with ammonium sulphate.

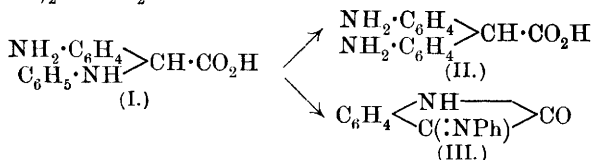
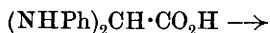
d- α -Bromopropionyl diglycylglycine, prepared from diglycylglycine and *d*-bromopropionyl chloride, crystallises in bunches of slender needles, m. p. 189.5°. *d*-Alanyldiglycylglycine,



crystallises in minute needles, m. p. 253.7° (corr., decomp.), $[\alpha]_D^{20} + 27^\circ$, and is rapidly attacked by pancreas juice. E. F. A.

Action of Dichloroacetic Acid on Aniline and its Homologues. II. IWAN OSTROMISSELSKY (*Ber.*, 1908, 41, 3019—3028. Compare this vol., i, 82).—In the direct action of dichloroacetic acid

with an excess of an arylamine, the various stages appear to be those represented by the following formulæ :



The dianilinoacetic acid is unstable, and undergoes the Hofmann rearrangement either singly or in duplicate. In the former case, the acid formed (I) loses water and yields imesatin (III), and in the latter case the product is 4 : 4'-diaminodiphenylacetic acid (II). The dianilinoacetic acid cannot be isolated from the products of the reaction on account of its instability in the presence of an excess of the amine ; it may, however, be obtained by the action of aniline on glyoxylic acid.

4 : 4'-*Diaminodiphenylacetic acid* crystallises from alcohol, in which imesatin is readily soluble, as soft, dark-coloured flakes, which, when powdered, have a pale canary-yellow colour. It melts at 73—74° to a dark brown oil, resolidifies, and then has m. p. 233—234° (decomp.). The crystals contain 1 mol. of alcohol, which they lose when heated for fifteen hours at 90°. The product is then dark yellow, and decomposes at 215°. The presence of amino-groups is shown by the readiness with which it can yield azo-dyes, and its constitution follows (a) from the fact that, when heated with dilute hydrochloric acid, it loses carbon dioxide and yields 4 : 4'-diaminodiphenylmethane, and (b) from the presence of four active hydrogen atoms (compare Zerewitinoff, this vol., i, 593).

A second modification (β) of the diamino-acid is obtained when ether is added to its alcoholic solution. It is excessively unstable, and, when brought into contact with the air, yields a dark-coloured oil, which is transformed into the original modification (α) when kept over sulphuric acid.

J. J. S.

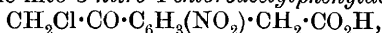
Action of Glyoxylic Acid and of Diacetylglyoxylic Acid on Aniline and its Homologues. IWAN OSTROMISSENSKY (*Ber.*, 1908, 41, 3029—3034).—The product described by Böttinger (*Abstr.*, 1879, 51) as the aniline salt of anilglyoxylic acid is shown to be the unstable dianilinoacetic acid. This follows (a) from the readiness with which aniline is eliminated, yielding anilglyoxylic acid, and (b) from the readiness with which it is transformed into 4 : 4'-diaminodiphenylacetic acid.

Di-p-toluidinoacetic acid, obtained from glyoxylic acid and *p*-toluidine, forms hard, colourless crystals, m. p. about 96°, becoming yellowish-red when kept. *Ethyl di-p-toluidinoacetate*, $\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2\cdot\text{CO}_2\text{Et}$, obtained from the base and ethyl glyoxylate, forms colourless crystals, m. p. 170°, and readily yields *p*-tolyl-*p*-methylimesatin when warmed with mineral acids.

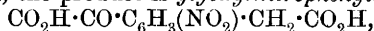
J. J. S.

The Three Chloroacetyl-benzyl Cyanides [Chloroacetyl-phenylacetonitriles] and Their Derivatives. FRANZ KUNCKELL [and F. Flos] (*Ber.*, 1908, 41, 3046—3050. Compare Abstr., 1906, i, 848).—Chloroacetyl chloride reacts much more vigorously with phenylacetonitrile in the presence of aluminium chloride than with acetyl chloride. When the condensation is carried out in the presence of carbon disulphide, the product consists of a mixture of o-, m-, and p-chloroacetylphenylacetonitriles. The para-compound solidifies when the crude product is kept, and is freed from the two isomerides by pressing on porous plate. It crystallises from a mixture of benzene and light petroleum in colourless needles, m. p. 93°. The ortho-compound is obtained as a solid when the oily residue from the para-compound is distilled under diminished pressure and kept for some days, or a large yield can be obtained from the acid liquor formed when the initial condensation product is added to water. It crystallises from water in glistening, snow-white needles, m. p. 47°. m-Chloroacetylphenylacetonitrile is an oil, b. p. 210—215°/25 mm. Each of the three compounds can be oxidised by alkaline hydrogen peroxide to the corresponding phthalic acid.

p-Chloroacetylphenylacetic acid, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by hydrolysing the nitrile with fuming hydrochloric acid at 120—130°, forms yellow needles, m. p. 130°. Fuming nitric acid converts the nitrile into 3-nitro-4-chloroacetylphenylacetic acid,



which crystallises from water in yellow, glistening needles, m. p. 149°. Its solutions in alkalis have a deep blue colour, but turn yellow when boiled. When the nitrile is heated for two hours at 70—100° with fuming nitric acid, the product is glyoxynitrophenylacetic acid,



which crystallises from ether in yellow needles, m. p. 214°. Its solutions in alkali hydroxides are blue, but in ammonia, yellow.

J. J. S.

A Dextrorotatory Resin Acid. W. SCHKATELOFF (*Chem. Zentr.*, 1908, ii, 807; from *Mon. Sci.*, 1908, 22, [ii], 548).—If a solution of crude β -sylvic acid, saturated with sulphur dioxide, is allowed to crystallise, the mother liquor will, after a time, deposit d-sylvic acid as a crystalline powder. When recrystallised from ether, it is obtained in rectangular plates, soluble in alkaline solutions, $[\alpha]_D + 78^\circ$.

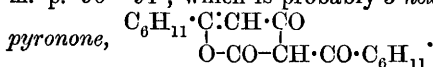
J. V. E.

Esters of Hexahydrobenzoylacetic Acid. ANDRÉ WAHL and A. MEYER (*Bull. Soc. chim.*, 1908, [iv], 3, 957—963).—Most of the results recorded have been published already (Abstr., 1907, i, 765), but detailed accounts of the methods of preparation and new constants for the various substances described are now given.

Ethyl hexahydrobenzoylacetate, $\text{C}_6\text{H}_{11}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b. p. 145—147°/19 mm., D_0^{20} 1.039, D_{18}^{20} 1.025 (compare Zelinsky and Schwedoff, Abstr., 1907, i, 704), is a colourless liquid, insoluble in water, soluble in most organic solvents, and gives a violet coloration with ferric chloride; the copper salt, m. p. 120°, separates from a

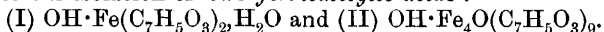
mixture of ether and light petroleum in green leaflets. The methyl ester, b. p. $138^{\circ}/20$ mm., yields a similar copper salt, m. p. $137-138^{\circ}$. With phenylhydrazine, the ethyl ester furnishes 1-phenyl-3-cyclohexyl-5-pyrazolone, $\text{NPh} \begin{array}{c} \text{N}=\text{C}\cdot\text{C}_6\text{H}_{11} \\ \text{CO}\cdot\text{CH}_2 \end{array}$, m. p. 126° , which crystallises in colourless spangles from boiling alcohol. With hydroxylamine, 3-cyclohexylisooxazolone, $\text{C}_6\text{H}_{11}\cdot\text{C} \begin{array}{c} \text{CH}_2\cdot\text{CO} \\ \text{N}-\text{O} \end{array}$, m. p. 42° , is produced. This crystallises in needles, several centimetres in length, and is readily soluble in alcohol or ether, less so in water or light petroleum.

The residues obtained in the preparation of ethyl hexahydrobenzoyl-acetate deposit eventually slender, silky, colourless needles of a substance, m. p. $90-91^{\circ}$, which is probably 3-hexahydrobenzoyl-6-cyclohexyl-2:4-



T. A. H.

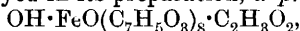
Salicylic Acid-Iron Reaction. KARL HOPFGARTNER (*Monatsh.* 1908, 29, 689—712).—An account is given of the views of various authors as to the cause of the violet coloration produced by adding salicylic acid to solutions of ferric salts. A new study of the reaction has led to the isolation of two *ferrisalicylic acids*:



The compound (I), which is obtained when slightly less than 3 mols. of sodium salicylate are added to 1 mol. of ferric chloride in moderately concentrated aqueous solution at the ordinary temperature, or on prolonged shaking of ferric hydroxide with salicylic acid and water, forms blackish-violet, microscopic needles, is stable at 100° , but decomposes at higher temperatures, and dissolves in water or dilute ferric chloride, forming a violet solution; hence it is to be considered as the cause of the violet coloration of the salicylic acid-iron reaction. The compound (II), formed by the action of sodium salicylate on ferric chloride, in hot concentrated solution, or by heating the acid (I) with salicylic acid at $155-160^{\circ}$, crystallises from ether-alcohol in scarlet, microscopic prisms containing ether, becomes blackish-brown when dried at 100° , decomposes at higher temperatures, and is converted into the acid (I) on prolonged shaking with water, the conversion being accelerated by gentle heating.

Ferric chloride and sodium 5-bromosalicylate form, in the same manner, two *ferribromosalicylic acids*, $\text{OH}\cdot\text{Fe}(\text{C}_7\text{H}_4\text{O}_3\text{Br})_2\cdot\frac{1}{2}\text{H}_2\text{O}$ and $\text{OH}\cdot\text{Fe}_2\text{O}(\text{C}_7\text{H}_4\text{O}_3\text{Br})_3$; *p*-hydroxybenzoic acid, on the other hand, is found to form only one *ferric*-compound, $\text{OH}\cdot\text{Fe}(\text{C}_7\text{H}_5\text{O}_3)_2\cdot\text{H}_2\text{O}$.

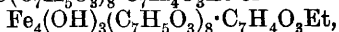
Hantzsch and Desch's ferrisalicylic acid (*Abstr.*, 1902, i, 708), prepared from ferric chloride, sodium acetate, and salicylic acid, is considered to have the constitution $\text{Fe}_4(\text{OH})_3(\text{C}_7\text{H}_5\text{O}_3)_9$, and to be related, therefore, to the ferrisalicylic acid (I). If insufficient salicylic acid is employed in its preparation, a *product*,



is obtained.

In agreement with Hantzsch and Desch's view, that in such

compounds the ferric atom displaces phenolic hydrogen atoms, it is found that, when heated with alcohol, ferrisalicilyc acid (II) forms an *ethyl* ester, $\text{OH} \cdot \text{Fe}_4\text{O}(\text{C}_7\text{H}_5\text{O}_3)_8 \cdot \text{C}_7\text{H}_4\text{O}_3\text{Et}$ or



which points to the presence of a free carboxyl in the original compound. A similar *ethyl* ester, $\text{OH} \cdot \text{Fe}_4\text{O}(\text{C}_7\text{H}_4\text{O}_3\text{Br})_8 \cdot \text{C}_7\text{H}_3\text{O}_3\text{BrEt}$, is obtained from the second ferribromosalicylic acid. Moreover, a crystalline *ferric*-compound, $\text{Fe}(\text{C}_7\text{H}_5\text{O}_2)_3$, is formed by the action of salicylaldehyde and 10% potassium hydroxide on ferric chloride in concentrated solution. On the other hand, the ferrisalicilyc acid (II) is of complex nature, since it does not form silver salicylate with silver nitrate in alcoholic solution, a reaction which takes place directly with sodium salicylate; the salicylic acid in the complex is considered to be "masked" in the same manner as is the sulphuric acid in green chromium sulphate. G. Y.

Methyl-carbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetical Operations. EMIL FISCHER (*Ber.*, 1908, 41, 2875—2891).—Chlorides of phenolcarboxylic acids cannot be prepared by ordinary methods, as the chlorides of phosphorus attack both carbonyl and hydroxyl, and yield products containing phosphorus. When, however, by means of methyl chlorocarbonate, the phenol group is first converted into a methyl-carbonato-compound, a normal acid chloride results, which is available for manifold synthetical purposes. On hydrolysis of the new products with cold alkali hydroxide, the original phenolic group is regenerated (compare this vol., i, 544).

p-Methyl-carbonatobenzoic acid, $\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, is obtained almost quantitatively from *p*-hydroxybenzoic acid and methyl chlorocarbonate. It crystallises in colourless, short needles, m. p. 179° (corr.), and gives no coloration with ferric chloride or with Millon's reagent. *p*-Methyl-carbonatobenzoyl chloride, prepared by the action of phosphorus pentachloride on the above, forms colourless, long needles, m. p. 82—83° (corr.), and distils without decomposition by 10—15 mm.

It combines with glycine ester to *ethyl p*-methyl-carbonatobenzoyl-glycine, $\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which crystallises in needles, m. p. 63° (corr.), and, when hydrolysed with sodium hydroxide, yields *p*-hydroxyhippuric acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. This separates in colourless, thin, glistening prisms, m. p. 240° (corr.), to a yellow liquid, and subsequently decomposes; it gives a brown coloration with ferric chloride, and is coloured red by Millon's reagent. It is, perhaps, identical with an acid, m. p. 228°, isolated from pathological urine.

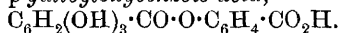
3 : 4-Dimethyl-carbonatobenzoic acid, $(\text{CO}_2\text{Me} \cdot \text{O})_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$, is obtained in colourless needles, m. p. 165—166°. 3 : 4-Dimethyl-carbonatobenzoyl chloride crystallises in bunches of needles, m. p. 118° (corr.), which sinter 2° or 3° lower.

3 : 4 : 5-Trimethyl-carbonatobenzoic acid, $(\text{CO}_2\text{Me} \cdot \text{O})_3 \cdot \text{C}_6\text{H}_2 \cdot \text{CO}_2\text{H}$, is obtained by the interaction of gallic acid and methyl chlorocarbonate in an atmosphere of hydrogen in a special apparatus. It forms colourless, thin prisms, which sinter about 130°, m. p. 136—141°. It forms a

crystalline, colourless *bromo*-derivative and a soluble *pyridine* salt, which is decomposed by excess of the base and liberates carbon dioxide. It is completely hydrolysed by acids, alkaline hydroxides, or ammonia to gallic acid; the methylcarbonato-group is eliminated as methyl carbamate by ammonia. Cautious partial hydrolysis in an atmosphere of hydrogen yields *hydroxydimethylcarbonatobenzoic acid*, $(\text{CO}_2\text{Me}\cdot\text{O})_2\cdot\text{C}_6\text{H}_2(\text{OH})\cdot\text{CO}_2\text{H}$. This has m. p. 160° (corr.), and gives a dark green coloration with ferric chloride.

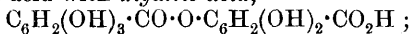
3:4:5-*Trimethylcarbonatobenzoic acid* crystallises in colourless, glistening plates, m. p. $96\text{--}97^\circ$ (corr.).

3:4:5-*Trimethylcarbonatobenzoyl chloride* forms long needles, m. p. 86° (corr.) to a clear liquid; it reacts with dimethylaniline and also with aniline, forming in the latter case *trimethylcarbonatobenzoic anilide*, which crystallises in needles pointed at both ends, m. p. $175\text{--}176^\circ$ (corr.) to a clear liquid. *p*-*Trimethylcarbonatobenzoyloxybenzoic acid*, $(\text{CO}_2\text{Me}\cdot\text{O})_3\cdot\text{C}_6\text{H}_2\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is obtained as an oil, which solidifies to thin prisms aggregated in bunches, m. p. 165° (corr.). On hydrolysis, for which purpose the crude product may be used with advantage, it yields *p*-*galloyloxybenzoic acid*,



This is obtained as a sandy, crystalline powder, consisting of obliquely cut plates, m. p. 260° (corr., decomp.). It gives similar colorations to gallic acid with ferric chloride or potassium cyanide.

On coupling trimethylcarbonatobenzoyl chloride with hydroxydimethylcarbonatobenzoic acid in alkaline solution, an amorphous mass was obtained, which contained much *pentamethylcarbonatobenzoyloxybenzoic acid*, and, on hydrolysis, yielded what appeared to be a mixture of gallic acid with *digallic acid*,



it formed short prisms or needles, m. p. $275\text{--}280^\circ$ (decomp.).

E. F. A.

Nitration. IV. Nitration of *N*-Acyl Compounds of Aniline derived from Certain Polybasic, Aliphatic, and Aromatic Acids. J. BISHOP TINGLE and F. C. BLANCK (*J. Amer. Chem. Soc.*, 1908, 30, 1587—1599. Compare this vol., i, 778).—A study has been made of the nitration of anilides of various di- and tri-basic acids, the experiments being carried out under the same general conditions as those described previously.

Oxanilic acid yields the *p*-nitro-derivative, both on direct nitration and also on nitration in presence of oxalic acid. Oxanilide gives the *m*-nitro-derivative in presence of sulphuric acid, and the *p*-dinitro-derivative in presence of acetic acid. Succinanilic acid yields the *m*-nitro-derivative in presence of sulphuric acid, and the *p*-nitro-derivative in presence of oxalic acid. By direct nitration of succinanil, a mixture of ortho- and para-derivatives is obtained, but in presence of sulphuric or oxalic acid, the *p*-nitro-derivative is formed. On direct nitration, succinanilide yields the *s*-*p*-dinitro-derivative, and tartranilide gives the *p*-nitro-derivative.

Phthalanil, both on direct nitration and in presence of oxalic acid,

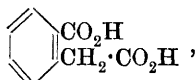
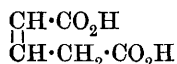
yields the *p*-nitro-derivative. Citranilide, on direct nitration, gives a trinitro-derivative.

The experiments so far carried out have led to the following generalisations. Direct nitration yields either the para-derivative or a mixture of ortho- and para-derivatives, except in the case of benzanilide, which gives some meta-derivative. Nitration in presence of sulphuric acid gives chiefly, or exclusively, the *m*-nitro-derivative. Oxalic acid does not affect the course of the nitration, and this is probably due to its small solubility in nitric acid.

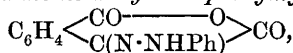
The possible modes of representing the disubstituted benzenes are discussed, and it is stated that the authors' results are fully and satisfactorily accounted for by Barlow and Pope's formula for benzene (*Trans.*, 1906, 89, 1697).

A discussion is also given of the mechanism of substitution, and leads to the conclusion that substitution must be regarded as essentially an additive phenomenon (compare Armstrong, *Proc.*, 1891, 7, 89). E. G.

Homophthalic Esters, Oxymethylenhomophthalic Esters, and their *iso*Coumarin and *iso*Carbostyryl Derivatives. WALTHER DIECKMANN and WILHELM MEISER (*Ber.*, 1908, 41, 3253—3269).—The structural analogy existing between homophthalic and glutaconic acids :

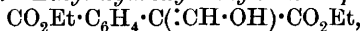


suggested an investigation into the properties of homophthalic acid with a view to comparing them with those of the other acid. The methylene group, which is very reactive in glutaconic acid (compare Henrich, *Abstr.*, 1902, i, 422), is markedly less reactive in the aromatic derivative. Sodium ethoxide and benzyl bromide are without action on ethyl homophthalate, as is also diazobenzene chloride. With homophthalic anhydride, however, the diazo-salt forms *benzeneazohomophthalic anhydride* [*phthalonic anhydride phenylhydrazone*],



which crystallises from benzene in long, reddish-yellow needles, m. p. 199°. It is hydrolysed by acids or alkalis to 3-phenylphthalazone-1-carboxylic acid. This marked difference between the acid and its anhydride is ascribed to the formation of the ring. Ethyl homophthalate yields naphthalene derivatives on condensation with sodium ethoxide (compare Pechmann, Bauer, and Obermiller, *Abstr.*, 1904, i, 592).

A comparison of the hydroxymethylene derivatives of the two acids shows a strong resemblance between them (compare Pechmann, *Abstr.*, 1893, i, 401), but the condensation proceeds more easily with the benzene compound. *Ethyl hydroxymethylenhomophthalate*,



obtained in good yield from ethyl formate, ethyl homophthalate, and sodium as a colourless, viscid oil, is converted by heating at 100° in two hours into *ethyl isocoumarin-4-carboxylate*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \text{---} \text{O} \\ \diagdown \quad \diagup \\ \text{C}(\text{CO}_2\text{Et}) \end{array} \text{CH},$

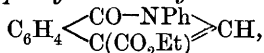
which crystallises in colourless needles from alcohol, m. p. 67—68°. Methyl-alcoholic potassium hydroxide hydrolyses it to formic and homophthalic acids. The corresponding *methyl ester*, $C_{11}H_8O_4$, forms colourless needles, m. p. 97°. *isocoumarin-4-carboxylic acid*, $C_{10}H_6O_4$, obtained by warming the ester with concentrated hydrochloric acid, forms slender needles, m. p. 244°, and yields *isocoumarin* on heating with 50% sulphuric acid. This acid is similar to the corresponding 3-carboxylic acid (Bamberger and Frew, Abstr., 1894, i, 192), but its ready conversion into formic and homophthalic acids by alkali is in marked contrast with the isomeric acid.

Ethyl isocarbostyryl-4-carboxylate, $C_6H_4 \begin{smallmatrix} \text{CO-NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{CH}$, prepared either from ethyl hydroxymethylenehomophthalate or from ethyl *isocoumarincarboxylate* by the action of ammonia, crystallises in colourless, slender needles, m. p. 227°. By shaking *isocoumarin-4-carboxylic acid* with ammonia and acidifying, *isocarbostyryl-4-carboxylic acid*, $C_{10}H_7O_3N$, is obtained as needles from glacial acetic acid, m. p. 290° (decomp.). If, however, the ammonia is warmed, *isocarbostyryl* is precipitated. *Ethyl 2-methylisocarbostyryl-4-carboxylate*, $C_6H_4 \begin{smallmatrix} \text{CO-NMe} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{CH}$, obtained from methylamine, crystallises from methyl alcohol in glistening needles, m. p. 98°. The corresponding acid, $C_{11}H_9O_3N$, forms small needles, m. p. 262°.

Aniline and ethyl hydroxymethylenehomophthalate form *ethyl anilinomethylenehomophthalate*,



which crystallises in needles, m. p. 102.5°. By heating them together for a long time, *ethyl 2-phenylisocarbostyryl-4-carboxylate*,



is produced; it forms crystals, m. p. 118°. The parent *acid*, $C_{16}H_{11}O_3N$, forms microscopic needles, m. p. 267°.

Experiments were carried out in the hope that stereoisomerides of hydroxymethylenehomophthalic ester would exist, but only with partial success. By the action of *m*-nitrobenzoyl chloride on the sodium salt of methyl hydroxymethylenehomophthalate, two isomeric *m*-nitrobenzoates were obtained. The α -*compound*, $C_{19}H_{15}O_8N$, obtained when the dry sodium salt in ether is treated with *m*-nitrobenzoyl chloride, crystallises from methyl alcohol in prisms, m. p. 139°. The β -*compound*, formed when the aqueous solution is treated with the chloride, crystallises in slender needles, m. p. 98°, but experiments to transform the one isomeride into the other were without the desired result.

When ethyl hydroxymethylenehomophthalate is coupled with diazobenzene chloride, ring formation takes place, *ethyl 3-phenylphthalazone-1-carboxylate*, $C_6H_4 \begin{smallmatrix} \text{CO-NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{N}$, being produced, which forms prisms, m. p. 115°.

W. R.

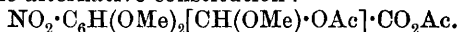
Methylenedioxyhydratropic Acid. Tiffeneau's Migration of the Phenyl Group. PAUL HOERING (*Ber.*, 1908, 41, 3081—3084. Compare this vol., i, 497).—From the investigations of Tiffeneau, it

was to be expected that derivatives of hydratropic acid could be prepared from α -ethoxy- α -phenylethylene, α -ethoxyanethole, and α -ethoxyisosafole by acting on them with mercuric oxide and iodine in alcoholic solution and treating the ethoxyiodohydrins so formed with alcoholic potassium hydroxide. The experiments carried out with the first two substances were unsuccessful, but methylenedioxyhydratropic acid was prepared from isosafole.

α -Methoxyisosafole is converted by mercuric oxide and iodine in methyl alcohol into the *iodohydrin*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}(\text{OMe})_2\cdot\text{CHMeI}$, which, however, could not be isolated, since it readily parts with iodine. The iodohydrin is converted by an alcoholic solution of potassium hydroxide into methylenedioxyhydratropic acid, $\text{C}_{10}\text{H}_{10}\text{O}_4$, m. p. $78\cdot5$ — 79° , identical with the acid obtained by Bougault from methylenedioxyhydratropaldehyde (Abstr., 1900, i, 495). α -Ethoxyisosafole, when similarly treated, yields the same acid. W. H. G.

Nitration of Opianic Esters and Derivatives of Nitro-opianic Acid. RUDOLF WEGSCHEIDER, NORL. MÜLLER, and EDUARD CHIARI (*Monatsh.*, 1908, 29, 713—747).—Whilst ψ -methyl nitro-opianate, which is remarkable in having a m. p. ($181\cdot5$ — $182\cdot5^\circ$; Abstr., 1904, i, 59) higher than that of the corresponding acid, is readily prepared, the methyl ester is formed only with difficulty, and only one ethyl ester, of uncertain constitution, has as yet been obtained. It was therefore of interest to study the formation of nitro-opianates by the nitration of the esters of opianic acid by means of various nitrating agents. It is found that ψ -methyl nitro-opianate is obtained by nitration of either methyl opianate, the normal ester undergoing transformation during the reaction. Since the nitration of ψ -ethyl opianate leads similarly to the formation of the known ethyl nitro-opianate, this is probably the ψ -ester.

The action of acetyl nitrate on ψ -methyl opianate leads directly to the formation of ψ -methyl nitro-opianate, but on methyl opianate, to that of a *diacetate*, $\text{NO}_2\cdot\text{C}_6\text{H}(\text{OMe})_2(\text{CO}_2\text{Me})\cdot\text{CH}(\text{OAc})_2$, which separates from benzene in crystals, m. p. 159 — 160° , yields nitro-opianic acid on hydrolysis, is stable towards boiling methyl alcohol, and is hydrolysed only slowly by boiling water or hot $0\cdot1N$ potassium hydroxide; when heated with sodium methoxide or with hydrogen chloride in methyl-alcoholic solution, it is converted into ψ -methyl nitro-opianate, and, on treatment with concentrated aqueous ammonia, yields nitro-opianamide. These properties show that the diacetate cannot have the alternative constitution:



The *diacetate*, $\text{C}_{16}\text{H}_{19}\text{O}_{10}\text{N}$, formed by the action of acetyl nitrate, or of nitric acid and acetic anhydride in glacial acetic acid solution, on ethyl opianate, crystallises in colourless plates, m. p. 100 — 101° , and has properties resembling those of the preceding diacetate. When treated with methyl alcohol, the crude product from the action of acetyl nitrate on ethyl opianate is converted into ψ -methyl nitro-opianate.

Energetic nitration of the normal opianates by means of fuming nitric acid alone or in concentrated sulphuric acid solution leads to the

formation of 4:5(or 5:6)-dinitro-2:3-dimethoxybenzoates (Wegscheider and Strauch, this vol., i, 794). *Ethyl dinitro-2:3-dimethoxybenzoate*, $C_{11}H_{12}O_8N_2$, crystallises from alcohol in white needles, m. p. $83.5-84.5^\circ$, and, on hydrolysis, yields an acid, m. p. $176-179^\circ$.

Nitro-opianic acid is now found to have the m. p. $169-170^\circ$ (corr.). The *sodium* salt, $C_{10}H_8O_7NNa \cdot 4H_2O$, loses $4H_2O$ at 100° . The *anhydride*, $C_{20}H_{16}O_{13}N_2$, is formed together with the two methyl esters by the action of diazomethane on nitro-opianic acid; it separates from glacial acetic acid in crystals, m. p. $231-233^\circ$. The action of concentrated aqueous ammonia on nitro-opianic acid at the laboratory temperature leads to the formation of a *product*, decomp. 320° , which is probably the imide, $CO \langle \begin{smallmatrix} N(C_8H_7O_4) \\ NH \end{smallmatrix} \rangle C:C \langle \begin{smallmatrix} N(C_8H_7O_4) \\ NH \end{smallmatrix} \rangle CO$, and may be identical with the substance described by Bistrzycki and Fink (Abstr., 1898, i, 427) as bisnitro-*m*-opindolone. G. Y.

Constitution of Tannin. N. MAXIMILIAN NIERENSTEIN (*Ber.*, 1908, 41, 3015—3019. Compare Abstr., 1905, 914; 1907, i, 331; this vol., i, 90).—When an aqueous solution of tannin is boiled with hydrogen peroxide, both ellagic acid and *pentahydroxydiphenylmethylolide-carboxylic acid* (*luteo-acid*), $CO_2H \cdot \begin{smallmatrix} C_6H(OH)_3 \cdot CO \\ C_6H(OH)_2 \cdot O \end{smallmatrix}$, are formed.

The latter is deposited, when the mother liquor from the ellagic acid is concentrated, as reddish-brown needles, which can be crystallised from pyridine and acetic acid. It turns brown at 305° , and decomposes at $338-342^\circ$. It dissolves in alkali hydroxide or hydrogen carbonate solutions, and also in concentrated sulphuric acid, and, when warmed with 10% sodium carbonate solution, yields its anhydride, ellagic acid.

The carboxyl group is eliminated when a pyridine solution of the luteo-acid is mixed with concentrated hydriodic acid and exposed to daylight for five days, pentahydroxydiphenylmethylolide being obtained.

Ellagic acid can be obtained by oxidising tetra-acetyldigallide with hydrogen peroxide, the reaction consisting in the elimination of two atoms of hydrogen and the union of the two benzene nuclei.

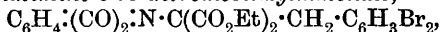
Tetra-acetyldigallide, $C_6H_2(OAc)_2 \langle \begin{smallmatrix} CO \cdot O \\ O \cdot CO \end{smallmatrix} \rangle C_6H_2(OAc)_2$, crystallises from alcohol and acetic acid in needles, m. p. $130-132^\circ$.

J. J. S.

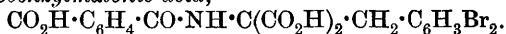
Halogen Amino-acids: 3:5-Dibromophenylalanine. HENRY L. WHEELER and SAMUEL H. CLAPP (*Amer. Chem. J.*, 1908, 40, 337—348).—The authors propose to study the halogen derivatives of phenylalanine with the view of deciding the question of the position of halogens in proteins, and in the present paper the preparation of the 3:5-dibromo-derivatives is described.

3:5-Dibromobenzyl bromide, $C_6H_3Br_2 \cdot CH_2Br$, prepared by adding bromine to 3:5-dibromotoluene at $170-180^\circ$, crystallises in prisms or long, felted needles, m. p. $95-96^\circ$, b. p. $173^\circ/19$ mm. and $169^\circ/15$ mm. It attacks the eyes violently. When heated with ethyl-sodio-

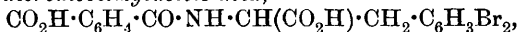
phthaliminomalonate (compare Sørensen, Abstr., 1903, i, 833), it yields *ethyl phthalimino-3:5-dibromobenzylmalonate*,



which forms aggregates of prisms and plates, m. p. 144—145°, and is hydrolysed by aqueous sodium hydroxide to *phthalamino-3:5-dibromobenzylmalonic acid*,



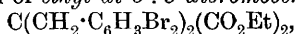
This forms snow-white, prismatic crystals, which lose carbon dioxide at 110°, or on boiling with water, with the production of *phthal-amino-3:5-dibromobenzylacetic acid*,



crystallising in clusters of minute prisms, m. p. 174° (decomp.).

When boiled with 20% hydrochloric acid, this substance is resolved into phthalic acid and 92% of the theoretical quantity of 3:5-*dibromophenylalanine*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Br}_2$; this dissolves in about 125 parts of water at 100°, and crystallises in long, hairy needles, m. p. 233—234° (decomp.). The aqueous solution tastes sweet and astringent. The substance is unchanged when heated with hydrochloric acid (D 1.19) in a sealed tube, but boiling aqueous barium hydroxide removes about 11% of the bromine. The *hydrochloride*, clusters of long prisms, changes on boiling with concentrated hydrochloric acid into stout prisms of a different habit, m. p. 254° (decomp.); the *barium* ($3\text{H}_2\text{O}$), *silver*, and *copper* ($1\frac{1}{2}\text{H}_2\text{O}$) salts are described; the *ethyl* ester is a viscid oil, b. p. 234—237°/24 mm., which forms a *picrate*, large, irregular prisms, m. p. 181—182°, and a *hydrochloride*, needle-like prisms, m. p. 186—187°.

The interaction of 3:5-dibromobenzyl bromide and ethylsodiummalonate leads to the formation of *ethyl di-3:5-dibromobenzylmalonate*,



crystallising in needle-like prisms, m. p. 99°.

3:5-*Dibromobenzylphthalimide*, $\text{C}_6\text{H}_4\text{:}(\text{CO})_2\text{:N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Br}_2$, is formed by heating potassium phthalimide and 3:5-dibromobenzyl bromide to 140°. It crystallises in colourless prisms, m. p. 185°.

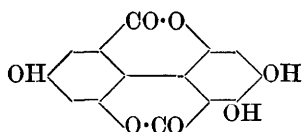
J. C. C.

Glycyrrhizic Acid. ALEXANDER TSCHIRCH and S. GAUCHMANN (*Arch. Pharm.*, 1908, 246, 545—558).—The paper discusses (1) the distribution of glycyrrhizic acid in the vegetable kingdom; (2) the best methods of preparing the acid from Russian liquorice root or the “glycyrrhizinium ammoniacale” of commerce, and (3) the nature of the hydrolytic products of the acid. It was shown previously that on hydrolysis by boiling dilute sulphuric acid, glycyrrhizic acid yields glycyrrhetic and probably glycuronic acids (Tschirch and Cederberg, Abstr., 1907, i, 545). Larger quantities of the hydrolytic products have now been prepared, and exhaustive examination shows that the second product is undoubtedly glycuronic acid.

Glycyrrhetic acid, $\text{C}_{32}\text{H}_{48}\text{O}_7$, contains one ethylene linking, possesses neither methoxyl nor ethoxyl groups, furnishes a crystalline hydrocarbon (? naphthalene) on distillation with zinc dust, an aromatic oily product when distilled with soda-lime, and, on oxidation with

permanganate, oxalic and picric acids. With nitric acid, no nitro-compound is formed, but only oxalic and picric acids. T. A. H.

Resoflavin. V. Lactone Dyes. JOSEF HERZIG and S. EPSTEIN (*Monatsh.*, 1908, 29, 661—675).—In the constitution ascribed to resoflavin by Herzig and Tscherne (this vol., i, 547) there remains doubtful whether one of the hydroxyls occupies the position 2 or 4.



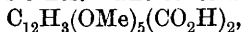
The analogy of the formation of resoflavin from 3:5-dihydroxybenzoic acid with that of flavellagic acid from gallic acid makes it probable that the hydroxyl in question occupies position 4, resoflavin having therefore the annexed constitution.

The behaviour of resoflavin when fused with potassium hydroxide is now found to be in agreement with this view of its constitution. Barth and Goldschmidt (*Abstr.*, 1879, 930) showed that ellagic acid, on fusion with potassium hydroxide, yields hexahydroxydiphenyl, pentahydroxydiphenylmethylolide (*Graebe*, *Abstr.*, 1903, i, 262; *Perkin and Nierenstein*, *Trans.*, 1905, 87, 1412) being formed intermediately. Resoflavin, on the other hand, when treated in the same manner, yields 3:5-dihydroxybenzoic acid, m. p. 237—240° (232—233°: *Böttger*, this *Journ.*, 1875, 567); the methyl ester, m. p. 163—165° (60°: *Meyer*, *Abstr.*, 1901, i, 628). 3:5-Dimethoxybenzoic acid, m. p. 185—186° (175—176°: *Tiemann and Streng*, *Abstr.*, 1882, 51); the methyl ester, m. p. 42—44° (81°: *Meyer*, *Abstr.*, 1888, 148).

As ellagic acid, which contains two pyrogallol groups, yields hexahydroxydiphenyl, and, as the resorcinol nucleus is more stable than the pyrogallol nucleus towards fused alkalis, a substance having the annexed constitution must under the same conditions yield pentahydroxydiphenyl.

The degradation of resoflavin to 3:5-dihydroxybenzoic acid must be explained, therefore, by the presence of a resorcinol and a hydroxyquinol grouping, the latter being more unstable towards the fused alkali than the carboxyl attached to the resorcinol portion of the complex.

When heated on the water-bath with alcoholic sulphuric acid, the ether ester of resoflavin yields a white substance, which, on treatment with diazomethane, forms trimethylresoflavin, and hence is the hydrolysis product of this ether. The ether acid,



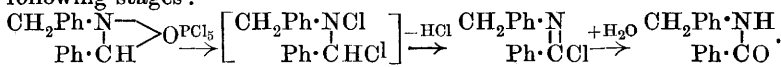
and trimethylresoflavin must be formed intermediately. In agreement with this, methyl 2:3:4:4':5':6'-hexamethoxydiphenyl-6:2'-carboxylate (*Herzig and Pollak*, this vol., i, 546), when treated with alcoholic sulphuric acid in the same manner, yields a yellow, crystalline substance, m. p. above 300°, which contains a slightly smaller percentage of methoxyl than tetramethylellagic acid, into which it is converted by the action of diazomethane.

G. Y.

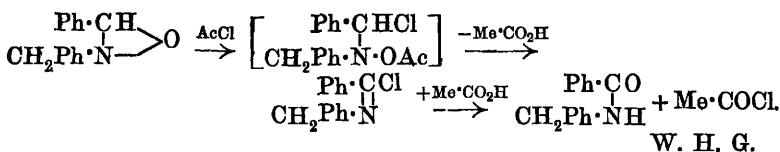
Nature and Constitution of Rhizocholic Acid. HUGO SCHRÖTTER and RICHARD WEITZENBÖCK (*Monatsh.*, 1908, 29, 749—751).—It is now found that the acid obtained by the successive action of sulphuric and nitric acids on cholesterol, cholic acid, camphor, or turpentine oil, and previously termed rhizocholic acid (this vol., i, 532, 636), is benzenepentacarboxylic acid. When heated it sublimes, losing carbon dioxide and forming pyromellitic anhydride. It is considered that the pentacarboxylic acid is a secondary product, formed by oxidation of primarily liberated carbon. Its formation, therefore, cannot be looked upon as evidence of any relationship between cholesterol and cholic acid, on the one hand, and the terpenes, on the other. G. Y.

Action of Hydrogen Persulphide on Organic Compounds. HEINRICH BRUNNER and V. VUILLEUMIER (*Chem. Zentr.*, 1908, ii, 588; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 436—438).—The authors have obtained the following substances by adding hydrogen persulphide to a solution of the organic compound in carbon disulphide, chloroform, or benzene. From *benzaldehyde*, long, colourless, prismatic crystals of the composition $(\text{Ph}\cdot\text{COH})_2\cdot\text{H}_2\text{S}_3$, which decompose at 28° into sulphur, hydrogen sulphide, and benzaldehyde. *Anisaldehyde*, similar crystals of the composition $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COH})_2\cdot\text{H}_2\text{S}_3$, decomposing at 18° . *Cinnamaldehyde* gives a solid, non-crystallisable product, $\text{C}_9\text{H}_8\text{O}_2\cdot\text{H}_2\text{S}_4$. *Benzoquinone*, a violet powder of the composition $(\text{C}_6\text{H}_4\text{O}_2)_4\cdot\text{H}_2\text{S}_5$, which is possibly a mixture of $(\text{C}_6\text{H}_4\text{O}_2)_2\cdot\text{H}_2\text{S}_2$ and $(\text{C}_6\text{H}_4\text{O}_2)_2\cdot\text{H}_2\text{S}_3$. Piperidine in chloroform gives a red solution with sulphur, which, on addition of carbon disulphide, yields $\text{C}_5\text{H}_{11}\text{N}\cdot\text{CS}\cdot\text{S}\cdot\text{NHC}_5\text{H}_{11}$. Many aldehydes and ketones simply cause the precipitation of white, prismatic sulphur. The compounds obtained with strychnine and brucine were found to be identical with those described by Hoffmann and Schmidt (*Abstr.*, 1877, ii, 789, 905). J. V. E.

Molecular Rearrangement of *N*-Benzylaldoxime. MITSURU KUHARA (*J. Coll. Sci. Tōkyō*, 1908, 25, xviii, 1—4).—The author has succeeded in isolating benzoylbenzylamine iminochloride (compare Pechmann and Heinze, *Abstr.*, 1897, i, 515) as an intermediate product of the rearrangement of *N*-benzylbenzaloxime by the action of phosphorus pentachloride, and in converting the iminochloride into benzylbenzamide by the action of water. The transformation of *N*-benzylbenzaloxime into benzylbenzamide under the influence of phosphorus pentachloride, therefore, probably takes place through the following stages:



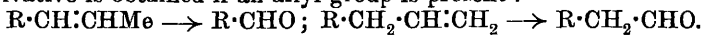
Kuhara and Kainosho (*Abstr.*, 1907, i, 1027) have shown that phenylbenzamide is formed by the action of acetic acid on chlorobenzylidenaniline. It is therefore probable that the rearrangement of *N*-benzylbenzaloxime by the action of acetyl chloride takes place thus:



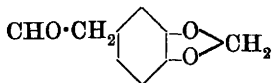
***β-p*-Methoxyphenylpropaldehyde** obtained from the **Isomeric *α-p*-Methoxyphenylpropylene-*αβ*-glycols** [*α-p*-Methoxyphenylpropane-*αβ*-diols]. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 259—269).—According to Tiffeneau and Daufresne (*Abstr.*, 1907, i, 701), the *β*-modification of *α-p*-methoxyphenylpropylene-*αβ*-glycol (compare Balbiano, *Abstr.*, 1907, i, 522) yields *p*-methoxyphenylacetone when dehydrated by means of 20% sulphuric acid. The author shows, however, that the compound is not a ketone, but *β-p*-methoxyphenylpropaldehyde, which is also obtained by dehydrating the isomeric *α*- and *β*-glycols by means of zinc chloride (compare Balbiano and Paolini, *Abstr.*, 1906, i, 186). When either method of dehydrating the glycol is used, this aldehyde is accompanied by a small quantity of a *dimeric* form, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \end{smallmatrix} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ (?), which crystallises from alcohol in microscopic prisms, m. p. 181—182°, has the normal molecular weight in freezing benzene, and exhibits no aldehydic properties. When treated with benzenesulphonylhydroxamic acid, the *α*- or *β*-form of *β-p*-methoxyphenylpropaldehyde yields a small amount of the corresponding hydroxamic acid, which was separated as *copper* salt, $\text{C}_{10}\text{H}_{11}\text{O}_8\text{NCu}$; when dissolved in dilute hydrochloric acid, this salt gives an intense violet coloration with ferric chloride, whilst, on hydrolysis, it yields anisic acid and a small quantity of a *substance*, $\text{C}_6\text{H}_7\text{O}_4\text{N}$, crystallising in shining laminae, m. p. about 150°.

T. H. P.

Constituents of Ethereal Oils. Homopiperonal and its Derivatives. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, 41, 2751—2753).—To distinguish between the aromatic constituents of ethereal oils containing an allyl or a propenyl group in the side-chain, the authors oxidise the substance with ozone, whereby rupture at the double linking occurs, with the formation of an aldehyde if a propenyl group is present, whilst the corresponding homoderivative is obtained if an allyl group is present:



Homopiperonal (annexed constitution), m. p. 69°, b. p. 143—144°/10 mm., D_{20} 1.295, n_D 1.57117, is obtained by passing ozone through a solution of safrole in benzene mixed with a small quantity of water, distilling the product



in steam to remove benzene and unchanged safrole, and extracting the non-volatile aldehyde with ether. The *semicarbazone*, m. p. 189°, *oxime*, m. p. 124—125°, b. p. 180—181°/10 mm., and *nitrile*, b. p. 153—156°/10 mm., D_{20} 1.231, n_D 1.53698, are described. Hydrolysis of the last by 10% alcoholic potassium hydroxide yields *homopiperonylic acid*, $\text{C}_9\text{H}_8\text{O}_4$, m. p. 127°, the *methyl ester* of which has b. p. 153—155°/10 mm.,

D_{20} 1.246, n_D 1.534, and is converted by sodium and absolute alcohol into *homopiperonyl alcohol*, $C_9H_{10}O_3$, b. p. $156^\circ/10$ mm., n_D 1.54780. By reduction, the nitrile yields the *amine*, $C_9H_{11}O_2N$, b. p. $146-148^\circ/10$ mm., D_{20} 1.225, n_D 1.5620, of which the *picrate* has m. p. 160° (decomp.). C. S.

Quinone Formation. RAYMOND VIDAL (*Chem. Zentr.*, 1908, ii, 240; from *Mon. Sci.*, 1908, [iv], 22, i, 368—372).—Quinone formation is considered as supporting the views expressed (Abstr., 1907, i, 1020) on the nature of the benzene ring. J. V. E.

Action of Piperidine on *l*-Pinene Chloroxime. P. G. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1015—1018).—The action of piperidine on the chloroxime of *l*-pinene isolated from the ethereal oil of the Siberian fir proceeds in two directions: (1) $C_{10}H_{16}\cdot NOCl + C_5H_{11}N = HCl + C_{10}H_{16}\cdot NO\cdot C_5H_{11}N$, yielding a compound identical with that given by *d*-pinene from American turpentine;

(2) $C_{10}H_{16}\cdot NOCl + C_5H_{11}N = HCl + C_5H_{11}N + C_{10}H_{15}ON$, yielding the nitrosopinene obtained by the action of diethylamine on *d*-pinene chloroxime. T. H. P.

Essential Oil of French Parsley and the Contained Ether, 2:3:4:5-Tetramethoxy-1-allylbenzene. HERMANN THOMS (*Ber.*, 1908, 41, 2753—2761. Compare Abstr., 1904, i, 47).—Experiments are in progress to ascertain whether the climate, the conditions of cultivation, or the degree of ripeness of the seeds, accounts for the fact that the essential oil of French parsley contains a large quantity of myristicin and a small amount of apiole, whilst the oil from German parsley is rich in the latter.

A large quantity of the oil of French parsley has been freed from phenols and acids, and the resulting liquid separated into two fractions, b. p. $160-165^\circ/15$ mm. and $165-170^\circ/15$ mm. The presence of myristicin in both is proved by the formation of dibromomyristicin dibromide (Abstr., 1904, i, 47), but a Zeisel estimation indicates the presence of a substance richer in methoxyl groups. This substance, ultimately isolated by the aid of solid carbon dioxide, has been proved to be 2:3:4:5-tetramethoxy-1-allylbenzene, m. p. 25° , D_{25}^{25} 1.087, n_D^{25} 1.51462. The presence of the allyl group is indicated by the dispersion and the molecular refraction, and by the formation of a red coloration with phloroglucinol and hydrochloric acid (compare Kobert, *Zeitsch. anal. Chem.*, 1908, 47, 711). The positions of the methoxyl groups are determined by oxidation with potassium permanganate, whereby 2:3:4:5-tetramethoxybenzoic acid, m. p. 87° , is obtained, and also by successive treatment with alcoholic potassium hydroxide (which changes the allyl to a propenyl group), reduction with sodium and alcohol, and nitration of the product, resulting in the formation of 4-nitro-2:3:5-trimethoxy-1-propylbenzene (Abstr., 1903, i, 558). By nitration, the methoxyl group in position 4 has been replaced by a nitro-group (compare Thoms and Herzog, Abstr., 1903, i, 415).

The same operations on the above-mentioned fractions yield the same compounds, as also does the oil from French parsley seeds grown in Dahlem.
C. S.

Ethereal Oil from *Salvia sclarea*. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1908, ii, 323; from *Wiss. ind. Ber. Roure-Bertrand Fils*, 1908, [ii], 7, 10—11).—The oil distilled in 1904 (*Chem. Zentr.*, 1906, ii, 535) has been saponified, and *l*-linalool is found to be the chief constituent, together with some resinous substances which render it insoluble in 96% alcohol, acetone, methyl alcohol, &c.

J. V. E.

Resin of *Antiaris toxicaria*. ADOLPH WINDAUS and A. WELSCH (*Arch. Pharm.*, 1908, 246, 504—508. Compare de Vrij and Ludwig, *Sitz. Wien. Akad.*, 1868, 57, 56, and Kiliani, *Abstr.*, 1897, i, 91).—The portion of the latex of *Antiaris toxicaria* soluble in light petroleum is composed principally of the cinnamic ester of α -amyrin, $C_{39}H_{56}O_2$, m. p. 176° , $[\alpha]_D^{25} + 78^\circ 45'$ (in chloroform), which crystallises from methyl alcohol in long, thick, colourless needles. From the products of hydrolysis of the amorphous portion of the resin, α -amyrin, cinnamic acid, and some stearic acid were obtained. No β -amyrin seems to be present in the resin.
T. A. H.

Decomposition of Amygdalin by Emulsin. KARL FEIST (*Arch. Pharm.*, 1908, 246, 509—510. Compare this vol., i, 437, and Rosenthaler, *ibid.*, i, 817).—Rosenthaler's observation, that emulsin is capable of forming *d*-benzaldehydecyanohydrin from benzaldehyde and hydrocyanic acid, is, contrary to that author's opinion, in reality a confirmation of Feist's statement that *d*-benzaldehydecyanohydrin is the first product of the action of emulsin on amygdalin, since the action probably reaches equilibrium in the two directions: *d*-benzaldehydecyanohydrin + emulsin \rightleftharpoons benzaldehyde + hydrocyanic acid + emulsin.
T. A. H.

New Glucoside (Erytaurin) obtained from the Common Century. HENRI HÉRISSEY and L. BOURDIER (*J. Pharm. Chim.*, 1908, [vi], 27, 252—255).—The glucoside, obtained from the plant by a lengthy extraction process, crystallises in small, colourless prisms on addition of ether to its solution in a mixture of chloroform and alcohol. It is bitter to the taste, has $[\alpha]_D -131.6^\circ$ to -134.4° , does not reduce Fehling's solution, but gives a blue coloration with a mixture of ferric chloride and potassium ferri-cyanide. Erytaurin is slowly hydrolysed by emulsin, yielding dextrose and a pale yellow precipitate.
T. A. H.

Glucosides of *Linaria*. TIMOTHÉE KLOBB (*Bull. Soc. chim.*, 1908, [iv], 3, 858—872. Compare *Abstr.*, 1907, i, 864; ii, 123).—The yield of linarin from the dried flowers of *Linaria vulgaris* amounts to 1.5—2.8%; it may be recrystallised from 50% acetic acid. Saturated solutions in boiling alcohol contain 0.30% of linarin; in cold alcohol,

0.24%; in boiling 50% acetic acid, 0.57%, and in the cold acid, 0.36%. The glucoside apparently forms an additive compound with phenol, and is readily absorbed from solution by animal charcoal. β -Linarin has m. p. 257—260°, and is more soluble than linarin in 50% acetic acid.

α -Pectolinarin is straw-yellow and amorphous, but sometimes forms hard, almost white, semi-crystalline aggregates. Saturated solutions in alcohol at 80° contain 0.582% of pectolinarin; in cold alcohol, 0.097%; in water at 100°, 0.24%. Pectolinarin is rapidly hydrolysed by dilute acids at 85°, giving a mixture of the two phenols. Both linarin and pectolinarin, when hydrolysed by concentrated hydrochloric acid, give linarinic phenol only.

Linarinic phenol crystallises from glacial acetic acid in needles or orange-red prisms, the latter containing both water and acetic acid of crystallisation, which are lost at 120—130°. Its m. p. is 277—279°, not 245° as stated previously; it gives a greenish-black coloration with alcoholic ferric chloride, and a greenish-grey precipitate with chloroform and potassium hydroxide, becoming reddish-brown on exposure to the air. It forms an *acetate*, $C_{19}H_{11}O_7Ac_3$, m. p. 248—250°.

Anhydrolinaric phenol is quite stable towards alkali hydroxides (difference from linarinic phenol), gives a violet-brown coloration with alcoholic ferric chloride, a bright red coloration with chloroform and potassium hydroxide, and a brown coloration in Liebermann's reaction. The *acetate* forms colourless needles, m. p. 198—200°, and the *benzoate*, $C_{19}H_{10}O_6(COPh)_2$, short, white needles, m. p. 199—201°. E. H.

Oleo-europein; a New Glucoside obtained from the Olive, *Olea Europa*. ÉMILE BOURQUELOT and J. VINTILESCO (*Compt. rend.*, 1908, 147, 533—535; *J. Pharm. Chim.*, 1908, [vi], 28, 303—314). [Compare Power and Tutin, *Trans.*, 1908, 93, 891, 904.] —Bourquelot's biological test (*Abstr.*, 1902, ii, 55) for the detection of glucosides shows the presence of a glucoside, *oleo-europein*, hydrolysable by emulsin in the fruits, leaves, and bark of the olive. This substance, which was only obtained as a slightly yellow powder, possesses a bitter taste, is readily soluble in cold water or warm alcohol, insoluble in ether, and has $[\alpha]_D - 5.166^\circ$. It reduces Fehling's solution on boiling, and its solution in water is coloured yellow by alkalis, red by sulphuric acid, and green by ferric chloride. The glucoside is hydrolysed by emulsin or by boiling with acids, yielding dextrose. Emulsin also occurs in the leaves and fruit of the olive. T. A. H.

***l*-Arabinose and Dextrose as Inversion Products of Saponin from the Leaves of *Polyscias nodosa*, Forst.** A. W. VAN DER HAAR (*Pharm. Weekblad*, 1908, 45, 1184—1191). —Anhydrous saponin from the leaves of *Polyscias nodosa* has the empirical constitution $C_{25}H_{42}O_{10}$, and contains an arabinose complex. On inversion, it takes up water, yielding *l*-arabinose, dextrose, and sapogenin. A. J. W.

The Hydrocarbon Nucleus of Frangula emodin, Aloe-emodin, and Rhein. OTTO A. OESTERLE and ED. TISZA (*Arch. Pharm.*, 1908, 246, 432—436).—A continuation of work on the constitution of the emodins obtained from the bark of *Rhamnus frangula* and from aloes respectively, showing that the former is a β -methylantracene derivative as already formulated (this vol., i, 350), and the latter probably derived from α -methylantracene.

Frangula emodin, on distillation with zinc dust, yields β -methylantracene (compare Liebermann, this Journ., 1876, i, 251; Perkin and Hummel, *Trans.*, 1894, 65, 924).

The hydrocarbon obtained when aloe-emodin is distilled with zinc dust forms greenish-yellow leaflets, has m. p. 208—209°, fluoresces green in acetic acid, gives a blood-red *picric acid* compound, m. p. 145°, and is polymerised in benzene solution on exposure to sunlight, yielding a *hydrocarbon*, m. p. 256°, crystallising in colourless needles. Since these characteristics are different from those of β -methylantracene, the authors suggest that the hydrocarbon thus obtained from aloe-emodin is probably α -methylantracene.

Rhein on distillation with zinc dust yields anthracene (compare Hesse, *Abstr.*, 1900, i, 41; Tschirch and Heuberger, *Abstr.*, 1903, i, 107; Oesterle, *Abstr.*, 1904, i, 80). T. A. H.

Pimpinellin. JOHANNES HERZOG and V. HÂNCU (*Arch. Pharm.*, 1908, 246, 402—414. Compare Heut, *Abstr.*, 1898, i, 598).—The preparation of pimpinellin from the root of *Pimpinella saxifraga* has been simplified, the characters of the substance definitely determined, and its oxidation by hydrogen peroxide studied. The results of this work indicate that pimpinellin is a naphthalene derivative.

Pimpinellin, $C_{15}H_{10}O_5$, m. p. 119°, obtained to the extent of 0.5% by extracting the ground root with benzene and treating the concentrated extract with light petroleum, crystallises in glancing, white needles, sublimes with slight decomposition, and becomes yellow on long exposure to light. It is probably a lactone, contains two methoxyl groups, and, on oxidation with hydrogen peroxide, furnishes a *tribasic acid*, $C_9H_6O_8$, m. p. 220° (decomp.). This crystallises in short, thick needles from acetic acid, is readily soluble in alcohol, less so in water, and can be sublimed, forming, then, long needles recalling those of phthalic anhydride, which it resembles in giving a fluorescein reaction. The acid contains no methoxyl groups; it yields a well-crystallised *pyridine* salt, m. p. 179° (decomp.), and this reacts with diphenylcarbonyl chloride (compare this vol., i, 268) to form the *diphenylated acid amide*, $C_6H_5O_2(CO \cdot NPh_2)_3$, m. p. 224.5—225.5°, which separates from boiling alcohol or toluene in splendid pale yellow crystals.

The second crystalline product isolated by Heut (*loc. cit.*) from the roots could not be obtained, although evidence of the existence of a minute quantity of a second substance, possibly a decomposition product of pimpinellin, was observed. T. A. H.

Formation and Chemistry of Anthocyanins. LEOPOLD VON PORTHEIM and EMIL SCHOLL (*Ber. deut. bot. Ges.*, 1908, 26a, 480—483).—Pure solutions of unstable, plant-colouring matters, such as that of

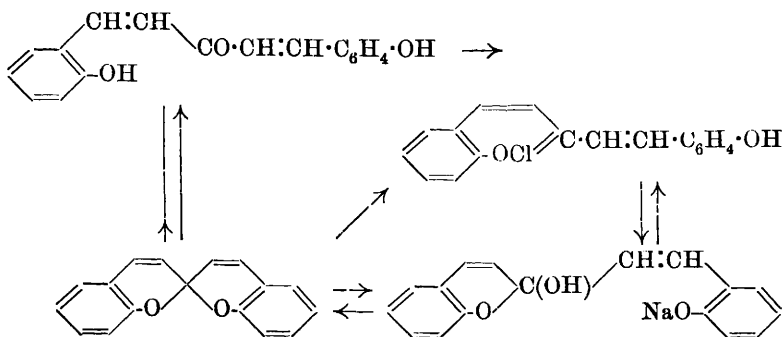
beetroot, can be prepared by dialysing the expressed juice or an aqueous extract of the plant (compare Weigert, Abstr., 1896, i, 387).

The colouring matter of the testa of the seed of *Phaseolus multiflorus* is insoluble in water. An alcoholic extract of the testæ deposits on slight concentration a small quantity of a yellow substance, crystallising in microscopic bundles of needles. The mother liquor from this deposits no more crystalline matter on further concentration, but, when boiled with a few drops of hydrochloric acid, yields a reddish-violet liquid, which, after some days, deposits ruby-red, microscopic crystals of a substance, readily soluble in alcohol, and turning blue on addition of ammonia.

The mother liquor referred to above may also be separated into three fractions by treatment with ether. Of these, (A) is a viscid, brown mass, which yields the crystalline, red colouring matter on hydrolysis by acids; (B) a reddish-violet, amorphous product, and (C) a brownish-yellow residue, insoluble in water. T. A. H.

Cyclic Oxonium Salts from Disalicylideneacetone, and spiroPyran Derivatives. HERMAN DECKER and HEINRICH FELSER (*Ber.*, 1908, 41, 2997—3007).—Tiemann and Kees' disalicylideneacetone (dicoumaro-ketone) (Abstr., 1885, 1073) is very easily obtained, in the form of the alkali salt, by adding alcoholic potassium hydroxide (3—4 mols.) to an alcoholic solution of salicylaldehyde (2 mols.) and acetone (rather less than 1 mol.). By treating an alcoholic solution of the ketone with hydrogen chloride or 50% sulphuric acid, a red solution of the 2-*o*-hydroxystyrylbenzopyrylium salt is obtained, from which ferric chloride precipitates the dark red *ferrichloride*, $C_{17}H_{13}O_2Cl_4Fe$, m. p. 180°. The very intense colour of these oxonium salts is due, in part, to the presence of the *o*-hydroxystyryl group. The red oxonium chloride gives with 10% sodium hydroxide a yellow solution of the sodium salt of 2-*o*-hydroxystyrylbenzopyranol-2, $C_6H_4 \begin{smallmatrix} \diagup CH:CH \\ \diagdown O \end{smallmatrix} C(OH) \cdot CH:CH \cdot C_6H_4 \cdot ONa$, from which the carbinol

itself cannot be isolated, since the carbinol and the phenolic hydroxyl groups eliminate water, and the stable, colourless, crystalline *dibenzo-spiropyran*, m. p. 102°, is formed, just as the carbinols of other cyclic oxonium salts react with alcohols to give ethers (Decker and



von Fellenberg, Abstr., 1907, i, 950). By treatment with concentrated acids, one pyran ring of the *spiro*pyran derivative is readily ruptured, yielding the coloured 2-*o*-hydroxystyrylbenzopyrylium salt, whilst warm alcoholic sodium hydroxide opens both rings, with the regeneration of disalicylideneacetone.

The constitutions and the transformations of the preceding compounds are indicated in the preceding scheme.

These changes are not readily explicable by Bülow's benzopyranol-(4) formula (Abstr., 1901, i, 400, 559; 1902, i, 113).

Perkin, Robinson, and Turner (Trans., 1908, 93, 1088), criticising Decker's formula of the benzopyrylium salts, contend that with this formula these should not be so highly coloured as they actually are, since the linkings in the skeleton formula are in a similar position to those in quinoline; they suggest an alternative *o*-quinonoid formula. The authors argue that this formula does not explain the formation of benzopyrylium salts from coumarin, the ready hydrolysis of the carbinol, the colour of the salts, and the absence of colour in the carbinol. It is known that in acridinium and xanthylium salts the replacement of the NMe group by O in the ring intensifies the colour. Just the same difference occurs with benzopyrylium and quinolinium salts, and the deeper colour of the former is regarded as a proof that they are oxonium salts isologous with quinolinium salts.

2-*o*-Hydroxystyrylbenzopyrylium chloride, $C_{17}H_{13}O_2Cl \cdot H_2O$, forms red needles with a bronze-green reflex, and, from its moderately-concentrated solution, other crystalline salts and double salts can be obtained. Dibenzospiropyran is formed when disalicylideneacetone is kept above its m. p., 168° , for ten minutes. C. S.

Brazanquinones. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, 41, 2800—2802).—As catechone trimethyl ether yields a well-crystallised nitro-derivative, the authors have investigated the action of nitric acid on the closely-allied 2:7:8-trimethoxybrazanquinone (this vol., i, 672), and find that it gives a trinitro-derivative; similarly, 2-methoxybrazanquinone yields a dinitro-derivative.

Trinitro-2:7:8-trimethoxybrazanquinone, $C_{19}H_{11}O_{12}N_3$, prepared by adding the quinone to nitric acid (D 1.5), crystallises in orange-yellow needles, m. p. 275° (decomp.). 1:3(?)*-Dinitro-2-methoxybrazanquinone* forms small, stout crystals, m. p. 253 — 254° (decomp.). In order further to characterise 2-methoxybrazanquinone, the authors have converted it by reduction and simultaneous acetylation into 5:10-*diacetoxy-2-methoxybrazan*, which crystallises in white, prismatic needles, m. p. 195 — 196° . Its solution in concentrated sulphuric acid is green, and shows an intense dark green fluorescence.

5:10-Diacetoxy-2:7:8-trimethoxybrazan (Kostanecki and Lloyd, Abstr., 1903, i, 646) gives the same colour reaction. When boiled with alcoholic potash and the product treated with dimethyl sulphate, 5:10-diacetoxy-2-methoxybrazan yields 2:5:10-*trimethoxybrazan*, crystallising in white leaflets, m. p. 165° . This shows the same colour reaction with sulphuric acid as the compound just described, and its alcoholic solution exhibits a weak blue fluorescence. J. C. C.

Morphine. XIX. Relationship between ψ -apoCodeine and apoMorphine. LUDWIG KNORR and FELIX RAABE (*Ber.*, 1908, 41, 3050—3054).— ψ -apoCodeine (Abstr., 1907, i, 790) stands in the same relationship to apomorphine as codeine to morphine; it is thus the 3-methyl ether of apomorphine, and is identical with Pschorr, Jäckel, and Fecht's methyl ether (Abstr., 1903, i, 193). The crystals obtained from alcoholic solutions contain 1EtOH, and melt and decompose at 105°, after sintering at 100°. In alcoholic solution it has $[\alpha]_D^{15} - 90^\circ$ ($c = 0.84$), and in chloroform solution, -103° ($c = 2.6$). The dimethyl ether of apomorphine has not been obtained crystalline, even after distillation under reduced pressure. It has b. p. 195—205° in the cathode ray vacuum, and $[\alpha]_D^{15} - 148^\circ$ ($c = 1.6395$) in alcoholic solution. The *hydriodide*, $C_{19}H_{22}O_2NI$, forms pale yellow prisms, m. p. about 220°.

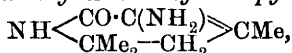
The rotatory power of methyl-apomorphine methiodide is $[\alpha]_D^{15} - 20^\circ$ ($c = 1.2573$) in methyl-alcoholic solution. Diacetylmethylapomorphine has m. p. 130°. J. J. S.

Protopine of Japanese Corydalis Roots (Corydalis Vernyi). K. MAKOSHI (*Arch. Pharm.*, 1908, 246, 401—402).—The root of this plant contains two alkaloids, the one, identical with protopine, occurring to the extent of 0.13%, and the other, obtained in the form of a yellow, crystalline mass and closely resembling dehydrocorydaline in appearance and properties, is present to the extent of 0.013%.

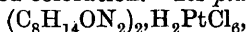
T. A. H.

Certain *o*-Amino- and *o*-Hydroxy-ketohydropyridines. I. GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1908, 43, 890—912).—The author describes various amino- and the corresponding hydroxy-tetrahydropyridine derivatives in which the amino- (or hydroxy-) group is in the 3 position, whilst the 2-position is occupied by what is most probably a carbonyl group.

3-Amino-4 : 6 : 6-trimethyl- Δ^3 -tetrahydro-2-pyridone,

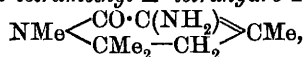


prepared by converting 4 : 6 : 6-trimethyl- Δ^3 -tetrahydro-2-pyridone-3-carboxylamide (compare this vol., i, 679) into the corresponding bromoamide by means of potassium hypobromite and then boiling with water, separates from benzene in friable, prismatic crystals, m. p. 130—131°, exhibiting a slight blue fluorescence, and yields an alkaline aqueous solution, which with ferric chloride gives an orange-red and, later, a blood-red coloration. Its *platinichloride*,



m. p. 235°, is decomposed when boiled with water, giving the corresponding hydroxy-compound (*vide infra*), $(C_8H_{14}ON_2)_2, H_2PtCl_6 + 2H_2O = 2C_8H_{18}O_2N + (NH_4)_2PtCl_6$. The hydroxy-compound is also formed by the action of nitrous acid on the amino-derivative.

3-Amino-1 : 4 : 6 : 6-tetramethyl- Δ^3 -tetrahydro-2-pyridone,



prepared from 1 : 4 : 6 : 6-tetramethyl- Δ^3 -tetrahydro-2-pyridone-3-

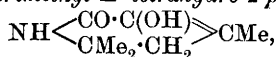
carboxylamide (*loc. cit.*), crystallises from ether in colourless or faintly yellow prisms, m. p. 60—61°, has an alkaline reaction, shows normal cryoscopic behaviour in benzene, and reacts with water or nitrous acid like the preceding compound. The *platinichloride*,
 $(C_9H_{16}ON_2)_2, H_2PtCl_6, H_2O$,
 has m. p. 196—197° (decomp.).

Both these amino-compounds are mono-acid bases rather weaker than ammonia; they do not absorb carbon dioxide from the air, but precipitate aluminium hydroxide from solutions of aluminium salts. The most striking properties of the bases are the ease with which they react with nitrous acid and the mobility of the amino-group towards hydrolysts, these being due to the presence of the group



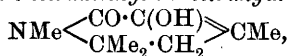
in a hydrogenated nucleus. They both readily reduce Fehling's solution, ammoniacal silver nitrate solution, &c.

3-Hydroxy-4 : 6 : 6-trimethyl- Δ^3 -tetrahydro-2-pyridone,



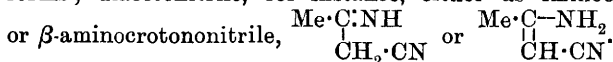
crystallises from water in shining leaflets, m. p. 143°, has a neutral reaction, gives a blue coloration with ferric chloride, and readily reduces Fehling's solution, ammoniacal silver nitrate solution, &c.

3-Hydroxy-1 : 4 : 6 : 6-tetramethyl- Δ^3 -tetrahydro-2-pyridone,

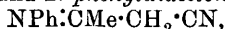


crystallises from alcohol in colourless needles, m. p. 95°, has the normal molecular weight in freezing benzene, gives a violet coloration with a little ferric chloride and an intense azure coloration with excess of the reagent, and readily reduces Fehling's solution, &c. T. H. P.

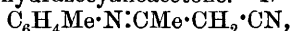
Bimolecular Nitriles. ERNST VON MEYER (*Chem. Zentr.*, 1908, ii, 591—594; from *Ber. K. Sächs. Ges. Wiss., Math.-phys. Kl.*, 1908, 60, 146—174. Compare *Abstr.*, 1895, i, 582—585).—The author has further investigated the behaviour of the so-called dinitriles which have long been shown (*loc. cit.*) to react as two tautomeric forms; diacetonitrile, for instance, either as iminoethylacetonitrile or β -aminocrotononitrile,



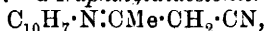
[With W. SCHUMACHER.]—*Action of Arylamines on Diacetonitrile.*—Aniline gives the compound *N-phenyldiacetonitrile*,



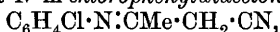
which crystallises in white needles, m. p. 115°; when treated with diazobenzene nitrate in pyridine solution, a *phenylhydrazone*, $NPh:CMe\cdot C:N\cdot NHPh\cdot CN$, is formed, crystallising in greenish-yellow leaflets, m. p. 149°, and this, when treated with hydrogen chloride, gives phenylhydrazocycanoacetone. *N-o-Tolyldiacetonitrile*,



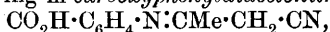
is prepared in a similar manner, and crystallises in leaflets, m. p. 73°. *N-m-Tolyldiacetonitrile*, white, prismatic needles, m. p. 109°. *N-p-Tolyldiacetonitrile*, white needles, m. p. 102°. *N-Benzoyldiacetonitrile*, white needles, m. p. 79°. *α -Naphthyldiacetonitrile*,



prepared from diacetonitrile and α -naphthylamine, crystallises in leaflets, m. p. 112°. β -Naphthyl-diacetonitrile, brown leaflets, m. p. 172°. The three isomeric mononitroanilines and *o*-chloroaniline do not react with diacetonitrile, but *N*-m-chlorophenyl-diacetonitrile,



was readily obtained as white needles, m. p. 136°, and *N*-p-chlorophenyl-diacetonitrile as white leaflets, m. p. 114°. With the three phenylenediamines, the following compounds have been obtained: *o*-phenylenebisdiacetonitrile, $\text{C}_6\text{H}_4(\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN})_2$, prismatic leaflets, m. p. 136°; *m*-phenylenebisdiacetonitrile, prisms, m. p. 185°; *p*-phenylenebisdiacetonitrile, square leaflets, m. p. 222°. *p*-Hydroxyphenyl-diacetonitrile, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$, crystallises in brown needles, m. p. 120°; *p*-ethoxyphenyl-diacetonitrile, white needles, m. p. 138°. No combination takes place with *o*-aminobenzoic acid, but the other isomerides react, giving *m*-carboxyphenyl-diacetonitrile,



white, prismatic needles, m. p. 206°; *p*-carboxyphenyl-diacetonitrile, needle-shaped crystals, m. p. 158°. All the above-mentioned compounds are decomposed by hydrogen chloride into acetic acid, ammonia, and arylamine.

[With H. LEHMANN.]—*Action of Hydrazine Derivatives on Diacetonitrile*.—Carbamidodiacetonitrile, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$, is produced from diacetonitrile and semicarbazide hydrochloride; it forms small, white plates, m. p. 165°, which re-melt at 220°; an isomeric modification crystallising in prisms, m. p. 134°, has been observed. Thiocarbamidodiacetonitrile, $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$, long needles, m. p. 106°. With thiosemicarbazide hydrochloride an isomeric form is obtained which crystallises in rhombic plates, m. p. 132°, re-melting at 162°. Benzoylamino-diacetonitrile, $\text{COPh}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CN}$, leaflets, m. p. 90°.

[With M. KLEINSTÜCK.]—*Action of Aldehydes on Dinitriles* (compare Mohr, Abstr., 1898, i, 26).—2:6-Dimethyl-3:5-dihydropyridine, prepared from diacetonitrile and formaldehyde, crystallises in yellow tablets, m. p. 222°, which are oxidised by nitric acid to 3:5-dicyano-2:6-dimethylpyridine, slender, white needles, m. p. 112°. Diacetonitrile with acetaldehyde (or paraldehyde) in presence of hydrogen chloride yields 3:5-dicyano-2:4:6-trimethyldihydropyridine, needle-shaped crystals, m. p. 170°, which also becomes oxidised by nitric acid to 3:5-dicyano-2:4:6-trimethylpyridine, m. p. 111°. Benzodiacetonitrile and benzaldehyde (or hydrobenzamide) react in presence of hydrogen chloride, forming 3:5-dicyano-2:4:6-triphenyldihydropyridine, small, yellow plates, m. p. 268°; when treated with nitric acid, 3:5-dicyano-2:4:6-triphenylpyridine is formed, which crystallises in needles, m. p. 238°. In a similar manner, 3:5-dicyano-2:6-diphenyl-4-*o*-nitrophenyldihydropyridine is produced from *o*-nitrobenzaldehyde; it forms small, yellow plates, m. p. 258°. From benzodiacetonitrile and hexamethyleneamine, 3:5-dicyano-2:6-diphenyldihydropyridine is obtained as small, yellow needles, m. p. 228°. With acetaldehyde or paraldehyde, 3:5-dicyano-2:6-diphenyl-4-methyldihydropyridine is obtained, needles, m. p. 267°.

[With W. HENNING.]—*Condensation of Diacetonitrile* (compare

Holtzwardt, Abstr., 1889, 577).—The substance $C_8H_9N_3$, obtained from diacetonitrile by withdrawal of ammonia, is found to be 6-amino-3-cyano-2:4-dimethylpyridine, white needles, m. p. 222° , which, when treated with nitric acid, give 3-cyano-6-hydroxy-2:4-dimethylpyridine, needles, which melt above 260° (decomp.). The last-named substance gives, with phosphorus pentachloride, 6-chloro-3-cyano-2:4-dimethylpyridine, crystallising in thin leaflets, m. p. 65° ; when boiled with methyl alcohol and sodium methoxide, 3-cyano-6-methoxy-2:4-dimethylpyridine is formed, needles, m. p. 96° , b. p. about 239° . This substance, when heated at 300° , changes to 3-cyano-1:2:4-trimethyl-6-pyridone, needle-shaped crystals, m. p. 125° . The above-mentioned chloro-compound (m. p. 65°), when reduced by zinc and hydrogen chloride, yields 3-cyano-2:4-dimethylpyridine, which forms colourless, prismatic crystals, m. p. 53° , b. p. $108^\circ/15\text{ mm.}$, b. p. 218° ; $C_8H_8N_2 \cdot HCl$, m. p. 187° ; $C_8H_8N_2 \cdot HAuCl_4$, m. p. 172° ; $C_8H_8N_2 \cdot HCl \cdot HgCl_2$, m. p. 178° ; $C_8H_8N_2 \cdot C_6H_5(NO_2)_3OH$, yellow prisms, m. p. 161° . When heated at 180° with alcoholic potassium hydroxide, lutidinamide is produced, which crystallises in needles with $\frac{1}{2}$ mol. H_2O , m. p. 191° ; when heated with hydrogen chloride at 220° , 2:4-dimethylpyridine (α -lutidine) is formed; hydrochloride, $C_5H_3Me_2N \cdot HCl$; platini-chloride, orange-red crystals, m. p. 208° . Contrary to Moir (Trans., 1902, 81, 10), the compound $C_8H_8ON_2$, which is isomeric with 3-cyano-6-hydroxy-2:4-dimethylpyridine (Holtzwardt, *loc. cit.*), is shown to be probably cyanodimethyl-6-pyridone; it gives with phosphorus pentachloride a compound, $C_8H_6N_2$, which is probably 2:4-dicyano-1:3-dimethylcyclobutane.

[With C. IRMSCHER.]—Condensation of Dinitriles with β -Keto-carboxylic Esters and Unsaturated Ketones.—Condensation is incomplete with ketonic esters. From diacetonitrile and ethyl acetoacetate in the presence of pyridine, there is obtained 3-cyano-2:6-dimethyl-4-pyridone, which crystallises in small, white needles, m. p. 280° . With benzodiacetonitrile in the presence of hydrogen chloride, the same ester gives 3-cyano-2-phenyl-6-methyl-4-pyridone, white leaflets, m. p. 244° . From unsaturated ketones and dinitriles, instead of dihydropyridine derivatives being produced, pyridine derivatives are obtained, owing to loss of two hydrogen atoms. Benzylideneacetophenone and diacetonitrile yield 3-cyano-4:6-diphenyl-2-methylpyridine, which crystallises in needles, m. p. 116° ; $(C_{19}H_{14}N_2)_2 \cdot H_2PtCl_6$, golden-yellow leaflets. When heated with concentrated hydrochloric acid at 260° , it gives 4:6-diphenyl-2-methylpyridine-3-carboxylic acid, leaflets, m. p. 264° ; the corresponding amide crystallises with 1 mol. H_2O , but the anhydrous substance, m. p. 216° . When the acid is distilled with soda-lime, 4:6-diphenyl-2-methylpyridine is produced, yellow needles, m. p. 156° . Potassium permanganate oxidises the acid compound to 4:6-diphenylpyridine-2:3-dicarboxylic acid, needles, m. p. 185° (decomp.). Diacetonitrile and anisylideneacetophenone with sodium ethoxide yield 3-cyano-4-p-methoxyphenylphenyl-6:2-methylpyridine, white needles, m. p. 157° . With piperonalacetophenone, 3-cyano-6-phenyl-4-methylenedioxyphenyl-2-methylpyridine, long, white needles, m. p. 238° ; phenyl-p-tolylpropenone gives 3-cyano-4-phenyl-6-p-tolyl-2-methylpyridine, needles, m. p. 165° . Benzodiacetonitrile gives

3-cyano-2:4:6-triphenylpyridine, crystallising in needles, m. p. 220°; *p*-toluidiacetonitrile gives 3-cyano-4:6-diphenyl-2-*p*-tolylpyridine, needles, m. p. 185°. From anisylideneacetophenone and benzodiacetonitrile there is obtained: 3-cyano-2:6-diphenyl-4-*p*-methoxyphenylpyridine, needles, m. p. 181°; and from anisylideneacetophenone and *p*-toluidiacetonitrile, 3-cyano-6-phenyl-4-*p*-methoxyphenyl-2-*p*-tolylpyridine, needle-shaped crystals, m. p. 195°. Piperonalacetophenone yields 3-cyano-2:6-diphenyl-4-methylenedioxyphenylpyridine, m. p. 233°; 3-cyano-6-phenyl-2-*p*-tolyl-4-methylenedioxyphenylpyridine crystallises in needles, m. p. 245°. From cinnamylideneacetophenone, 3-cyano-2:6-diphenyl-4-cinnamylpyridine, needles, m. p. 184°; 3-cyano-6-phenyl-2-*p*-tolyl-4-cinnamylpyridine, needles, m. p. 181°. Benzylideneacetone, benzylidenecamphor, and benzylidenepyrrolone react in a different manner to benzylideneacetophenone.

[With W. SCHUMACHER.]—*Triazole Derivatives from Dinitriles*.—Diacetonitrile condenses with phenylazoimide, forming 1-phenyl-5-methyltriazole-4-carboxylic acid, which crystallises with $\frac{1}{2}$ H₂O, m. p. 111°; the anhydrous substance has m. p. 146°. Benzodiacetonitrile gives 4-cyano-1:5-diphenyltriazole, crystallising in nearly white needles, m. p. 242°, together with 1:5-diphenyltriazole-4-carboxylamide, yellow leaflets, m. p. 173°. J. V. E.

Action of Methyl Iodide on 2:6-Substituted Pyridine-carboxylic Acids. RICHARD TURNAU (*Monatsh.*, 1908, 29, 845—852).—An extension of the author's previous work on abnormal salts of betaines and pyridinecarboxylic acids (*Abstr.*, 1905, i, 546).

2-Methylpyridine-6-carboxylic acid yields a basic hydriodide, HI, C₅NH₃Me·CO·O·C₅NH₄Me·CO₂H, which crystallises from alcohol in long needles and from water in stout prisms, turning brown above 200°, and decomposing at 230°; the same salt is also produced by the interaction of methyl iodide and the anhydrous acid. When shaken with silver chloride, the hydriodide yields 2-methylpyridine-6-carboxylic acid and the normal hydrochloride, m. p. 201° (decomp.) (Pinner and Lewin, *Abstr.*, 1900, i, 409, give 138°).

2-Methylpyridine-6-carboxylic chloride, prepared by the action of thionyl chloride on the acid, forms slender, white needles, m. p. 195° (decomp.).

Quinoline-2-carboxylic acid does not react with methyl iodide at 100°, either with or without the presence of methyl alcohol. Pyridine-2:6-dicarboxylic acid does not react with methyl iodide at 100°, but in methyl-alcoholic solution gives the dimethyl ester. The author was unable to obtain a methiodide of 2-phenylcinchoninic acid as described by Claus and Büttner (*Abstr.*, 1893, i, 731).

Nicotinic acid hydriodide is almost colourless and rather unstable; *isonicotinic acid hydriodide* forms slender, yellow needles, turning brown at 180°, and decomposing above 200°; both these are normal salts. J. C. C.

Electrolytic Reduction of the Indoles. ORESTE CARRASCO (*Gazzetta*, 1908, 38, ii, 301—308).—Tetrahydrocarbazole, 2:3-dimethylindole, 2-methylindole, and 1-methylindole can be completely

reduced electrolytically in an acid solution by means of lead electrodes separated by a porous diaphragm, but indole itself, although largely reduced to the corresponding indoline, undergoes secondary condensations or polymerisations apparently analogous to those occurring during the reduction of quinoline (compare Ahrens, Abstr., 1897, i, 368).

Thus tetrahydrocarbazole yields the carbazoline obtained by Graebe and Glaser (this Journ., 1872, 302); 2:3-dimethylindole gives 2:3-dimethylindoline, the *oxalate* of which, $C_{10}H_{13}N, H_2C_2O_4$, m. p. 134° , was prepared; 2-methylindole yields 2-methylindoline; 1-methylindole, 1-methylindoline, and indole, indoline. In the last case, a solid basic substance is also obtained, which is probably a polymeride of the hypothetical indolenine, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CH}$.

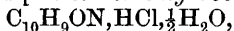
The electrolytic reducing action is related to the number and position of the alkyl groups in the pyrrole nucleus. Thus 2:3-methylindole is reduced more easily than 2-methylindole, and the latter more easily than 1-methylindole, further proof being so afforded of the great stability of the 1-indole derivatives compared with the 2- or 3-derivatives.

T. H. P.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid. II. GUSTAV HELLER and APOSTOLOS SOURLIS (*Ber.*, 1908, 41, 2692—2703. Compare this vol., i, 867).—When *o*-nitrophenyl-hydroxyethyl methyl ketone is reduced with zinc dust and 33% acetic acid in the cold, it yields 4-*keto*-2-methyl-1:4-dihydroquinoline,

$C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{CO} - \text{CH} \end{smallmatrix}$, which crystallises from water in long, colourless,

hydrated needles, m. p. $77-78^\circ$. After remaining over sulphuric acid, it loses all but $\frac{1}{2}H_2O$. 2-Methylquinoline is formed on heating it with methyl sulphate. The *hydrochloride*,



forms small, white rods, which darken at 190° , and decompose at 202° . The *hydriodide*, $C_{10}H_9ON, HI, \frac{1}{2}H_2O$, separates in long, cherry-red rods, m. p. 167° . The *zincichloride*, $(C_{10}H_9ON)_2HCl, ZnCl_2, H_2O$, has m. p. 211° . The *platinichloride*, $(C_{10}H_9ON)_4, H_2PtCl_6, 2H_2O$, forms lemon-yellow prisms, m. p. 207° (decomp.). The *dichromate* occurs in small, orange-yellow rods, m. p. $133-134^\circ$ (decomp.). The *picrate* crystallises in lemon-yellow, six-sided rhombohedra, m. p. 173° . When the base is treated with phosphoryl chloride and phosphorus pentachloride, 4-chloro-2-methylquinoline (Conrad and Limpach, Abstr., 1887, 680) is formed. This crystallises with $1H_2O$, which is lost in a desiccator. 4-*Keto*-1:4-dihydroquinoline-2-carboxylic acid, prepared by oxidising the base with potassium permanganate in alkaline solution, crystallises in colourless needles, m. p. 167° (decomp.); on reduction with hydriodic acid and red phosphorus, it yields quinoline-2-carboxylic acid. When 4-*keto*-2-methyl-1:4-dihydroquinoline is reduced with zinc dust and hydrochloric acid, it yields 2-methylquinoline, of which the following salts are described and some inaccurate statements concerning them in the literature corrected. The hydrochloride (mentioned by the author as not having previously been described, but referred to by

Doebner and von Miller, Abstr., 1883, 602), colourless needles, m. p. 224° (decomp.); the dichromate, yellow needles, m. p. 110° ; the methiodide darkens at 230° , m. p. 234° (decomp.) (Doebner and von Miller, Abstr., 1884, 184, give 195°); the *zincichloride*, colourless rhombohedra, darkens at 205° and decomposes at 245° ; this salt is formed in the reduction of *o*-nitrophenylhydroxyethyl methyl ketone, and if this process is carried on with addition of 1 part of hydrochloric acid, a yield of 52% of the theoretical amount of 2-methylquinoline is obtained. The mercurichloride of 2-methylquinoline has m. p. 184° (Pictet and Bunzl, Abstr., 1889, 971, give 165.5°), and the picrate, m. p. 194° .

2-Methyldihydroquinoline, prepared by reducing 2-methylquinoline with hydrochloric acid and zinc dust, forms feathery crystals, m. p. 178° , and is bimolecular. It differs from the 2-methyldihydroquinoline described by Doebner (Abstr., 1898, i, 385), and the termolecular compound prepared by Ahrens (Abstr., 1897, i, 370). The *picrate* forms small, dark brown rods, which sinter at 95° and decompose at 110° .
J. C. C.

Constitution of Cyanine Dyes. EDUARD VONGERICHTEN and C. HÖFCHEN (*Ber.*, 1908, 41, 3054—3062. Compare Miethe and Book, Abstr., 1904, i, 622, 776).—The authors are in favour of Miethe and Book's constitutional formula for diethylisocyanine iodide (ethyl-red). Their support is based on the following considerations: (1) *Diethylchloroisocyanine iodide*, obtained from the ethiodides of 6-chloroquinoline and 2-methylquinoline, has the formula $C_{23}H_{24}N_2ClI$. It crystallises from alcohol in a mixture of dark reddish-violet, flat needles, and of green crystals resembling ethyl-red, or from chloroform in homogeneous, green crystals. (2) Ethyl-red is a tertiary amine, since it forms a *methiodide*, $C_{24}H_{28}N_2I_2$, which crystallises in minute, brown needles, m. p. about 230° . It is decomposed by solution in alcohol, yielding ethyl-red. (3) In the condensation of the ethiodides of quinoline and 2-methylquinoline, the methyl group of the latter is concerned, as when two hydrogen atoms of this methyl group are replaced by the benzylidene group or by two methyl groups, the condensation with quinoline ethiodide does not take place.

The action of the alkali on the 2-methylquinoline ethiodide is supposed to give the ammonium hydroxide derivative, which is then transformed into the carbinol base, and this by loss of water gives the isobase, $C_6H_4 \begin{smallmatrix} \text{NEt} \cdot \text{C} : \text{CH}_2 \\ \text{CH} : \text{CH} \end{smallmatrix}$, which then condenses with the quinoline ethiodide. The presence of this grouping in ethyl-red is demonstrated by the formation of 1-ethyl-2-quinolone by the oxidation of ethyl-red, or its chloro-derivative with excess of cold potassium ferricyanide solution.

In the preparation of ethyl-red, the yield of dye is considerably lessened when more than two molecular proportions of potassium hydroxide are used for one of 2-methylquinoline methiodide and two of quinoline ethiodide.

6-Chloroquinoline *nitrate* forms colourless, glossy needles, m. p. 176° ; the *chromate*, which can be used for purifying the base, golden-yellow

needles, m. p. 168° , and the *ethiodide*, C_9H_6ClN, EtI , yellow plates, m. p. $168-169^{\circ}$.

α -isoPropylcinchoninic acid has m. p. 150° , not 146° , and α -iso-propylquinoline methiodide, $C_{15}H_{16}NI$, m. p. 182° .

Ethyl-red is not formed when 2-methylquinoline ethiodide is added to a hot solution of quinoline ethiodide and alcoholic potash solution, but is formed when cold solutions are used. This indicates that 1-ethyl-2-quinolone and 1-ethyltetrahydroquinolone, which are formed by the action of hot alkali on the carbinol base, cannot be intermediate products in the formation of the dye.

Cold aqueous potassium hydroxide reacts with 2-methylquinoline ethiodide, yielding a base which is soluble in ether or benzene, and the base appears to be a carbinol base, as it yields 2-methylquinoline ethochloride and water when its dry benzene solution is treated with hydrogen chloride.

1-Methyl-4-quinaldone reacts with phosphorus pentachloride, yielding a crude product, which condenses with 2-methylquinoline ethiodide and alkali to ethyl-red. J. J. S.

Formation of 4-Oxycarbostryl from *o*-Nitrobenzoylactic Acid. KŌICHI MATSUBARA (*J. Coll. Sci. Tōkyō*, 1908, 25, xvii, 1—3).—4-Oxycarbostryl (or 2:4-dihydroxyquinoline) is formed by adding an ammoniacal solution of *o*-nitrobenzoylactic acid to an aqueous solution of ferrous sulphate to which an excess of ammonia has been added. W. H. G.

Action of Acid Esters on Quinoline Bases. JOHANN SPADY (*Ber.*, 1908, 41, 2902—2907).—On heating methyl salicylate with 2-methylquinoline at 180° , a quinaldine dye, $C_{22}H_{20}N_2$, phenol, and carbon dioxide are formed. The reaction is analogous to that between alkyl salicylates and primary or secondary amines studied by Tingle. The *dye* forms microscopic, yellow prisms from benzene, m. p. $190-191^{\circ}$; it dyes silk or cotton yarn similarly to quinaldine-yellow; it yields a sparingly soluble, crystalline hydrochloride and sulphate, and dissolves in concentrated sulphuric acid to a yellow solution having a bluish-green fluorescence.

Methyl salicylate reacts with quinoline at 150° , and energetically at $180-190^{\circ}$, forming a *compound*, $C_{20}H_{22}O_2N_2, \frac{1}{2}H_2O$, crystallising in minute, glistening, orange needles, which sinter at $281-282^{\circ}$, and melt and decompose at a higher temperature. It is soluble in water and alkaline hydroxides, and its solutions, particularly in alcohol or benzene, have a green fluorescence. E. F. A.

Quinonoid Compounds. XVII. *meri*-Quinoneimines. II. RICHARD WILLSTÄTTER and JEAN PICCARD (*Ber.*, 1908, 41, 3245—3252. Compare this vol., i, 475).—as-*meri*-Quinonedimethyldi-*imonium nitrate*, $NO_3 \cdot NH_2 : \langle \text{benzene ring} \rangle : NMe_2 \cdot NO_3, NH_2 \langle \text{benzene ring} \rangle NMe_2$, is prepared by the action of nitrous gases on a solution of *p*-phenylenedimethyldiamine in alcohol and nitric acid, cooled by a mixture of ice

and calcium chloride. The leaflets are green by transmitted light, and show a copper metallic lustre; the solution is red.

Potassium ferri cyanide in aqueous solution, when stirred into an acetic acid solution of the phenylenedimethyldiamine, forms green, rectangular plates of as-*meri-quinonedimethyldi-imonium ferricyanide*, $\text{H}_2\text{Fe}(\text{CN})_6 \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot 2\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$.

Wurster and Schobig obtained a blue dye from tetramethylphenylenediamine which could only be analysed as the ferricyanide (Abstr., 1880, 111). Two *meri-quinonoid* compounds have been obtained by the authors, the blue salt, $\text{C}_{10}\text{H}_{16}\text{N}_2 \cdot \text{H}_3\text{Fe}(\text{CN})_6$, and the new violet salt, $3\text{C}_{10}\text{H}_{16}\text{N}_2 + \text{H}_3\text{Fe}(\text{CN})_6$ minus H_2 .

From benzidine, two *meri-quinonoid* chromates have been obtained: the first, $\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot 4\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot 4\text{H}_2\text{CrO}_4$, is formed when a chromic acid solution is treated at 0° with an excess of an acetic acid solution of benzidine. It is blue, the other is brownish-violet, and is obtained when excess of chromic acid is employed. It has the composition:

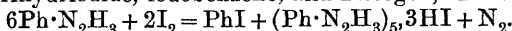
$\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot 3\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot 5\text{H}_2\text{CrO}_4$
(compare Willstätter and Kalb, Abstr., 1906, i, 996).

The quinonoid derivatives of tetramethylbenzidine prepared by Willstätter and Kalb (Abstr., 1904, i, 1050) have been re-examined by the new titration method with stannous chloride. The formula of the yellow *holo-quinonoid* disulphate has been confirmed; the green *meri-quinonoid* dichloride has the constitution:

$\text{NMe}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{Cl} \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot 6\text{H}_2\text{O}$.

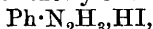
W. R.

Action of Halogens and Hydrogen Halides on Phenylhydrazine. GEORG LOCKEMANN and E. WEINIGER (*Ber.*, 1908, 41, 3102—3108. Compare Fischer, this Journ., 1877, ii, 887; von Meyer, Abstr., 1887, 1042; Stollé, Abstr., 1903, ii, 100).—Iodine acts on phenylhydrazine dissolved in absolute ether, yielding pentaphenylhydrazine trihydriodide, iodobenzene, and nitrogen, thus:

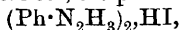


Bromine acts in a similar manner, but chlorine yields only the normal hydrochloride.

Pentaphenylhydrazine trihydriodide, $(\text{Ph} \cdot \text{N}_2\text{H}_3)_5 \cdot 3\text{HI}$, crystallises in thin, colourless leaflets, m. p. 137° . An alcoholic solution of the substance when treated with ether yields the *monohydriodide*,



crystallising in colourless leaflets, m. p. 165° . The *basic salt*,



is prepared by passing small quantities of hydrogen iodide into an ethereal solution of phenylhydrazine; it crystallises in small, colourless needles, m. p. 132° .

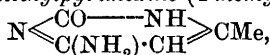
Pentaphenylhydrazine trihydrobromide, $(\text{Ph} \cdot \text{N}_2\text{H}_3)_5 \cdot 3\text{HBr}$, is obtained as a white, crystalline precipitate, m. p. 194 — 197° . Phenylhydrazine hydrobromide and the basic salt, $(\text{Ph} \cdot \text{N}_2\text{H}_3)_2 \cdot \text{HBr}$, melt at 218° and 183° respectively. These differ from the m. p.'s recorded by Le Canu (Abstr., 1903, i, 778), Broche (Abstr., 1894, i, 562), and Ponzio (Abstr., 1906, i, 482).

W. H. G.

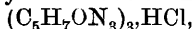
Action of Nitrous Esters on Hydrazine, Phenylhydrazine, and Benzylhydrazine in Alkaline Solution. ROBERT STOLLÉ (*Ber.*, 1908, 41, 2811—2813).—The author had already patented the same process as that since described by Thiele (this vol., ii, 940) for the preparation of azoimide. The best yields (80%) are obtained by boiling an alcoholic solution of hydrazine hydrate with amyl nitrite and sodium ethoxide. By neutralising hydrazine sulphate with aqueous potassium hydroxide and shaking the solution with alcohol, potassium hydroxide, and amyl nitrite, a 70% yield is obtained, and yields of 60% (of the hydrazine sulphate used) result when no alcohol is used. The author has also prepared *isodiazobenzene* salts by the action of ethyl nitrite on phenylhydrazine in presence of sodium or potassium ethoxide (compare Thiele, this vol., i, 927). The *silver* salt is white. Benzylhydrazine when treated with ethyl nitrite and sodium ethoxide in alcoholic solution yields, after some days, a mixture of sodium azoimide and sodium dibenzylhydrazine. J. C. C.

Pyrimidines. XXXVII. Synthesis of 4-Methylcytosine. CARL O. JOHNS (*Amer. Chem. J.*, 1908, 40, 348—355).—Of the two methyl derivatives of cytosine having the methyl group attached to carbon, the 5-methyl compound has already been prepared (Wheeler and Johnson, *Abstr.*, 1904, i, 624), and the 4-methyl compound is described in the present paper. When 6-oxy-2-ethylthiol-4-methylpyrimidine (obtained in an 80—90% yield by condensing ψ -ethylthiocarbamide hydrobromide with ethyl acetoacetate in aqueous sodium hydroxide) is heated with phosphoryl chloride, it is converted into 6-chloro-2-ethylthiol-4-methylpyrimidine, $N \begin{smallmatrix} \swarrow C(SeEt):N \\ \searrow CCl-CH \end{smallmatrix} \triangleright CMe$, b. p. 142°/15 mm., which, with sodium ethoxide, furnishes 6-ethoxy-2-ethylthiol-4-methylpyrimidine, $N \begin{smallmatrix} \swarrow C(SeEt):N \\ \searrow C(OEt)-CH \end{smallmatrix} \triangleright CMe$, b. p. 154°/20 mm.

When 6-chloro-2-ethylthiol-4-methylpyrimidine is heated with alcoholic ammonia under pressure, it yields 6-amino-2-ethylthiol-4-methylpyrimidine, $N \begin{smallmatrix} \swarrow C(SeEt):N \\ \searrow C(NH_2)-CH \end{smallmatrix} \triangleright CMe$, which forms crystals with a tetrahedral outline and a tendency to twinning, m. p. 115—116°. On evaporating this substance with concentrated hydrochloric acid, it gives 2-oxy-6-amino-4-methylpyrimidine (4-methylcytosine),



crystallising in anhydrous, slender, brittle prisms, which do not melt at 310°, but decompose slowly at higher temperatures. At 24°, 0.36 gram is dissolved by 100 c.c. of water. The *monohydrochloride* forms blunt, flat prisms with a hexagonal appearance; it sinters at 280°, and decomposes slowly above 300°. The *basic hydrochloride*,



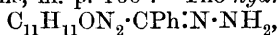
forms pearly scales, which do not melt at 310°. The *nitrate*, clusters of blunt prisms, the *sulphate*, $(C_5H_7ON_3)_2 \cdot H_2SO_4 \cdot H_2O$, large, flat prisms, and the *picrate*, yellow needles, decomposing above 265°, are also described. J. C. C.

4-Keto-compounds of Pyrines. AUGUST MICHAELIS and F. ENGELHARDT (*Ber.*, 1908, 41, 2668—2676).—The authors have prepared keto-compounds of the pyrines by a similar method to that used for the preparation of the azo-derivatives of antipyrine and thiopyrine (Michaelis and Schlecht, *Abstr.*, 1906, i, 614), namely, by treating the corresponding ketopyrazolones or their chloropyrazoles with methyl sulphate. In the present paper, the 4-benzoyl derivatives of the pyrines are described.

4-Benzoyl-1-phenyl-3-methyl-5-pyrazolone is best prepared by converting 1-phenyl-3-methyl-5-pyrazolone into the 5-benzoyl derivative, transforming the recrystallised substance into the 4:5-dibenzoyl derivative, and heating this with alcoholic potash according to Nef's method (*Abstr.*, 1892, 146). Nef (*loc. cit.*) describes 4-benzoyl-1-phenyl-3-methylpyrazolone as forming yellow needles, m. p. 86°, and Knorr (*Abstr.*, 1895, i, 396) gives m. p. 116—117°. The authors find that it exists in two isomeric modifications; the one separates from a mixture of light petroleum and chloroform in large, yellow, quadratic columns, m. p. 86°, and the other crystallises from alcohol in asbestos-like, white needles, m. p. 118°.

4-Benzoylantipyrine, $\begin{array}{c} \text{CMe:NMe} \\ | \text{O} < \text{---} \text{---} \text{---} \text{NPh} \\ \text{CBz:C} \end{array}$, prepared from 4-benzoyl-1-

phenyl-3-methylpyrazolone and methyl sulphate, forms colourless, rhombic columns, m. p. 148°. Its aqueous solution gives a red coloration with ferric chloride. The *hydrochloride* crystallises in hexagonal tablets, m. p. 218°. The *phenylhydrazone*, $\text{C}_{11}\text{H}_{11}\text{ON}_2\cdot\text{CPh:N:NHPh}$, forms quadratic columns, m. p. 160°. The *hydrazone*,



crystallises in hexagonal prisms, m. p. 215°; with nitrobenzaldehyde it gives a yellow, insoluble compound, m. p. 350°; the *hydrochloride* of the hydrazone forms yellow, quadratic columns, m. p. 202°. The *oxime* of benzoylantipyrine, $\text{C}_{11}\text{H}_{11}\text{ON}_2\cdot\text{CPh:N}\cdot\text{OH}$, crystallises in long, hexagonal prisms, m. p. 197°.

4-*a*-Hydroxybenzoylantipyrine, $\begin{array}{c} \text{CMe} = = = = \text{N}\cdot\text{Me} \\ | \text{O} < \text{---} \text{---} \text{---} \text{NPh} \\ \text{C(CHPh}\cdot\text{OH):C} \end{array}$, prepared

by reducing 4-benzoylantipyrine with sodium amalgam, crystallises in long, white, hexagonal prisms, m. p. 173°. It gives a strong antipyrine reaction with ferric chloride, and, on warming with dilute hydrochloric acid, furnishes benzylideneantipyrine hydrochloride (Knorr, *Abstr.*, 1884, 1378), which is found to have the formula $\text{C}_{20}\text{H}_{28}\text{O}_2\text{N}_4\cdot 2\text{HCl}\cdot 7\text{H}_2\text{O}$. Benzoylantipyrine and *a*-hydroxybenzoylantipyrine have no striking poisonous effects when administered to dogs.

5-Chloro-4-benzoyl-1-phenyl-3-methylpyrazole methiodide, prepared by treating the pyrazole (Michaelis and Bender, *Abstr.*, 1903, i, 288) with methyl sulphate and subsequently adding potassium iodide to the aqueous solution, forms glistening, quadratic tablets, m. p. 166°. With sodium hydroxide, it yields 4-benzoylantipyrine, and with potassium

hydrogen sulphide it gives 4-benzoylthiopyrine, $\begin{array}{c} \text{CMe:NMe} \\ | \text{S} < \text{---} \text{---} \text{---} \text{NPh} \\ \text{CBz:C} \end{array}$, crystallising in flat, quadratic prisms, m. p. 217°. The *phenylhydr-*

azone, $C_{11}H_{11}N_2S \cdot CPh \cdot N \cdot NHPh$, crystallises in microscopic, yellowish-white needles, m. p. 280° , and the *methiodide* forms long, hexagonal prisms, m. p. 168° . When the latter is heated, it yields 4-benzoyl- ψ -thiopyrine (Michaelis and Lehmann, this vol., i, 691).

4-Benzoylanilopyryne, $\begin{array}{c} \text{OMe}=\text{NMe} \\ | \text{NPh} \diagup \quad \diagdown \text{NPh} \\ \text{OBz}=\text{C} \end{array}$, prepared from 5-chloro-

4-benzoyl-1-phenyl-3-methylpyrazole methiodide and aniline, forms dark yellow, rhombic tablets, m. p. 159°; the *phenylhydrazone*,

$\text{C}_{17}\text{H}_{16}\text{H}_3\cdot\text{CPh}\cdot\text{N}\cdot\text{NHPH}$,
forms long, yellowish-white needles, m. p. 178°. The *methiodide*
crystallises in large, colourless or pale rose-coloured, quadratic tablets,
m. p. 172°, and, on heating, furnishes 4-benzoyl- ψ -anilopyrrole (4-benzoyl-5-
methylanilino-1-phenyl-3-methylpyrazole), $\text{N} \begin{smallmatrix} \text{NPh} \cdot \text{C} \cdot \text{NMePh} \\ \text{CMe} \cdot \text{CBz} \end{smallmatrix}$, which
forms hexagonal columns, m. p. 144.5°.

The *methiodide* of 5-amino-4-benzoyl-1-phenyl-3-methylpyrazole (Michaelis and Bender, *loc. cit.*) crystallises in glistening, quadratic tablets, m. p. 238°. The *methochloride* forms glistening, white leaflets, and with aqueous sodium hydroxide gives 4-benzoyliminopyrine (2:5-imino-4-benzoyl-1-phenyl-2-methyldihydropyrazole),

$$\begin{array}{c} \text{CMe} \equiv \text{NMe} \\ | \quad \text{NH} \quad \diagup \quad \diagdown \\ \text{CBz} \equiv \text{C} \quad \text{NPh} \end{array}$$

which crystallises in small, yellow needles, m. p. 155°. J. C. C.

Piperazine Phosphates and Arsenates. A. ASTRUC and R. BRENTA (*Bull. Soc. chim.*, 1908, [iv], 3, 963—966).—Piperazine forms with phosphoric acid the two salts: $C_4H_{10}N_2, H_2PO_4, H_2O$ and

$$\text{C}_4\text{H}_{10}\text{N}_2, 2\text{H}_3\text{PO}_4.$$

Of these, both are acid to phenolphthalein, and the first is alkaline and the second neutral to helianthin. The potassium salt,

$$\text{C}_4\text{H}_{10}\text{N}_2, \text{KH}_2\text{PO}_4,$$

is neutral to phenolphthalein and alkaline to helianthin. The two arsenates are similar in constitution to the phosphates, and show like behaviour with the indicators named. The salts of the type

$$\text{C}_4\text{H}_{10}\text{N}_2, \text{H}_3\text{PO}_4, \text{H}_2\text{O}$$

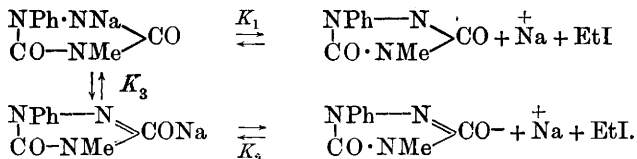
may be regarded as analogous with disodium hydrogen phosphate or arsenate, and those of the type $C_4H_{10}N_2 \cdot 2H_3PO_4$ may perhaps be regarded as salts of the acid, $2H_3PO_4$, mentioned by Giran (this vol., ii, 686).

T. A. H.

T. A. H.

Urazoles XIV. Reactions between Tautomeric Acids and Salts with Diazomethane and Alkyl Haloids. SALAMON F. ACREE, J. M. JOHNSON, R. F. BRUNEL, G. H. SHADINGER, and SIDNEY NIRDLINGER (*Ber.*, 1908, 41, 3199—3236. Compare this vol., ii, 163).—1-Phenylurazole and its derivatives are moderately strong acids, and yield salts not markedly hydrolysed, the dissociation constants of which are easily determined. They also react easily with alkyl halides, and as no slow tautomeric changes occur and the isomeric ethers so obtained are stable, these compounds are very

suitable for an investigation of tautomeric phenomena. It has now been proved with practical certainty that both forms of the salts of 1-phenyl-4-methylurazole exist in solution, and that the alkyl halide reacts with the enolic as well as with the ketonic anion to form the O- and N-ethers.



If K_3 is the alkylation constant, x the velocity of formation of the N-ether, and x' that of the O-ether, then

$$\frac{dx}{dt} = K(C_{\text{salt}} - x - x')(C_{\text{EtI}} - x - x');$$

$$\frac{d(x+x')}{dt} = K + K'(C_{\text{salt}} - x - x')(C_{\text{EtI}} - x - x'), \quad \text{and} \quad K/K' = x/x' = \text{N-ether/O-ether}.$$
The ratio between the quantities of the two stable alkyl or other derivatives from tautomeric substances must be independent of the time, and the ratio between the quantity of ethers and the alkylating reagent is dependent on three factors: (1) the relative reactivities of the tautomeric isomerides with the reagent; (2) the ratio of the isomerides if these exist in equilibrium, and (3) the velocity of transformation of one isomeride into the other as soon as the equilibrium is disturbed.

The hypotheses of Comstock, Wheeler, and Nef are discussed from this point of view, and considered to be erroneous. The theory (*loc. cit.*) has been confirmed and extended to all tautomeric phenomena. It would appear that the equilibrium is established between the molecules of the salt, and not the anions, as the addition of sodium iodide to solutions of ethyl iodide and sodium urazole does not cause a catalytic alteration in the ratio of O-ether to N-ether, although the nature of the urazole salt has a large effect. Thus ethyl iodide gives with the sodium, potassium, barium, and zinc salts of 1-phenyl-4-methylurazole in a 0.3*N* solution in 40% alcohol at 60°, velocity constants: 0.42, 0.36, 0.28, and 0.05. The sodium salt of 1-phenyl-2-methylurazole yields with methyl iodide, 98% of the N-ether and 2% of the O-ether, whereas the silver salt gives a 50% yield of both. Experiments are quoted to show that by using the potassium and silver salts of 1-phenyl-4-methylurazole with ethyl iodide at 22°, 60°, and 90°, constant values of the ratio of two ethers are obtained; thus indicating that the equilibrium in solution is not markedly affected by temperature.

The effect of solvent has also been studied; thus the silver salt with ethyl iodide at 60° gives the ratio of the two ethers: in 40% alcohol, 40:60; in absolute alcohol, 33:67; in acetone, 39.5:60.5; in water, 37:63, and in ether, 35:65.

When different alkyl iodides are employed, this ratio of N- to O-ether is altered. The silver salt of 1-phenyl-2-methylurazole reacts quickly with methyl iodide to form 50% of each, and with ethyl iodide only slowly to give 90% O- and 10% N-ether.

Concentration has practically no effect; thus the sodium salt of

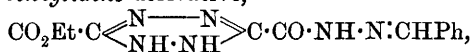
1-phenyl-4-methylurazole with ethyl iodide in 0.3, 0.15, 0.1, and 0.075*N* solutions gave the ratio 94 N- : 6 O-ether. W. R.

Action of Hydrazine Hydrate on Ethyl Bisdiazooacetate. THEODOR CURTIUS and EUGEN RIMELE (*Ber.*, 1908, 41, 3108—3116).—In continuation of the investigation of Curtius, Darapsky, and Bockmühl (this vol., i, 144), the behaviour of ethyl bisdiazooacetate towards hydrazine has been studied. It is found that the carbethoxy-groups of ethyl bisdiazooacetate are attacked by hydrazine hydrate, the first compound formed being ethyl bisdiazooacetate hydrazide, which is acted on by further quantities of hydrazine, yielding bisdiazooacetic acid dihydrazide. In this respect, ethyl bisdiazooacetate behaves like ethyl terephthalate; in both compounds, the carbethoxy-groups occupy 1 : 4-positions.

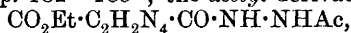
Ethyl bisdiazooacetate hydrazide is converted by nitrous acid into ethyl tetrazinedicarboxylate azoimide, and the dihydrazide into tetrazinedicarboxylic acid diazoimide. Ethyl bisdiazooacetate is most readily prepared by the action of diazomethane on an ethereal solution of bisdiazooacetic acid.

Ethyl bisdiazooacetate hydrazide, $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$,

prepared by the action of hydrazine hydrate on ethyl bisdiazooacetate in alcoholic solution, crystallises in small, soft, pale yellow needles, m. p. 228—231° (decomp.); the *hydrochloride*, $\text{C}_6\text{H}_{10}\text{O}_3\text{N}_6 \cdot \text{HCl}$, crystallises in slender, golden-yellow needles, m. p. 212°. The corresponding *methyl ester*, $\text{C}_5\text{H}_8\text{O}_2\text{N}_6$, has m. p. 211°. The following derivatives of the ethyl ester are prepared by shaking its solution in dilute hydrochloric acid with the aldehyde or by heating the hydrazide with the ketone: the *benzylidene* derivative,



is obtained as a yellow, crystalline powder, decomposing at 233—234°; the *p-methoxybenzylidene* derivative, $\text{C}_{14}\text{H}_{16}\text{O}_3\text{N}_6$, sinters and melts at 237°; the *propylidene* derivative, $\text{CO}_2\text{Et} \cdot \text{C}_2\text{H}_5\text{N}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe}_2$, crystallises in slender, pale yellow needles, m. p. 115°; the *α-phenylethylidene* derivative, $\text{C}_{14}\text{H}_{16}\text{O}_3\text{N}_6$, crystallises in small, glistening, pale yellow needles, m. p. 182—185°; the *acetyl* derivative,

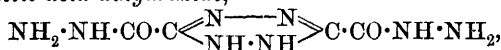


prepared by acting on the hydrazide with acetic anhydride, forms a yellow powder, m. p. 166°.

Ethyl tetrazinedicarboxylate azoimide, $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{N} \cdot \text{N} \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{N}_3$, pre-

pared by treating a solution of the hydrazide hydrochloride with sodium nitrite, crystallises in violet-red leaflets, decomposes when heated, and liberates 2 mols. of nitrogen when its alcoholic solution is boiled.

Bisdiazooacetic acid dihydrazide,



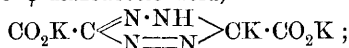
obtained by the action of a large excess of hydrazine hydrate on ethyl bisdiazooacetate, crystallises in golden-yellow spangles, m. p. 265—275°

(decomp.); the *hydrochloride*, $C_6H_5O_2N_8 \cdot 2HCl$, and *dibenzylidene* derivative, $C_2H_2N_4(CO \cdot NH \cdot N : CHPh)_2$, a yellow powder, m. p. above 290° , were prepared and analysed.

Hydrazine bisdiazooacetate, $C_2H_2N_4(CO_2 \cdot N_2H_5)_2$, prepared by adding hydrazine hydrate to an alcoholic solution of bisdiazooacetic acid, crystallises in small, yellow needles, m. p. $183-188^\circ$. *Ammonium hydrogen bisdiazooacetate*, $CO_2H \cdot C_2H_2N_4 \cdot CO_2NH_4$, prepared by adding the acid (1 mol.) to the neutral ammonium salt (1 mol.), crystallises in orange-red needles, m. p. 192° . In the same way are obtained: *sodium hydrogen bisdiazooacetate*, $C_4H_8O_4N_4Na \cdot H_2O$, yellow needles, and *potassium hydrogen bisdiazooacetate*, $C_4H_8O_4N_4K$. *Barium bisdiazooacetate*, $C_4H_2O_4N_4Ba \cdot 2H_2O$, is obtained as a yellow precipitate by adding barium chloride to an alcoholic solution of the acid. Attempts to prepare acid barium and silver salts were unsuccessful.

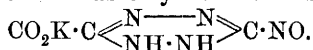
W. H. G.

ψ -Diazooacetic Acid. ERNST MÜLLER (*Ber.*, 1908, 41, 3116—3139). —A continuation of the investigations by Curtius, Darapsky, and Müller (compare Abstr., 1906, i, 939; 1907, i, 21, 262, 359, 450, 451). When ethyl diazoacetate is treated with a concentrated aqueous solution of potassium hydroxide, it is converted into a tripotassium salt of ψ -diazooacetic acid,



the formation of this salt is greatly accelerated by the presence of ethyl alcohol. It is converted by dilute acetic acid into the dipotassium salt, $CO_2K \cdot C \begin{array}{c} \text{N} \cdot \text{NH} \\ \text{N} = \text{N} \end{array} > CH \cdot CO_2K$, which, with glacial acetic acid, yields

the potassium hydrogen salt, $CO_2K \cdot C \begin{array}{c} \text{N} \cdot \text{NH} \\ \text{N} = \text{N} \end{array} > CH \cdot CO_2H$. That the latter has this constitution follows from the fact that it yields a nitroso-derivative which undoubtedly has the constitution



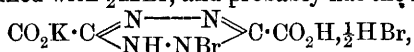
Potassium ψ -diazooacetate is hydrolysed by boiling acids, yielding glyoxylic acid (2 mols.), hydrazine (1 mol.), and nitrogen (1 mol.).

ψ -Diazooacetic acid has not yet been isolated, but an aqueous solution of the acid is obtained by treating the lead salt with hydrogen sulphide; the yellow solution thus obtained has a decided acid reaction, and gives the reaction characteristic of the ψ -series, namely, evolution of nitrogen and formation of hydrazine and glyoxylic acid when warmed with acids.

Unlike ψ -diazooacetamide, which is readily converted by a warm solution of potassium hydroxide into bisdiazooacetamide (compare Abstr., 1906, i, 939), potassium ψ -diazooacetate is converted only with difficulty into potassium bisdiazooacetate. The formation of potassium bisdiazooacetate from potassium diazoacetate observed by Hantzsch and Lehmann (Abstr., 1901, i, 678) must therefore take place through the intermediate ψ -diazooacetate.

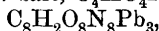
An aqueous solution of potassium ψ -diazooacetate is converted by bromine into potassium hydrogen bromodihydratetrazinedicarboxylate;

it is always obtained with $\frac{1}{2}$ HBr, and probably has the formula



since it is also formed by the action of bromine on potassium bisdiazooacetate, and is reduced by hydrogen sulphide to bisdiazooacetic acid. All attempts to remove the $\frac{1}{2}$ HBr lead to the decomposition of the substance; thus it is converted by an aqueous solution of potassium acetate into potassium tetrazinedicarboxylate, and by sulphurous acid into tetrazinecarboxylic acid.

Tripotassium ψ -diazooacetate, $\text{C}_4\text{HO}_4\text{N}_4\text{K}_3 \cdot 2\text{H}_2\text{O}$, is obtained as a pale yellow precipitate, which becomes brownish-yellow when exposed to light; the *dipotassium* salt, $\text{C}_4\text{H}_2\text{O}_4\text{N}_4\text{K}_2 \cdot \text{H}_2\text{O}$, as a lemon-yellow precipitate; the *potassium hydrogen* salt, $\text{C}_4\text{H}_3\text{O}_4\text{N}_4\text{K} \cdot \text{H}_2\text{O}$, as a bright yellow precipitate; the *silver* salt, $\text{C}_4\text{HO}_4\text{N}_4\text{Ag}_3$, and *lead* salt,

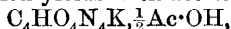


as yellow precipitates by adding silver nitrate or lead acetate to aqueous solutions of the dipotassium salt. *Dipotassium ammonium ψ -diazooacetate*, $\text{C}_4\text{HO}_4\text{N}_4\text{K}_2\text{NH}_4$, is obtained as hard, yellow leaflets by saturating a cold aqueous solution of the potassium salt with ammonia.

Potassium hydrogen bromodihydrotetrazinedicarboxylate,



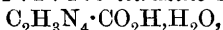
forms a brick-red powder; it is converted by an aqueous solution of potassium acetate into *potassium tetrazinedicarboxylate*, $\text{C}_4\text{O}_4\text{N}_4\text{K}_2$, a violet-red precipitate, which yields with acetic acid the salt,



obtained as an orange powder; the latter loses acetic acid at 90° , yielding *potassium hydrogen tetrazinedicarboxylate*, $\text{C}_4\text{HO}_4\text{N}_4\text{K}$, a carmine-red powder.

Ethyl tetrazinedicarboxylate, $\text{C}_2\text{N}_4(\text{CO}_2\text{Et})_2$, is prepared by the action of nitrous gases on an ethereal solution of ethyl bisdiazooacetate; it crystallises in long, purple prisms, m. p. $105\text{--}106^\circ$ (decomp.).

Potassium nitrosodihydrotetrazinecarboxylate, $\text{CO}_2\text{K} \cdot \text{C}_2\text{H}_2\text{N}_4 \cdot \text{NO}$, is obtained by adding acetic acid to an aqueous solution of potassium ψ -diazooacetate and nitrite as a bright yellow precipitate, m. p. 170° (decomp.). It is converted by hydrogen sulphide into a *sulphur dioxide additive* compound of *potassium 1:2-dihydro-1:2:4:5-tetrazine-3-carboxylate*, obtained as a pale yellow, crystalline substance. A strong aqueous solution of this substance, when treated with sulphuric acid, yields *1:2-dihydro-1:2:4:5-tetrazine-3-carboxylic acid*,



which crystallises in glistening, yellow scales, m. p. $93\text{--}105^\circ$ (decomp.). When heated at $60\text{--}70^\circ$ for forty-five minutes, it is converted into 1-amino-3:4-triazole (compare Bülow, Abstr., 1906, i, 905; 1907, i, 99).

W. H. G.

So-called Ethyl *iso*Diazooacetate. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1908, 41, 3140—3160).—Contrary to the statement of Hantzsch and Lehmann (*Abstr.*, 1901, i, 678), the compound described by these authors as ethyl

potassioisodiazacetate, $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{N} \\ \diagup \\ \text{N} \end{smallmatrix}\text{K}$, when treated with dilute acid liberates nitrogen; the solution is then found to contain ethyl glyoxylate (2 mols.) and hydrazine (1 mol.). If the solution is boiled for some time, the ethyl glyoxylate is hydrolysed, and the glyoxylic acid reacts with the hydrazine, yielding ammonia and oxalic acid. It is therefore evident that the compound is not ethyl potassioisodiazacetate, since this substance when hydrolysed would yield only ethyl oxalate and hydrazine. The compound prepared according to the directions of Hantzsch and Lehmann is shown to have the composition $\text{CO}_2\text{Et}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{NH} \\ \text{N}=\text{N} \end{smallmatrix}\text{CK}\cdot\text{CO}_2\text{Et}, \text{KOEt}$; that is, it is an additive product of *potassium ethoxide* with *potassium diethyl ψ -diazacetate* (compare Müller, preceding abstract), which, when hydrolysed decomposes, thus: $\text{C}_2\text{H}_5\text{N}_4(\text{CO}_2\text{Et})_2 \xrightarrow{2\text{H}_2\text{O}} 2\text{CO}_2\text{Et}\cdot\text{CHO} + \text{N}_2\text{H}_4 + \text{N}_2$. An aqueous solution of this substance, contrary to the statements of Hantzsch and Lehmann (*loc. cit.*), yields with silver nitrate the *silver* salt, $\text{C}_8\text{H}_{11}\text{O}_4\text{N}_4\text{Ag}, \frac{1}{2}\text{Ag}_2\text{O}$, obtained as a greenish-black precipitate, and with mercuric chloride a dense, yellowish-brown precipitate of a complex *mercury* salt. The potassium salt is converted by an aqueous solution of potassium hydroxide (1 : 1) into potassium ψ -diazacetate (compare Müller, *loc. cit.*).

Sodium diethyl ψ -diazacetate, $\text{CO}_2\text{Et}\cdot\text{C}_2\text{HN}_4\text{Na}\cdot\text{CO}_2\text{Et}, \text{NaOEt}$, described by Hantzsch and Lehmann as ethyl sodioisodiazacetate, $\text{CO}_2\text{Et}\cdot\text{CNaN}_2, \frac{1}{2}\text{H}_2\text{O}$, is best prepared by the action of sodium ethoxide, prepared by Brühl's method, on ethyl diazoacetate.

The substance which separates as an oil when an aqueous solution of either of the above salts is treated with dilute acids could not be purified, and all attempts to prepare derivatives were unsuccessful.

W. H. G.

Products of the Transformation of Ethyl Diazoacetate under the Influence of Alkalis. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1908, 41, 3161—3172).—A summary of the results obtained during the investigation on the behaviour of ethyl diazoacetate towards alkalis (compare Curtius, Darapsky, and Müller, *Abstr.*, 1906, i, 939; 1907, i, 21, 262, 359, 450, 451, and preceding abstract; Müller, preceding abstract).

W. H. G.

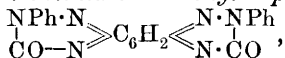
Ethylenediguanide. EMIL DITTLER (*Monatsh.*, 1908, 29, 645—652).—Whilst monoamines form additive compounds (the mono-substituted diguanides) with dicyanodiamide, Ziegelbauer observed (*Abstr.*, 1897, i, 142) that the action of *o*-phenylenediamine on dicyanodiamide leads to the formation of ammonia and *o*-phenylene-diguanide, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{NH}\cdot\text{C}(\text{NH}) \\ \text{NH}\cdot\text{C}(\text{NH}) \end{smallmatrix}\text{NH}$. With the object of determining if this formation of a disubstituted diguanide is a general reaction of diamines, the author has studied the action of ethylenediamine on dicyanodiamide, and has found that here, also, the reaction leads to the formation of ammonia and a disubstituted diguanide.

Ethylenediguanide, $C_2H_4 \left\langle \begin{smallmatrix} NH \cdot C(NH) \\ NH \cdot C(NH) \end{smallmatrix} \right\rangle NH$, formed by the action of ethylenediamine on dicyanodiamide at 80—150°, is isolated as the *sulphate* of the copper derivative, $(C_4H_8N_5)_2Cu \cdot H_2SO_4 \cdot 3H_2O$, which separates in rose-red, microscopic needles, and dissolves sparingly in water, but readily in aqueous alkalis, forming red solutions. The *hydrogen sulphate*, $C_4H_9N_5 \cdot H_2SO_4$, forms hygroscopic, white needles, and gives characteristic reactions with nickel, cobalt, gold, and platinum salts, and with chromic, picric, and picrolonic acids. The *sulphate*, $(C_4H_9N_5)_2 \cdot H_2SO_4$, *hydrogen chloride*, $C_4H_9N_5 \cdot 2HCl$, *chromate*, $(C_4H_9N_5)_2 \cdot H_2CrO_4$, and *picrolonate*, $C_4H_9N_5 \cdot C_{10}H_8O_5N_4$, are described. The free base, liberated from the sulphate by cold baryta water, is obtained as a syrup, which decomposes above 150°, yielding complicated products. The action of boiling baryta water on the sulphate, on the other hand, leads to the formation of ethylenediamine. G. Y.

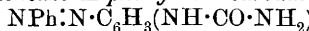
Aromatic Monatomic Cyanamides. PAUL PIERRON (*Ann. Chim. Phys.*, 1908, [viii], 15, 145—278).—Mainly a résumé of work already published (Abstr., 1905, i, 125; 1906, i, 772; 1907, i, 121); the following compounds are described for the first time: *ψ-cumylcyanamide*, $C_6H_2Me_3 \cdot NH \cdot CN$, colourless prisms, m. p. 126°; the *carbamide* and the *benzoyl* derivatives melt at 237° and 94° respectively; *p-iodophenylcyanamide*, $C_6H_4I \cdot NH \cdot CN$, m. p. 110°, and the *carbamide*, m. p. 244°; *benzeneazo-m-ethoxycyananilide*, $CN \cdot NH \cdot C_6H_3(OEt) \cdot N : NPh$, m. p. 81—82°; and the following corrections in melting points are recorded: the benzoyl derivative of benzeneazo-*p*-cyananilide has m. p. 191°, and not 161°; benzeneazo-*m*-tolylcarbamide has m. p. 186°, and not 152°, and benzeneazo-*p*-cyano-*o*-ethoxyanilide has m. p. 120°, and not 121° (compare Abstr., 1906, i, 772).

With the view of preparing the corresponding dicyanamides and their derivatives, the author has examined the behaviour of the phenylenediamines with cyanogen bromide.

m-Phenylenediamine yields *m-phenylenedicyanamide*, $C_6H_4(NH \cdot CN)_2$, m. p. 205—207°. When heated rapidly, it condenses with diazobenzene chloride to yield the following products: (1) *benzeneazo-m-phenylenedicyanamide*, $C_6H_2(CN \cdot NH)_2(N : NPh)_2$, m. p. 250—252°; (2) *m-bis-keto-2-phenylbenzotriazine* (*dibenzeneazodicarbonyl-m-phenylenediamine*)



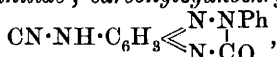
m. p. 310°; (3) *benzeneazo-m-phenylenedicarbamide*,



m. p. 238—240°; (4) *imino-m-cyanamido-2-phenylbenzotriazine* (*benzeneazoaminocarbonylaminophenylcyanamide*; *iminocarbonylcyanochrysoidine*), $CN \cdot NH \cdot C_6H_3 \begin{array}{c} N \cdot NPh \\ \diagup \quad \diagdown \\ N \cdot C(NH) \end{array}$, m. p. 200° when heated rapidly, or 290° when gradually heated; the *hydrochloride* has m. p. 230°.

m-Cyanaminophenylcarbamide, $CN \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, m. p. 210°, has a pronounced sweet taste, and condenses with diazobenzene chloride to form *keto-m-cyanamido-2-phenylbenzotriazine* (*benzeneazo-*

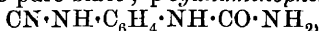
carbonyl-*m*-amidocyananilide; carbonylcyanochrysoidine),



m. p. 258°; the corresponding *carbamide* has m. p. 300°, and, on reduction, it yields *keto-m-cyanamido-2-phenyldihydrobenzotriazine* (*dihydrocarbonylcyanochrysoidine*), $\text{CN} \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \llcorner \\ \text{NH} \cdot \text{NPh} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, m. p. 210°.

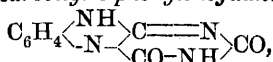
m-Cyanoaminoacetanilide, $\text{CN} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, m. p. 205—207°, condenses with diazobenzene chloride to form *benzeneazoacetamido-cyananilide* (*acetylcyanochrysoidine*), $\text{CN} \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NAc}) \cdot \text{N} \cdot \text{NPh}$, m. p. 246°; *cyanochrysoidine*, $\text{CN} \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NH}) \cdot \text{N} \cdot \text{NPh}$, has m. p. 186°, and the *benzoyl* derivative has m. p. 233°.

In the case of *p*-phenylenediamine, the dicyanamide derivative could not be isolated in the pure state; *p*-cyanaminophenylcarbamide,



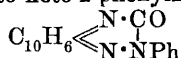
has m. p. 255°, and does not form a stable compound with diazobenzene chloride.

o-Phenylenediamine does not form cyanamide derivatives, but yields *o*-phenyleneguanidine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \llcorner \\ \text{NH} \\ \text{NH} \end{smallmatrix} > \text{C} \cdot \text{NH}$, m. p. 222°, when treated with cyanogen bromide; the *benzoyl* derivative has m. p. 236°; it is converted into *iminodicarbonyl-o*-phenyleneguanidine,

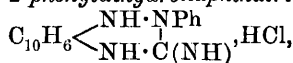


by the further action of cyanogen bromide, and the same compound is obtained by the action of cyanogen bromide on *o*-phenylenediamine in the presence of sodium hydrogen carbonate, or by the condensation of *o*-phenyleneguanidine with biuret.

β -Naphthylcyanamide condenses with diazobenzene chloride to form *imino-2-phenylnaphthatriazine* (*benzeneazoiminocarbonyl- β -naphthylamine*), $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \llcorner \\ \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{C}(\text{NH}) \end{smallmatrix}$, m. p. 160°, and the same compound is obtained by the action of cyanogen bromide on benzeneazo- β -naphthylamine; the *hydrochloride*, m. p. 230°, and the *dichromate* have been prepared. When the base is treated with acids, alkalis, or benzoyl chloride, it is converted into *keto-2-phenylnaphthatriazine*,



(compare Goldschmidt and Rosell, *Abstr.*, 1890, 614; Busch, *Abstr.*, 1900, i, 59), and, on reduction with stannous chloride, it yields the *hydrochloride* of *imino-2-phenyldihydronaphthatriazine*,



m. p. 242—245°.

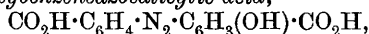
M. A. W.

Azo-compounds of Salicylic Acid. EUGÈNE GRANDMOUGIN and JULIEN GUISAN (*Chem. Zentr.*, 1908, ii, 310—311; from *Rev. gén. Matières Colorantes*, 1908, 12, 129—137. Compare *Abstr.*, 1907, i,

987).—When aminosalicyclic acid and *p*-phenylenediamine are reduced by means of sodium hydrogen sulphite in hot aqueous solution, *p*-nitrobenzeneazosalicyclic acid, m. p. 256°, is formed.

m-Tolueneazosalicyclic acid is a yellow, crystalline substance, m. p. 208°; *acetyl* compound, m. p. 155°. *p*-Tolueneazosalicyclic acid forms yellowish-brown needles, m. p. 214°; the sodium salt is known as flavazole, and the *acetyl* compound, $C_{16}H_{14}O_3N_2$, pale yellow crystals, m. p. 159·5°. *m*-Nitrotolueneazosalicyclic acid, $C_{14}H_{11}O_5N_3$, prepared from diazotised *m*-nitro-*p*-toluidine and salicylic acid in alkaline solution, forms yellow needles, m. p. 242°; the *acetyl* compound, $C_{16}H_{13}O_6N_3$, large, yellow crystals, m. p. 171°.

o-Nitrotolueneazosalicyclic acid, prepared in like manner, crystallises in brown needles, m. p. 210°, which, when reduced with hydrogen sulphite, form a *triazole* compound; the *acetyl* compound crystallises in brownish-yellow needles, m. p. 180°. *p*-Acetylaminobenzeneazosalicyclic acid, $C_{15}H_{13}O_4N_3$, forms a brownish-yellow, crystalline powder, m. p. 245° (decomp.); the *diacetyl* compound, yellow needles, m. p. 200° (decomp.). When this is treated with strong sulphuric acid, *p*-aminobenzeneazosalicyclic acid, $NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H$, is produced, which forms a grey, crystalline powder, m. p. 230° (decomp.), and gives with carbonyl chloride the diaminodiphenyl derivative of carbamide, $CO[NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H]$. *p*-Hydroxybenzeneazosalicyclic acid, $C_{13}H_{10}O_4N_2$, prepared by the diazo-reaction from *p*-aminobenzeneazosalicyclic acid, or from *p*-aminophenol and salicylic acid, or from aminosalicyclic acid and phenol, crystallises in brown needles, m. p. 236°. *p*-Ethoxybenzeneazosalicyclic acid, $C_{15}H_{14}O_4N_2$, prepared from diazotised phenetidine and salicylic acid, is a green, crystalline powder, m. p. 208°; the *acetyl* compound, yellow crystals, m. p. 158·5°. *m*-Carboxybenzeneazosalicyclic acid,



prepared from *m*-aminobenzoic acid, has m. p. about 280° (decomp.). *o*-Carboxybenzeneazosalicyclic acid, from anthranilic acid, forms yellow crystals, m. p. 219° (with sublimation). *m*-Sulphobenzeneazosalicyclic acid, prepared from metanilic acid, gives a crystalline sodium salt of the composition $Na \cdot C_{13}H_9O_5N_2S \cdot 3H_2O$. When diazotised nitroaniline and diazotised 2-naphthylamine-7-sulphonic acid act on salicylic acid, some tris-azo-compound and phenol-bis-azo-compound are found together with the bis-azo-derivative. J. V. E.

Aromatic and Aliphatic *iso*Diazo-compounds (*iso*Azotates) from Hydrazines. JOHANNES THIELE (*Ber.*, 1908, 41, 2806—2811).—When phenylhydrazine is treated with an alkyl nitrite and alkali, it is smoothly converted into the corresponding metallic salt of *iso*-diazobenzene, nitrogen monoxide being formed at the same time. In the well-known production of diazonium salts from phenylhydrazine salts and nitrous acid and from nitrosophenylhydrazine, the author has been able to show that nitrogen monoxide is formed here also, and he considers that the process involves the intermediate formation of dinitrosohydrazines, $R \cdot N(NO) \cdot NH \cdot NO$, or the alkali salts of their tautomerides. It is probable, also, that in the interaction of hydrazine

and nitrous acid (Dennstedt and Göhlich, Abstr., 1898, ii, 425), dinitrosohydrazine is formed, which, with the possible intermediate formation of a compound $N_3 \cdot NO$, may decompose according to the equation: $NO \cdot NH \cdot NH \cdot NO = N_2O + N_2 + H_2O$. Further, azoimide and nitrous acid decompose, thus: $N_3H + HNO_2 = N_2 + N_2O + H_2O$, so that for each molecule of nitrogen monoxide formed in the above reaction one molecule of azoimide is lost.

Nitrosophenylhydrazine forms salts with bases, and, on heating its solutions in indifferent solvents, it decomposes into aniline and nitrogen monoxide; moreover, it does not form nitrosohydrazones with acetaldehyde or benzaldehyde, and it is suggested that its constitution may be represented as $C_6H_5 \cdot NH \cdot NH \cdot NO$, or the tautomeric expression.

Nitrosobenzylhydrazine gives the first two reactions, but gives the normal hydrazone with benzaldehyde, so that the symmetrical formula $CH_2Ph \cdot NH \cdot NH \cdot NO$ cannot be assigned to it. Benzylhydrazine also gives the corresponding isodiazotate, and, as this may be regarded as belonging to the aliphatic series, it is termed *sodium benzylisozazotate*, $C_6H_5 \cdot CH_2 \cdot N : N \cdot ONa$. This compound, which forms white needles, resembles sodium benzeneisodiazotate in its reactions, except that it cannot be converted into a diazonium salt and does not yield azo-dyes; with acids, nitrogen is evolved.

Sodium benzeneisodiazotate, prepared by adding ethyl nitrite mixed with ether to a cold mixture of phenylhydrazine, sodium methoxide, and ether, gives, in aqueous solution, with ferric chloride a brown, with copper sulphate a blackish-violet, and with mercuric nitrate a white, precipitate. Sodium *p*-nitrobenzeneisodiazotate and sodium benzylisozazotate give similar reactions.

An aqueous solution of nitrosophenylhydrazine gives with ferric chloride a transient violet coloration, with copper acetate a precipitate followed by reduction, and with mercuric nitrate a yellow precipitate sparingly soluble in dilute nitric acid. The *sodium* salt, $C_6H_5 \cdot N_3HONa$, obtained by adding sodium methoxide to the ethereal solution, is white; with water, nitrosophenylhydrazine is regenerated.

Nitrosobenzylhydrazine gives with copper acetate a pale precipitate soluble in dilute acids, which reddens on warming. With mercuric nitrate, a yellow precipitate, soon turning white, is produced, which is sparingly soluble in nitric acid. The *sodium* salt, $C_7H_8N_3 \cdot ONa$, resembles that of nitrosophenylhydrazine. J. C. C.

Hydrolysis of Legumelin from the Pea (*Pisum sativum*).
 THOMAS B. OSBORNE and FREDERICK W. HEYL (*J. Biol. Chem.*, 1908, 5, 197—206).—Legumelin is the albumin which occurs in many leguminous seeds. The following table compares the percentage of hydrolytic products in legumelin and leucosin, the albumin of wheat:

Legumelin. Leucosin.		Legumelin. Leucosin.	
Glycine	0.50 0.94	Glutamic acid ...	12.96 6.73
Alanine	0.92 4.45	Tyrosine	1.56 3.34
Valine	0.69 0.18	Arginine	5.45 5.94
Leucine	9.63 11.34	Histidine	2.27 2.83
Proline	3.96 3.18	Lysine	3.03 2.75
Phenylalanine ...	4.79 3.83	Ammonia	1.26 1.41
Aspartic acid	4.11 3.85		
		Total	51.15 50.53

Tryptophan is present in both; serine and cystine were not estimated.

W. D. H.

Hydrolysis of Vicilin from the Pea (*Pisum sativum*). THOMAS B. OSBORNE and FREDERICK W. HEYL (*J. Biol. Chem.*, 1908, 5, 187—196).—Vicilin is a globulin occurring in the pea, horse-bean, and lentil. It differs from legumin in containing more carbon, less nitrogen, and much less sulphur. It contains the smallest proportion of sulphur yet found in any protein (0.1—0.2%). The following table compares the percentage of hydrolytic products of the two proteins:

Vicilin. Legumin.		Vicilin. Legumin.	
Glycine	0.0 0.38	Cystine	not determined
Alanine	0.5 2.08	Oxyproline	„ „
Valine	0.15 ?	Tyrosine	2.38 1.55
Leucine	9.38 8.00	Arginine	8.91 11.71
Proline	4.06 3.22	Histidine	2.17 1.69
Phenylalanine ...	3.82 3.75	Lysine	5.40 4.98
Aspartic acid	5.30 5.30	Ammonia	2.03 2.05
Glutamic acid	21.34 16.97	Tryptophan	present present
Serine	? 0.53		
		Total	65.44 62.22

W. D. H.

Applicability of the Laws of Amphoteric Electrolytes to Serum Globulin. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1908, 5, 155—162).—Polemical against H. Lundén (*ibid.*, 267).

W. D. H.

The Swelling of Fibrin. MARTIN H. FISCHER (*Pflüger's Archiv*, 1908, 125, 99—110. Compare Abstr., 1907, i, 1095).—Fibrin swells more in acids than in distilled water; various acids produce this effect better than others; for instance, hydrochloric acid is the most and sulphuric acid the least effective of those investigated. The amount of swelling is dependent on the concentration of the acids. Alkalis also cause fibrin to swell in various degrees in proportion to the concentration. Beyond a certain point in the case both of acid and alkali, the swelling decreases. Alkalis produce more swelling than acids of the same strength. The addition of salts lessens the swelling, as also do non-electrolytes (urea, sugar, &c.). The taking up and giving out of water is a reversible phenomenon.

W. D. H.

Solubility of Zein in Different Solvents. GINO GALEOTTI and G. GIAMPALMO (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 118—126).—Zein (a protein which occurs in maize) is insoluble in water and in alcohol, but is readily soluble in a mixture of them. The maximum solubility is observed with 60% alcohol. The solutions

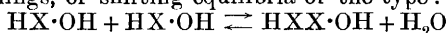
in alcohol stronger than 45% are clear and mobile, those in weaker alcohols are turbid and viscous. The addition of xylene, ether, or light petroleum does not precipitate zein from these solutions unless enough is added to form a second liquid phase. The solubility curve for mixtures of chloroform and 85% alcohol is found to possess two maxima, one about 16% and the other about 54% of chloroform. The solubility of zein in mixtures of water, alcohol, and acetone is very thoroughly studied, and the results represented by a diagram. The mixtures containing acetone dissolve less zein than the corresponding mixture of water and alcohol. The two series of solutions (clear and easily filtered—turbid and not readily filtered) are also found in the acetone mixtures. Zein is insoluble in all the pure solvents tried.

T. E.

Another Method of Measuring Large Molecular Masses. WILLIAM SUTHERLAND (*Phil. Mag.*, 1908, [vi], 16, 497—512).—From a relationship, previously deduced by the author, between the molecular conductivity, the concentration, the viscosities of the solvent and solution, the mass of the atom of hydrogen, the dielectric capacity of the solvent, and the dissociating force which causes complete ionisation, the author has deduced the molecular masses of globulin and casein. The globulin ions produced by hydrochloric acid in aqueous solutions are found to be bivalent, and their molecular mass about 10,000. The molecular mass of the casein ion is given as 2605. On the assumption that the casein ion is bivalent, this result agrees freely well with the value 1135 obtained by Laqueur and Sackur for its equivalent weight.

H. M. D.

Influence of Temperature on the Solubility of Casein in Alkaline Solutions. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1908, 5, 147—154).—The solubility of casein in alkaline solutions is increased at temperatures over 40°. This fact is not in harmony with the view that heat increases the degree of hydrolytic dissociation of solutions of the caseinates. Osborne showed that heating increases the alkalinity and electrical conductivity of caseinate solutions; it is, therefore, suggested that the influence of heat on proteins consists, among other things, of shifting equilibria of the type:



in the direction of higher complexes, and that heat coagulation is a result of repeated condensations of this type. The solubility of casein in solutions of various concentrations of potassium hydroxide, lithium hydroxide, and calcium hydroxide at various temperatures is given.

W. D. H.

Products of Hydrolysis of Casein. ZDENKO H. SKRAUP (*Monatsh.*, 1908, 29, 791—798. Compare Abderhalden and Funk, *Abstr.*, 1907, i, 1095).—In the products of hydrolysis of casein with hydrochloric acid, three substances occur, which have the composition of leucylvalylimide. The one is fairly strongly laevorotatory, the second is weakly rotatory, and the third is practically inactive. It is not yet certain whether these compounds are pure or mixtures.

The ether-alcoholic extract of the hydrolysed casein, on distillation, left a residue which was esterified and distilled in a vacuum; three fractions were collected up to 115° , and the residue on extraction with alcohol gave a substance, $C_{11}H_{20}O_2N_2$, sintering at 283° , m. p. 289° , $[\alpha]_D - 53.0^{\circ}$ (Abderhalden and Funk give $[\alpha]_D - 44.27^{\circ}$).

The mother liquor from this yielded a substance, $C_{11}H_{20}O_2N_2$, forming needle-shaped crystals, m. p. 250° , $[\alpha]_D - 17.6^{\circ}$. The alcoholic extract from which the first substance was obtained yielded, with light petroleum, a third substance, $C_{12}H_{20}O_2N_2$, forming crystals, m. p. 275° . The mother liquor from this gave leucine, and amines of the composition of butyl- and amyl-amine. After separating the leucine, the solution furnished a basic aurichloride, $C_4H_{12}NCl_3Au$, m. p. 195° (decomp.), the corresponding hydrochloride of which crystallises only in a vacuum, and a platinichloride, $(C_5H_{13}N)_2H_2PtCl_6$, large, yellow leaves, m. p. 210° (decomp.); the corresponding hydrochloride crystallises more readily than that prepared from the aurichloride, and both give the carbamide reaction.

J. C. C.

Formation of Thymine by Heating Intestinal Nucleic Acid. KATSUJI INOUE (*Zeitsch. physiol. Chem.*, 1908, 57, 313).—If nucleic acid (from the intestines) is burnt, a white material collects on the walls of the tube. This was collected and identified as thymine.

W. D. H.

Pyrimidines. X. Action of Diazobenzenesulphonic Acid on Thymine, Uracil, and Cytosine. TREAT B. JOHNSON and SAMUEL H. CLAPP (*J. Biol. Chem.*, 1908, 5, 163—172).—Thymine, uracil, and cytosine all give, in the presence of alkali, a red solution with diazobenzene-sulphonic acid. The colour given by thymine is most intense. Substitution in position 3 in the pyrimidine ring prevents the formation of a red colour, and the absence of this colour reaction in nucleic acids (Burian) indicates that thymine, and probably also cytosine and uracil, are linked in nucleic acids at position 3. Whether the pyrimidines are linked to phosphorus, a carbohydrate complex or otherwise, is not yet settled.

W. D. H.

Cleavage Products of Nucleic Acid. PHÆBUS A. LEVENE (*Zeitsch. physiol. Chem.*, 1908, 57, 154—156; HERMANN STEUDEL, *ibid.*, 157—160).—Polemical between the two authors, mainly in reference to priority.

W. D. H.

Inosic Acid. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1908, 41, 2703—2707).—When hydrolysed with 5% sulphuric acid and the products isolated by means of their barium salts, inosic acid furnishes a complex phosphoric acid, of which two barium salts were analysed. The one, $(C_5H_8O_8P)_2Ba_3$, is amorphous, has $[\alpha]_D^{20} + 4.4^{\circ}$, and reduces Fehling's solution on heating, and the other, $C_5H_7O_8PBa, 5H_2O$ or $C_5H_9O_8PBa, 5H_2O$, forms bundles of needles and readily reduces Fehling's solution. By hydrolysis of inosic acid with 5% potassium hydroxide, 30% of the original phosphoric acid is eliminated. The conclusion is drawn that in inosic acid the carbohydrate forms a

glucophosphoric acid with the phosphoric acid, and that the base is combined with the aldehyde group of the sugar. The authors are unable to confirm the observations of Neuberg and Brahn (Abstr., 1907, i, 1097), or of Bauer (Abstr., 1907, i, 1098), as to the nature of the sugar.

J. C. C.

Hydrolysis of Witte's Peptone. PHÆBUS A. LEVENE and D. D. VAN SLYKE (*Biochem. Zeitsch.*, 1908, 13, 440—457).—The peptone was hydrolysed by hydrochloric acid. The following yields of amino-acids were obtained (in parts per cent. of the peptone), the corresponding yields from fibrin being given in brackets: tyrosine, 3.25 (3.3); glycine, 0.78 (2.2); alanine, 2.83 (3.1); valine and leucine, 14.70 (13.0); phenylalanine, 2.60 (1.2); glutamic acid, 8.24 (6.6); aspartic acid, 1.70 (1.7); proline, 4.56 (2.4); serine, 1.18; histidine, 0.75; lysine, 2.71; arginine, 1.48. Total yield of amino-acids, 47.78%.

S. B. S.

Polypeptides Containing Tryptophan. EMIL ABDERHALDEN and LOUIS BAUMANN (*Ber.*, 1908, 41, 2857—2860).—*Iodoacetyl-L-tryptophan*, prepared by coupling the components in alkaline solution, crystallises in needles, m. p. 175—176° (decomp.), and has $[\alpha]_D^{20} + 31.3^\circ$. *Chloroacetyl-L-tryptophan* has $[\alpha]_D^{20} + 32.9$, not -32.9° as previously stated in error (Abstr., 1907, i, 652). *Methyl-dl- α -iodopropionyl-L-tryptophan* crystallises in needles aggregated in rosettes, m. p. 145—146°. *dl-Alanyl-L-tryptophan anhydride*, prepared by the action of methyl-alcoholic ammonia on the foregoing, crystallises in minute needles, m. p. 290° (corr.), $[\alpha]_D^{20} + 87^\circ$.

E. F. A.

Plastein. PHÆBUS A. LEVENE and D. D. VAN SLYKE (*Biochem. Zeitsch.*, 1908, 13, 458—474).—The plastein was made by treatment of a 20% solution of Witte's peptone in 0.2% hydrochloric acid. It was submitted to hydrolysis, and the following percentages of amino-acids were obtained, the corresponding numbers for fibrin being given in brackets: tyrosine, 3.03 (3.1); glycine, 0.50 (2.2); alanine? (3.1); valine and leucine, 15.59 (13.0); phenylalanine, 1.0 (1.2); glutamic acid, 10.02 (6.8); aspartic acid, 2.15 (1.7); proline, 2.55 (2.4); histidine, 0.43; arginine, 2.06; lysine, 1.42. Total yield of amino-acid, 38.75%. The numbers indicate that plastein is a complex protein, not far removed in composition from fibrin. It is not possible to determine, however, whether the plastein is a synthetic product, or a coagulated form of one of the fibrin albumoses.

S. B. S.

Organic Chemistry.

A New Reaction of Petroleum. ETTORE MOLINARI and P. FENAROLI (*Ber.*, 1908, 41, 3704—3707).—It has been found that Russian petroleum yields ozonides by the action of ozonised oxygen at 8—10°. An oil, b. p. 135—290°, gave 12% of ozonide, whereas one boiling at 295—300° gave 32%. The ozonide forms a white or pale yellowish-red powder soluble in ether, chloroform, or benzene. It can be kept for several days at low temperatures, but decomposes rapidly at 20°, and at 45—50° yields a soft, red substance which is converted into a brown resin at 150°.

The analyses of the ozonide agree with the conclusion that it is derived from a naphthene, $C_{17}H_{20}$, containing two ethylene linkings.

A Roumanian oil gave a similar ozonide, whereas an Italian oil, b. p. 140—265°, gave a small amount of an ozonide, probably derived from a hydrocarbon, $C_{15}H_{16}$.

The ozone also produces a certain amount of oxidation, and the residue left after the removal of the ozonide is still optically active, indicating that this activity cannot be due to unaltered cholesterol in the original oil.

J. J. S.

Preparation of Acetylene Di- and Tetra-chlorides. JOHANN H. LIDHOLM (D.R.-P. 201705).—A mixture of 2 vols. of chlorine and 1 vol. of acetylene, diluted with 10% of carbon dioxide, reacts quite quietly to furnish acetylene tetrachloride with about 10% of acetylene dichloride when exposed to radium emanations or to the light from a quartz-mercury lamp fed with a current of 3 to 5 amperes and 60—75 volts.

G. T. M.

Constitution of Copper Acetylide. JOHANNES SCHEIBER [with R. FLEBBE] (*Ber.*, 1908, 41, 3816—3828).—Makowka has assigned

the constitution $\begin{array}{c} \text{Cu} \\ | \\ \text{Cu} \end{array} \text{ > CH} \cdot \text{CHO}$ to the copper acetylene compound

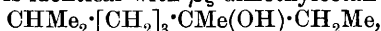
obtained by precipitation of a cuprous salt by acetylene (this vol., i, 328). It is now shown that the freshly-prepared compound can be converted into a dehydrated form, C_2Cu_2 , by heating for two hours at 100° over calcium chloride (compare Keiser, *Abstr.*, 1892, 1416). This result is not in accordance with the aldehyde formula. Further, no acetaldehyde can be detected when the compound is dissolved in hydrochloric acid, whereas trichloromercuriacetaldehyde yields the aldehyde, but no acetylene, under corresponding conditions (Biltz and Mumm, *Abstr.*, 1905, i, 2). It would also appear that the water is firmly held in the molecule, as after drying in a desiccator for twenty-eight days it still has $1H_2O$. Inasmuch as the compound is amorphous, it is unlikely that the compound contains water of crystallisation, and

of two suggested formulæ, $\begin{array}{c} \text{Cu} \cdot \text{C} \\ | \\ \text{Cu} \cdot \text{C} \end{array} \text{H}_2\text{O}$ and $\text{CH} : \text{CCu} \cdot \text{CuOH}$, preference

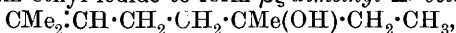
is given to the latter.

The carbonaceous residue left after dissolution of the acetylide in hydrochloric acid is not an impurity, but is due to secondary changes. Analysis of one preparation led to the formula $(C_{11}H_8O_4)_x$, but it is uncertain whether it is of definite composition. W. R.

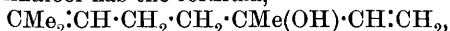
Hydrogenation of Linalool by means of Nickel and Hydrogen. Synthesis of Tetrahydrolinalool ($\beta\zeta$ -Dimethyloctan- ζ -ol). C. J. ENKLAAR (*Rec. trav. chim.*, 1908, 27, 411—417. Compare this vol., i, 664).—When linalool is directly hydrogenated in the presence of nickel at 130—140°, $\beta\zeta$ -dimethyloctane (compare Willstätter and Meyer, this vol., i, 383) is obtained together with the saturated alcohol, tetrahydrolinalool, $C_{10}H_{22}O$, b. p. 88—88.5°/14 mm., D_4^{15} 0.8360, n_D^{15} 1.4388, which is identical with $\beta\zeta$ -dimethyloctan- ζ -ol,



prepared synthetically from methylheptenone (Barbier and Bouveault, Abstr., 1896, i, 445; Verley, Abstr., 1898, i, 557; Leser, Abstr., 1898, i, 512; Tiemann, Abstr., 1898, i, 374; Ipatieff, Abstr., 1901, i, 256) by the following series of reactions: methylheptenone reacts with magnesium ethyl iodide to form $\beta\zeta$ -dimethyl- Δ^8 -octene- ζ -ol,



b. p. 94—94.5°, D_4^{15} 0.8695, n_D^{15} 1.4569, which, on direct hydrogenation in the presence of nickel, yields $\beta\zeta$ -dimethyloctan- ζ -ol; it follows therefore that linalool has the formula,



ascribed to it by Tiemann and Semmler (Abstr., 1895, i, 646).

M. A. W.

α -Methylallyl Alcohol (Δ^a -Butene- γ -ol). ALFRED WOHL and M. S. LOSANITSCH (*Ber.*, 1908, 41, 3621—3622. Compare Reif, this vol., i, 847).—The action of magnesium methyl iodide on acraldehyde in ethereal solution leads to the formation of α -methylallyl alcohol, $CH_2 \cdot CH \cdot CHMe \cdot OH$, which is obtained as a viscid, colourless oil, b. p. 96—97°/756 mm. or 28—31°/35 mm., does not reduce ammoniacal silver or Fehling's solution, and when treated with permanganate is only partly oxidised, evolving carbon dioxide. Neither by this reaction nor by oxidation of the unsaturated alcohol with chromic acid and very dilute sulphuric acid can the corresponding ketone be obtained. G. Y.

Complex Compounds of Multivalent Alcohols. A Class of Cyclic Complex Metallic Salts. ADOLF GRÜN and F. BOCKISCH (*Ber.*, 1908, 41, 3465—3478).— $\alpha\beta$ -Glycols and glycerol show a marked tendency to combine with metallic salts. Such compounds are regarded as having a cyclic structure, and are classed with the saccharates formed by sugars with metallic oxides. Ethylene glycol displaces water from the hydrates of copper, cobalt, nickel, and chromium salts, $C_2H_4(OH)_2$ replacing $2H_2O$.

Diethyleneglycolcuprosulphate, $CuSO_4 \cdot 2C_2H_4(OH)_2 \cdot 2H_2O$, prepared by warming the constituents together on the water-bath, crystallises in minute, bright blue needles, which melt to a clear blue liquid. On warming at 60°, it loses 25% of its weight, but still contains 11.3% of water. On prolonged heating at 125°, copper sulphate alone remains.

Triethyleneglycolcobaltosulphate, $\left[\text{Co} \left(\begin{array}{c} \text{CH}_2 \cdot \text{OH} \\ | \\ \text{CH}_2 \cdot \text{OH} \end{array} \right)_3 \right] \text{SO}_4 \cdot \text{H}_2\text{O}$, is best

obtained by heating the constituents at the water-bath temperature, diluting the saturated, purplish-red solution with a little alcohol after cooling, and adding acetone until the solution is decolorised. A red oil is precipitated, which forms minute, red, hygroscopic crystals on drying over sulphuric acid. It decomposes in aqueous solution, or on heating to 80° .

Glycerol monomethyl ether (α -monomethylin), prepared by the action of sodium methoxide on α -monochlorohydrin in cold methyl-alcoholic solution, forms a colourless, pleasant ethereal-smelling liquid, less viscid than glycerol. It has b. p. $196^\circ/728 \text{ mm.}$, $115\text{--}120^\circ/18 \text{ mm.}$

Dimethylincobaltosulphate, $\text{CoSO}_4 \cdot 2\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{C}_2\text{H}_5(\text{OH})_2$, prepared by mixing the components in the cold and precipitating the saturated solution with ether, is obtained as a dark red, microcrystalline mass, which is very hygroscopic.

Glycerol gives rise to compounds with metallic sulphates having the general formula $\left[\text{M} \left(\begin{array}{c} \text{HO} \cdot \text{CH}_2 \\ | \\ \text{HO} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{array} \right)_3 \right] \text{SO}_4 \cdot \text{H}_2\text{O}$.

They are obtained by heating glycerol on the water-bath with the hydrated salt, and precipitated from the saturated solution by means of alcohol.

Triglycerolcuprisulphate is a clear, blue mass of the consistence of colophony. *Triglycerolcobaltosulphate* forms a red, gelatinous mass, which melts on heating; it dissolves in water, and is reprecipitated unchanged by alcohol. *Triglycerolnickelosulphate* is obtained as a transparent, emerald-green, glass-like mass, which is very hygroscopic, but extremely stable. Barium chloride removes the sulphate from this compound, and the corresponding *chloride* results, which is very similar in appearance. *Triglycerolzincisulphate* is an amorphous, colourless mass.

Triglycerol calcium hydroxide forms slightly yellow, granular crystals, which are very hygroscopic and absorb carbon dioxide with great avidity. It dissolves easily in water, sparingly in methyl or ethyl alcohol, all three solutions having an alkaline reaction.

The compounds formed between borates and glycerol in the ordinary analytical procedure are considered to be complex salts of the above type, and not salts of the hypothetical glyceroboric acid.

On mixing boric acid, glycerol and lithium carbonate, and precipitating with alcoholic silver nitrate, bright yellow crystals of the *silver salt*, $\text{AgBO}_2 \cdot 2\text{C}_3\text{H}_5(\text{OH})_3$, are obtained.

$\alpha\beta$ -Glycols, when treated with hydrogen iodide, are only partly converted into alkyl iodide, the rest being reduced to hydrocarbon. They cannot therefore be estimated in this manner. E. F. A.

Alkylated Halohydrin and Vinylethyl Ethers. JOSEF HOUBEN (*Ber.*, 1908, 41, 3708—3712).—Polemical. A reply to Hoering (this vol., i, 497). J. J. S.

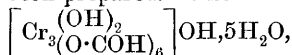
Metallic Salts of Organic Acids. I. Formates and Acetates of Chromium. ALFRED WERNER [with J. JOVANOVIĆ, G. ASCHKINASY, and J. POSSELT] (*Ber.*, 1908, 41, 3447—3465).—The

author has commenced a systematic examination of the capacity of the metallic salts of organic acids to form complex compounds. The present communication deals mainly with the formates and acetates of chromium. Two types of salts have been obtained: (a) normal salts; (b) complex salts.

The normal salts are prepared by triturating *dihydroxotetra-aquochromium sulphate*, $\left[\text{Cr} \begin{smallmatrix} (\text{OH})_2 \\ (\text{OH}_2)_4 \end{smallmatrix} \right]_2 \text{SO}_4$ (which is obtained by the addition of pyridine to an aqueous solution of chromium alum and sodium sulphate), with an organic acid. In this way *hexa-aquochromium formate*, *acetate*, *propionate*, and *butyrate* have been prepared, $[\text{Cr}(\text{H}_2\text{O})_6](\text{O}\cdot\text{CO}\cdot\text{R})_3$. The colour of these salts varies in a remarkable way, the formate being greyish-green, the acetate bluish-violet, the propionate Turkey-blue, and the butyrate silver-grey. The acetate is identical with Recoura's compound (Abstr., 1899, ii, 661), but contains 6 instead of 5 H_2O . All the salts are hydrolytically dissociated by excess of water, giving bluish-green solutions, from which sodium sulphate precipitates dihydroxotetra-aquochromium sulphate. By trituration with mineral acids, the salts are converted into the corresponding hexa-aquochromium salt of the mineral acid, proving that the organic acid group is in the ionogenic state.

The complex salts are of the type $\left[\text{Cr}_3 \begin{smallmatrix} (\text{OH})_2 \\ (\text{O}\cdot\text{CO}\cdot\text{R})_6 \end{smallmatrix} \right] \text{X}, x\text{H}_2\text{O}$, the constitution of the metallic complex being as yet unknown.

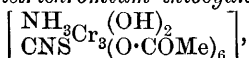
Hexaformatodioltrichromium formate, $\left[\text{Cr}_3 \begin{smallmatrix} (\text{OH})_2 \\ (\text{O}\cdot\text{COH})_6 \end{smallmatrix} \right] \text{O}\cdot\text{COH}, 5\text{H}_2\text{O}$, is prepared by dissolving freshly-precipitated, moist chromium hydroxide in formic acid, D 1.15—1.20 (compare Häussermann, Abstr., 1895, i, 15). By solution in concentrated nitric acid, the air-dried formate is converted into the *nitrate*, $\left[\text{Cr}_3 \begin{smallmatrix} (\text{OH})_2 \\ (\text{O}\cdot\text{COH})_6 \end{smallmatrix} \right] \text{NO}_3, 5\text{H}_2\text{O}$, from which the corresponding *chloride*, *bromide*, *iodide*, *sulphate*, *dithionate*, and *aurichloride* have been prepared. The free base,



obtained from the nitrate and ammonium hydroxide, crystallises in light green needles.

Hexa-acetatodioltrichromium nitrate, $\left[\text{Cr}_3 \begin{smallmatrix} (\text{OH})_2 \\ (\text{O}\cdot\text{COMe})_6 \end{smallmatrix} \right] \text{NO}_3, 6\text{H}_2\text{O}$, is prepared by dissolving equal quantities of recently-precipitated chromium hydroxide in nitric acid (1 mol.) and in glacial acetic acid (6 mols.) respectively, and heating the mixed solutions on the water-bath until a pure dark green colour is produced; the nitrate slowly separates, after cooling, in tufts of dark green leaflets. The corresponding *chloride*, *bromide*, *iodide*, *aurichloride*, and *platini-chloride* are described; the last three salts contain only $5\text{H}_2\text{O}$. *Hexa-propionatodioltrichromium chloride*, $\left[\text{Cr}_3 \begin{smallmatrix} (\text{OH})_2 \\ (\text{O}\cdot\text{CO}\cdot\text{C}_2\text{H}_5)_6 \end{smallmatrix} \right] \text{Cl}, 5\text{H}_2\text{O}$, forms dark green crystals.

Hexa-acetatodiolamminetrichromium thiocyanate,

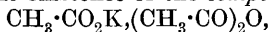


prepared from chloropentamminechromium chloride, aqueous potassium thiocyanate, and glacial acetic acid, separates from acetone in tufts of glistening, pale green needles. The thiocyanate group is probably within the metallic complex, since an aqueous solution of the salt does not immediately precipitate silver thiocyanate by treatment with silver nitrate. The mother liquor contains *hexa-acetatodiol-aquo-amminetricobalt nitrate*, $\left[\begin{smallmatrix} \text{NH}_3\text{Cr}(\text{OH})_2 \\ \text{H}_2\text{O} \end{smallmatrix} \text{Cr}_3(\text{O}\cdot\text{COMe})_6 \right] \text{NO}_3$, which is also obtained by oxidising the thiocyanate with concentrated nitric acid; the corresponding *iodide* is also described. C. S.

Double Compounds of Acetates with Acetic Anhydride. HARTWIG FRANZEN (*Ber.*, 1908, 41, 3641—3644).—When a recently fused and powdered acetate is boiled for a short time with acetic anhydride and the filtered solution allowed to cool, crystals of a compound of the acetate and anhydride separate. Two series of compounds appear to exist, namely, $(\text{Ac}\cdot\text{OR})_2, \text{Ac}_2\text{O}$ and $\text{Ac}\cdot\text{OR}, \text{Ac}_2\text{O}$; the latter have been obtained only in the case of potassium and sodium acetate. The conditions according to which the one or the other compound is produced are unknown in the case of sodium acetate, but in general the compound $(\text{Ac}\cdot\text{ONa})_2, \text{Ac}_2\text{O}$ is formed when crystallisation begins in the warm solution, whilst the compound $\text{Ac}\cdot\text{ONa}, \text{Ac}_2\text{O}$ is obtained when crystallisation is started in a super-cooled solution. The acetic anhydride may be combined with the acetate in a manner similar to that of water of crystallisation, or the compounds may be regarded as salts of acetylorthoacetic acids, thus: $\text{NaO}\cdot\text{CMe}(\text{OAc})_2$ and $\text{CMe}(\text{ONa}_2)\cdot\text{O}\cdot\text{CMe}(\text{OAc})_2$. This explanation may throw some light on the constitution of bimolecular fatty acids; thus bimolecular acetic acid may be an acetylorthoacetic acid, $\text{CMe}(\text{OH})_2\cdot\text{OAc}$.

The *compound*, $(\text{CH}_3\cdot\text{CO}_2\text{Na})_2, (\text{CH}_3\cdot\text{CO})_2\text{O}$, forms compact, colourless crystals, m. p. 160° , becoming solid on further heating. It loses acetic anhydride gradually in a vacuum desiccator. The *compound*, $\text{CH}_3\cdot\text{CO}_2\text{Na}, (\text{CH}_3\cdot\text{CO})_2\text{O}$, forms slender, colourless, matted needles, sintering at 80° , m. p. $150\text{--}160^\circ$; at $180\text{--}200^\circ$, the substance boils and begins to solidify, and the whole is completely solid at 220° . It loses acetic anhydride rapidly in a vacuum desiccator.

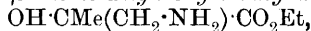
The *compound*, $(\text{CH}_3\cdot\text{CO}_2\text{K})_2, (\text{CH}_3\cdot\text{CO})_2\text{O}$, forms slender, colourless crystals; evidence of the existence of the *compound*,



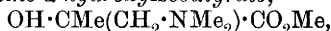
is also adduced. The *compound*, $(\text{CH}_3\cdot\text{CO}_2\text{Rb})_2, (\text{CH}_3\cdot\text{CO})_2\text{O}$, forms slender, colourless crystals. The *compound*, $(\text{CH}_3\cdot\text{CO}_2\text{Cs})_2, (\text{CH}_3\cdot\text{CO})_2\text{O}$, is also obtained in colourless crystals. J. C. C.

Preparation of the Esters of the Amino- α -hydroxy-acids. LES ÉTABLISSEMENTS POULENC FRÈRES and ERNEST FOURNEAU (D.R.-P. 198306).—The esters of the amino- α -hydroxy-acids having the general formula $\text{NRR}'\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{R}''$ (where R'' is an alkyl group and R and R' either hydrogen atoms or alkyl groups) are produced by the esterification of the corresponding acid with aliphatic alcohols in the presence of mineral acids. The starting point in these syntheses

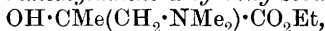
is chloroacetone, which, when treated successively with hydrocyanic acid and hydrolytic agents, furnishes β -chloro- α -hydroxyisobutyric acid, $\text{OH}\cdot\text{CMe}(\text{CH}_2\text{Cl})\cdot\text{CO}_2\text{H}$. This chloro-acid, on treatment under pressure with ammonia or primary or secondary aliphatic amines, gives rise to a series of amino- α -hydroxyisobutyric acids. The following compounds are described: *Ethyl β -amino- α -hydroxyisobutyrate*,



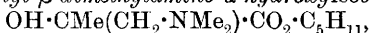
oil, b. p. 107—109°/15 mm.; *hydrochloride*, needles, m. p. 105°; *urethane derivative*, $\text{OH}\cdot\text{CMe}(\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CO}_2\text{Et}$, b. p. 164—165°/16 mm. *Methyl β -dimethylamino- α -hydroxyisobutyrate*,



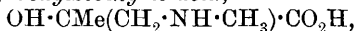
oil, b. p. 107°/35 mm.; *hydrochloride* of its *benzoyl* derivative, m. p. 149—150°. *Ethyl β -dimethylamino- α -hydroxyisobutyrate*,



oil, 88—89°/16 mm., 108—110°/32 mm.; the *hydrochlorides* of its *benzoyl* and *isovaleryl* derivatives melt respectively at 137° and 134—135°. *isoAmyl β -dimethylamino- α -hydroxyisobutyrate*,



b. p. 121°/12 mm.; the *hydrochloride* of its *benzoyl* derivative, m. p. 134°. *β -Methylamino- α -hydroxyisobutyric acid*,



m. p. 230—231°; *ethyl ester*, b. p. 112°/38 mm.

β -Diethylamino- α -hydroxyisobutyric acid, $\text{OH}\cdot\text{CMe}(\text{CH}_2\cdot\text{NEt}_2)\cdot\text{CO}_2\text{H}$, transparent prisms, m. p. 223°; *ethyl ester*, m. p. 212°/760 mm.

Propyl β -dimethylamino- α -hydroxyisobutyrate, b. p. 94°/13 mm.; *hydrobromide* of its *isovaleryl* derivative, m. p. 165°. G. T. M.

Oxalyl Chloride. HERMANN STAUDINGER (*Ber.*, 1908, 41, 3558—3566).—Oxalyl chloride (Fauconnier, *Abstr.*, 1892, 588) is obtained in a 50% yield by the action of phosphorus pentachloride (2 mols.) on anhydrous oxalic acid (1 mol.). It is considered that the intermediate product of the reaction cannot be the half-chloride, as this is unstable at -80° , but may be a compound, $\text{C}_2\text{O}_2(\text{OPCl}_4)_2$, corresponding with that of oxalic acid with antimony pentachloride (Rosenheim and Loewenstamm, *Abstr.*, 1902, i, 358). Oxalyl chloride forms white crystals, m. p. -12° , b. p. 64°/763 mm., reacts quantitatively with water, yielding carbon dioxide, carbon monoxide, and hydrogen chloride, but forms oxalic acid when treated in the gaseous state with water vapour, and is converted into oxalates by alcohols and into oxamides by amines. It is stable towards fuming sulphuric acid, but decomposes, forming carbonyl chloride and carbon monoxide, when distilled through a glass tube heated at 600°, or when boiled with aluminium chloride in carbon disulphide solution, and may therefore be employed in place of carbonyl chloride in the Friedel-Crafts synthesis. When treated with hydrogen sulphide in ethereal solution, oxalyl chloride remains unchanged, but if quinoline is added, carbon monoxide is evolved.

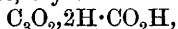
The action of ethyl mercaptan on oxalyl chloride in cold ethereal solution leads to the formation of *ethyl dithio-oxalate*, $\text{C}_2\text{O}_2(\text{SEt})_2$, which is obtained as a viscid, yellow oil, b. p. 238—240°/757 mm., solidifying at 24—25° to light yellow crystals. G. Y.

Electrolytic Decomposition of Dicarboxylic Organic Acids:
Pimelic Acid. B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 331—333. Compare Abstr., 1907, i, 823).—When neutral salts of the normal acids of the oxalic acid series are electrolysed, lengthening of the carbon atom-chain of the acids is accompanied by increasing complexity of the secondary phenomena of anodic oxidation. Synthesis occurs, owing to the demolition of the anion as it becomes discharged at the anode, alcohols and unsaturated acids being formed, together with their esterification products, hydroxy-acids and lactones, and substances containing aldehydic and ketonic carbonyl groups, formed by the action of the anodic oxygen. Further, with succinic acid, ethylene is formed in appreciable quantity, whilst glutaric acid yields a little propylene, and adipic acid small amounts of two butylenes having normal carbon atom-chains; suberic acid, however, does not yield hydrocarbons in appreciable quantity. Variation of the conditions of electrolysis never leads to the formation of the corresponding cyclic hydrocarbons, tri-, tetra-, and hexa-methylene, which would be expected if the two CO_2 groups of the anion leave the latter simultaneously.

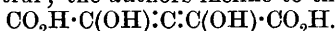
In the case of pimelic acid, now studied, the electrolytic decomposition products consist of ethylene and propylene in approximately equal proportions, and of other compounds analogous with those formed with suberic acid. No *cyclopentane* is obtained, although the closing of the carbon atom-ring should take place more readily with five carbon atoms than in the other cases. T. H. P.

Diethylmalonic Anhydride. HERMANN STAUDINGER and E. OTT (*Ber.*, 1908, 41, 3829—3830).—By purifying crude diethylmalonic anhydride by extraction with ether during forty-eight hours, it has decomp. 95—97°, and gives only a very slight depression of the freezing point in benzene solution. It is therefore very highly polymerised, and the conclusion previously drawn that it is higher than duodecimolecular is confirmed (this vol., i, 603). W. R.

Carbon Suboxide. IV. OTTO DIELS and LEONID LALIN (*Ber.*, 1908, 41, 3426—3434).—Carbon suboxide shows little tendency to combine with aldehydes, hydrogen cyanide, or the Schiff bases; additive compounds with formic acid and with acetic acid have been obtained. In liquid sulphur dioxide at -40° to -50° , carbon suboxide and formic acid combine to give a white, crystalline *additive* compound,



which is stable in the absence of moisture, and can be recrystallised from acetyl chloride, formic acid, or methylal and light petroleum. Water instantly decomposes the substance, formic and malonic acids being formed. The molecular formula is established by analysis and by titration with sodium hydroxide (4 equivalents). The constitutional formula is still doubtful; the authors incline to the formula



The substance melts at 78° , gives off a gas, mainly carbon monoxide, just above the m. p., resolidifies, and again melts at 133 — 134° , the

m. p. of malonic acid; various other products, however, are also obtained.

The additive compound of carbon suboxide and acetic acid, obtained in a similar manner, has not yet been thoroughly examined. It is a faintly coloured syrup, which, in a vacuum at the ordinary temperature, evolves acetic anhydride, leaving a viscous residue, probably malonic anhydride, $\text{CH}_2\text{C}(\text{CO})_2\text{O}$, since it is converted by water into nearly the quantitative amount of malonic acid. C. S.

Preparation of Arylthioglycollic [Arylthiolacetic] Acids. KALLE & Co. (D.R.-P. 199619).—Aromatic compounds containing a reactive halogen or nitro-group interact with alkali thiolacetates to give rise to arylthiolacetic acids, in which the reactive substituent is displaced by the radicle $\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

p-Nitrophenylthiolacetic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, yellow needles, m. p. 152° , was obtained by heating in alcoholic soda solution, *p*-chloronitrobenzene and thiolacetic acid.

o-Nitrophenylthiolacetic acid, m. p. 157° , was similarly prepared from *o*-chloronitrobenzene.

2:4-Dinitrophenylthiolacetic acid, yellow needles, m. p. $167\text{--}168^\circ$, was produced from 1-chloro-2:4-dinitrobenzene. The crude dinitrobenzene from the mother liquors of crystallised *m*-dinitrobenzene, when condensed in this way with α -thiolacetic acid, gave rise to *o*-nitrophenylthiolacetic acid. G. T. M.

New Reaction of Formaldehyde. F. TODTENHAUPT (*Chem. Zeit.*, 1908, 32, 1045).—When a strong solution of formaldehyde is added to a concentrated ammonium sulphide solution, the mixture becomes heated, and, after a few seconds, there separates a white, soft, sticky substance which, when cooled, forms white, glassy, resinous material with a lustrous fracture; m. p. about 45° . It is soluble in hot glacial acetic acid and in chloroform, and from the former solution, long, white needles separate, m. p. 208° . When heated, the substance (m. p. 45°) has the property of dissolving large quantities of sulphur, becoming brown in colour. J. V. E.

Hyposulphites. V. Rongalitic Acid, Bases, and Formaldehyde. ARTHUR BINZ and ED. ISAAC (*Ber.*, 1908, 41, 3381—3387. Compare Reinking, Dehnel, and Labhardt, *Abstr.*, 1905, i, 261).—Sodium formaldehydesulphoxylate is termed *Rongalite* by the Badische Anilin- & Soda-Fabrik, and the author uses the name *Rongalitic acid* for the corresponding acid.

When aqueous solutions of ammonium chloride, rongalite, and formaldehyde are mixed, a white, powdery substance, $\text{C}_5\text{H}_{12}\text{O}_5\text{N}_2\text{S}_2$, probably $\text{CH}_2\text{C}(\text{N}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{S})_2\text{O}$, is formed.

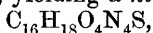
It decomposes between 135° and 140° , reduces indigo-carmin, and when kept for some time undergoes spontaneous decomposition, yielding sulphur dioxide. It is also decomposed by hot water. When suspended in boiling alcohol and decomposed by the addition of a

small amount of water, it yields aminomethylsulphurous acid, m. p. 193° (compare Reinking, Dehnel, and Labhardt, *loc. cit.*).

Rongalite, aniline hydrochloride, and formaldehyde react in aqueous solution and yield a colourless compound, $C_{25}H_{28}O_4N_4S_2$, m. p. 138–142°, which rapidly decomposes and turns yellow. The compound appears to be formed by the action of rongalite on the hydrochloride of anhydro-*p*-aminobenzyl alcohol, obtained by the action of formaldehyde on aniline hydrochloride. The salts of other primary amines behave in much the same manner as aniline hydrochloride.

Aqueous solutions of rongalite and aniline hydrochloride react in the absence of formaldehyde, and when the mixture is heated in a boiling water-bath it yields a colourless precipitate, $C_{27}H_{32}O_6N_4S_2$, m. p. 159–160°. When thoroughly dried, it remains colourless, but otherwise turns yellow. It does not reduce indigo-carmin, and when heated with acetic anhydride and water yields diacetaminodiphenyl-methane.

Dimethylaniline hydrochloride, rongalite, and formaldehyde, when heated together in aqueous solution, yield a base, *tetramethyldiaminobenzylphenylsulphone*, $C_{17}H_{22}O_2N_2S$, which crystallises from alcohol or benzene in long needles, m. p. 199°. It does not reduce indigo-carmin, but reacts with nitrous acid, yielding a *nitro-nitroso*-derivative,



m. p. 170°.

J. J. S.

Action of Bromine on Ether. Bromoacetaldehyde. CHARLES MAUGUIN (*Compt. rend.*, 1908, 147, 747–749).—The action of dry bromine on dry ethyl ether has been investigated by Löwig (*Ann. Phys. Chem.*, 1829, 16, 376), Völckel (*Annalen* 1842, 41, 119), and Schützenberger (*Bull. Soc. chim.*, 1873, [ii], 19, 8). The author has studied the reaction in the presence of water. A mixture of ethyl ether (60 grams), bromine (10 grams), and water (30 grams) is decolorised by one hour's exposure to July sunlight. The velocity of the reaction depends on the intensity of the light (it does not occur in the dark), and is diminished by reducing the quantity of water present. When the reaction is complete, the ethereal layer gives the reactions of an aldehyde, and reacts with urethane, forming bromoacetaldehyde diurethane, m. p. 146°, $CH_2Br \cdot CH(\cdot NH \cdot CO_2Et)_2$, described by Bischoff (*Ber.*, 1872, 5, 85) and by Hantzsch (*Abstr.*, 1894, i, 363). This urethane gives the aldehyde on distillation with 10% sulphuric acid, and the latter is identified by transformation into glycollaldehyde and glyoxalosazone in the manner described by Fischer and Landsteiner (*Abstr.*, 1892, 1424). The reaction affords a method of readily preparing bromoacetaldehyde. E. H.

The Tricarbon Series. ALFRED WOHL (*Ber.*, 1908, 41, 3599–3612).—Studies in the synthesis of oxygenated acyclic derivatives of propane.

1. *Derivatives of Propaldehyde*.—[With H. SCHWEITZER].— β -Hydroxypropaldehyde, obtained in small yield by hydrolysis of β -hydroxypropaldehydediethylacetal (*Abstr.*, 1900, i, 627) by means of dilute sulphuric acid, has b. p. 75–78°/12 mm. (corr.) (90°/10 mm. :

Nef, Abstr., 1905, i, 3), reduces cold ammoniacal silver nitrate solutions, but not Fehling's solution until after the lapse of some days, when it has commenced to undergo condensation with formation of $\alpha\beta$ -unsaturated aldehydes.

β -Iodopropaldehydedimethylacetal, $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})_2$, prepared by heating the β -chloro-compound with potassium iodide in methyl-alcoholic solution in a sealed tube at 100° , forms a colourless oil, b. p. $85^\circ/60$ mm., has an intense odour, and is comparatively stable.

α -Bromopropaldehydedimethylacetal, $\text{CHMeBr}\cdot\text{CH}(\text{OMe})_2$, prepared by bromination of propaldehydedimethylacetal, is obtained as an oil, b. p. $52^\circ/12$ mm. Attempts to prepare α -hydroxypropaldehydeacetal from this or from the diethylacetal were unsuccessful.

2. *Derivatives of $\alpha\alpha$ -Dichloroacetone*.—[With A. KÖPPEN.]— *$\alpha\alpha$ -Dichloroacetonedietiylacetal*, $\text{CHCl}_2\cdot\text{C}(\text{OEt}_2)\cdot\text{CH}_3$, prepared by Claisen's method (Abstr., 1898, i, 421), is obtained as a liquid, b. p. $76^\circ/8$ mm. or $183\text{--}184^\circ/767$ mm., has an odour resembling camphor, and is miscible with the usual organic solvents.

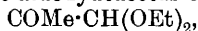
$\alpha\alpha$ -Dichloroacetonedimethylacetal, $\text{C}_5\text{H}_{10}\text{O}_2\text{Cl}_2$, forms a colourless liquid, b. p. $63^\circ/9$ mm. or $170\text{--}171^\circ/767$ mm., and resembles the diethylacetal.

3. *Derivatives of Dichloroisopropyl Alcohol*.—[With H. RORR.]—The action of sodium methoxide or ethoxide on dichloroisopropyl alcohol leads to the formation of mixtures of derivatives containing varying amounts of chlorine. The *benzoyl* derivative, formed by heating the alcohol with benzoyl chloride, has b. p. $92\text{--}94^\circ/0.15\text{--}0.17$ mm.; this also, when treated with sodium methoxide, yields mixtures of products which cannot be separated.

s-Tetrachlorodiisopropylformal, $\text{CH}_2(\text{O}\cdot\text{CHMe}\cdot\text{CHCl}_2)_2$, prepared by Henry's method (Abstr., 1905, i, 558), has b. p. $81^\circ/0.2$ mm., and when treated with sodium methoxide or ethoxide yields a *product*, b. p. $80\text{--}300^\circ$ (indefinite), which reduces Fehling's solution and decolorises permanganate.

4. *Lactaldehyde*.—[With M. LANGE.]—*Lactaldehyde*, $\text{C}_3\text{H}_6\text{O}_2$, obtained by hydrolysis of *lactaldehydeacetal* (see following abstract) by means of dilute sulphuric acid, crystallises in flat needles, sinters at 101° , m. p. 105° on prolonged heating, has a bitter flavour, gives a yellow to brown coloration with alkalis, and reduces Fehling's and Tollen's solutions in the cold. When heated under 9 mm. pressure in a bath at $115\text{--}125^\circ$, the aldehyde distils, chiefly at $58\text{--}66^\circ$, yielding a mobile distillate which rapidly becomes viscid, undergoing polymerisation. Rosaniline gives a red coloration with the freshly distilled aldehyde in ten seconds, with the crystallised aldehyde in one minute, and with the viscid polymeride, seven days after distillation, in two minutes; the three colorations are of equal depth in ten minutes. In freshly prepared aqueous solution, the aldehyde is bimolecular, and gradually becomes unimolecular, slowly at the ordinary temperature, but more quickly when heated. The *phenylhydrazone*, prepared from the acetal, crystallises in prismatic leaflets, m. p. $90\text{--}92^\circ$, or when prepared from the aldehyde, m. p. $128\text{--}129^\circ$; the corresponding *acetol*, m. p. $97\text{--}98^\circ$. The osazone is identical with methylglyoxalosazone. The *nitrophenylhydrazone* crystallises in yellow prisms, m. p. 124° (corr.); the corresponding *acetol*, m. p. $190\text{--}191^\circ$. G. Y.

Synthesis of Lactaldehyde. ALFRED WOHL and M. LANGE (*Ber.*, 1908, 41, 3612—3620).—Ethyl diethoxyacetate is obtained in a 69·5% yield from dichloroacetic acid by a modification of Schreiber's method (*Jahresb.*, 1870, 641), or in a 52% yield by the action of alcoholic hydrogen chloride on calcium glyoxylate. The *piperidide*, $\text{CH}(\text{OEt})_2 \cdot \text{CO} \cdot \text{C}_5\text{NH}_{10}$, prepared by boiling the ester with piperidine, forms a viscid, colourless, strongly refracting oil, b. p. 87—90°/0·12—0·15 mm., and when treated with magnesium methyl iodide in ethereal solution yields the aldehydeacetal of methylglyoxal,



which is obtained as a colourless liquid, b. p. 54—55°/13—15 mm. (corr.) or 161·7—161·8°/761 mm. (corr.), D 0·937. In sodium hydrogen carbonate solution, it forms a *monosemicarbazone*, white needles, m. p. 132°, and in acid solution, a *disemicarbazone*, m. p. 254° (corr.) (compare Harries and Türk, *Abstr.*, 1905, i, 413). With phenylhydrazine in hot acetic acid solution, the acetal yields methylglyoxal-osazone. When treated with alkalis, the acetal forms a *polymeride*, b. p. 158—159°/16 mm., and on reduction with sodium and alcohol yields *lactaldehydeacetal*, which is obtained as a clear, mobile liquid, b. p. 67°/12—13 mm. (corr.) or 167—170°/758 mm. (corr.) (slight decomp.). G. Y.

Desmotropy and Merotropy. ARTHUR MICHAEL (*Annalen*, 1908, 363, 20—35).—An attempt to refer to the laws of entropy, the phenomena of desmotropy, the existence of two isomerides which can change each into the other by intramolecular wandering of a hydrogen atom, and of merotropy, the formation of derivatives of an isomeride by a substance of stable constitution. It is considered that a correct theoretical view of the whole field can be gained only if the two classes of phenomena are kept strictly separated (compare following abstracts). G. Y.

Tertiary Amines as Reagents for Distinguishing between Stable Enolic and Ketonic Derivatives. ARTHUR MICHAEL and HOWARD D. SMITH (*Annalen*, 1908, 363, 36—63).—Hantzsch and Dollfuss drew attention (*Abstr.*, 1902, i, 223, 675) to the advantage of employing trimethylamine instead of ammonia as a reagent for the recognition of ψ -acids, as an addition of the base to a carbonyl group appeared improbable. They found, however, that their expectations as to the solubilities of trimethylammonium salts in ether and benzene were in many cases not fulfilled. In the present work a rise in temperature on addition of the substance to the reagent, and the formation of a new compound, are taken as the signs of chemical reaction. This method is independent of the solubilities of the substances concerned, and permits of the study of the problem without the introduction of complications by the use of a solvent. As triethylphosphine and trimethylamine unite with carbon disulphide, the formation of similar additive compounds of tertiary amines with aldehydes and ketones was not impossible, but is found not to take place.

A number of stable enolic and ketonic compounds have been investigated as to their behaviour towards triethyl-, tripropyl-, tri-

methyl-, triisooamyl-, triisobutyl-, and tribenzyl-amines. These bases are found to be incapable of enolising stable ketonic compounds. They differ in their capacity to form ammonium salts with enolic compounds, as this property depends on their structure. This capacity is found to diminish in the order in which the bases are named: triisobutylamine reacts only with the most acid enolic compounds, whilst tribenzylamine does not in any case form an ammonium salt. Triethyl- and tripropyl-amines are to be preferred as reagents, because the formation of their additive compounds is accompanied by the development of the greatest amounts of heat, and because they form the most stable salts, an advantage in the case of feebly acid enolic compounds.

The behaviour of merotropic compounds towards amines is discussed, and the conclusion is drawn that a merotropic compound has the enolic form if it reacts with a tertiary amine in absence of a solvent, and the original substance is again formed by the action of hydrochloric acid on the product, but that it has the ketonic form if, whilst not reacting with tertiary amines, it yields with primary and secondary amines, products from which the parent substance is again formed by treatment with hydrochloric acid.

The matter is less simple in the case of desmotropic compounds. The experimental results show that, as was to be expected on theoretical grounds when the conditions of stability of the enolic and the ketonic forms approximate to each other ($K \rightleftharpoons E$), the ketonic form is enolised by tertiary amines, and consequently forms ammonium salts. The action of triethylamine on the ketonic form of dibenzoylacetylmethane leads to the formation of an unstable ammonium salt of the enolic form, which undergoes intramolecular transformation into a stable salt, also of the enolic form. It is considered that the tertiary base acts in the first place on the acetyl carbonyl, which possesses the most energy (see Claisen, Abstr., 1896, i, 557), forming the salt, $CBz_2 \cdot CMe \cdot O \cdot NHEt_3$, the tendency towards better intramolecular neutralisation then causing the triethylammonium group to wander to the benzoyl carbonyl, $CBzAc \cdot CPh \cdot O \cdot NHEt_3$. As was to be expected, the enolic form of dibenzoylacetylmethane forms only one salt with triethylamine.

The behaviour of desmotropic compounds of the group $K \rightleftharpoons E$ towards tertiary amines agrees with the theoretical expectation, the enolic forms being converted into the ketonic. The ketonic forms of ethyl diacetyl- and dibenzoyl-succinates contain each two asymmetric carbon atoms; Knorr considered (Abstr., 1899, i, 673) therefore that the two forms in which each of these esters are obtained are racemic and inactive modifications. This view is tenable no longer, as Michael and Murphy found (Abstr., 1906, i, 179) that the ketonic modification of dibenzoylacetylmethane, which does not contain an asymmetric carbon atom, also exists in two forms. The ketonic form of ethyl diacetylsuccinate behaves in the same manner as that of dibenzoylacetylmethane towards tertiary amines; the modification melting at the higher temperature is converted, completely by triethylamine, partly by triisobutylamine, into the modification melting at the lower temperature. The enolic modification of ethyl dibenzoyl-

succinate, which is only slowly and partly ketonised by sodium carbonate solution (Knorr, *loc. cit.*), is transformed rapidly by traces of triethylamine, forming a mixture of the two ketonic forms. The conditions of stability of the ketones are the converse of those of the acetyl compounds, in that the modification, m. p. 75° , is transformed by triethylamine partly into the modification, m. p. 128° , whereas this is stable towards triethylamine.

The question whether merotropic ketones, which are stable towards tertiary amines alone, can be enolised by these in conjunction with an organic solvent has also been studied. It is found that an organic solvent has no influence on the enolisation of stable merotropic ketones at the ordinary temperature. This conclusion and the classification of many of the substances investigated as ketonic compounds are in disagreement with views which have been founded on the results of physico-chemical investigations. In the present state of their development, however, physical methods cannot be relied on for the decision of such problems, and views founded on the results obtained by these methods can be accepted as correct only when in agreement with the results of chemical investigations.

Ketones.—Diacetylmethane, diacetyethane, acetylheptoylmethane, benzoylacetylmethane, and dibenzoylmethane, oxalyldiacetone, oxalyldimesityl oxide, oxalyldiacetophenone, ethyl acetoacetate, methylacetoacetate, ethylacetoacetate, benzoylacacetate, α -diphenyl acetoacetate, benzoylsuccinate, succinylsuccinate, acetonedicarboxylate, acetylmalonanilate, and cyanoacetate are stable towards tertiary amines in the absence of a solvent. In some cases, solution takes place on heating with triethylamine or on treatment with a concentrated solution of the base, but the unchanged ketone is then regained on cooling or on evaporation at the ordinary temperature. Ethyl diacetoacetate, which is stable towards tertiary amines, reacts with primary and secondary amines, forming carbonyl *additive* compounds.

Ethyl oxalacetate is converted by tertiary amines into ethyl oxalocitrolactone (Wislicenus and Beckh, *Abstr.*, 1897, i, 397). *Methyl oxalocitrolactone*, $C_{11}H_{12}O_9$, obtained in the same manner from methyl oxalacetate, forms white crystals, m. p. 63° ; the *triethylammonium*, m. p. 103° , *tripropylammonium*, m. p. $88-89^{\circ}$, and *barium*, m. p. $225-227^{\circ}$, salts are described.

Ethyl methylloxalacetate and triethylamine form, with development of heat, a brown *oil*, from which the original ester cannot be regained.

Enolic Compounds.—The following compounds react with tertiary amines with development of heat:

Ethyl α -hydroxymethylenepropionate forms unstable *salts*, which decompose in a vacuum, yielding the ester.

Hydroxymethylenacetophenone forms oily *products*, which, on treatment with hydrochloric acid, yield a nitrogen-free *substance*, m. p. $73-74^{\circ}$, gradually becoming resinous.

Hydroxymethylenecamphor reacts with triethyl-, tripropyl-, and triisobutylamines, but not with triisobutylamine, forming *oils*.

With triethylamine, ethyl phenylloxalacetate forms a colourless,

viscid oil, $(C_{14}H_{16}O_5)_2 \cdot NEt_3$, from which hydrochloric acid liberates the original ester.

Ethyl acetylpyruvate reacts with trimethylamine in benzene-toluene solution, forming a yellow oil, which solidifies when rubbed. Similar yellow oils are formed also with other tertiary amines, but only slowly with triisobutylamine. The action of hydrochloric acid on these oily salts leads to the formation of Claisen and Stylos's decomposition product (Abstr., 1887, 918), but of copper acetate in concentrated aqueous-alcoholic solution to the formation of the copper derivative of the pyruvate.

Tetric acid yields a white, crystalline triethylammonium, $(C_5H_6O_3)_2 \cdot NEt_3$, m. p. 30—35°, and an oily triisobutylammonium salt.

With tertiary bases, ethyl acetylmalonate and benzoylacetoacetate form salts, which decompose slowly in a vacuum.

Ethyl dibenzoylacetate does not react with tripropyl-, triisoamyl-, or triisobutylamine, but yields a yellow, crystalline trimethylammonium, m. p. 75—80°, and a triethylammonium, $C_{18}H_{16}O_4 \cdot NEt_3$, m. p. 69—70°, salt, decomposing slowly in a vacuum.

In contrast to ethyl diacetylacetate, which is a stable lactone, diacetylacetanilide behaves as an enolic compound, forming an oily salt with triethylamine.

Triacetylmethane forms salts with trimethyl- and triethylamine, but not with other tertiary bases.

The yellow trimethylammonium salt of benzoyldiacetylmethane is unstable; the triethylammonium salt, $C_{12}H_{12}O_3 \cdot NEt_3$, m. p. 55—58°, decomposes slowly in a vacuum.

Ethyl hydroxymethyleneacetoacetate and diacetylhydroxymethylene-methane form moderately stable, red and dark green oily salts with triethylamine.

Methyl oxalylsuccinate combines with tertiary fatty amines, with the exception of triisobutylamine, forming oils, from which hydrochloric acid liberates apparently the parent ester.

Ethyl acetonedioxyate forms with trimethylamine a yellow salt, m. p. 81—83°, with triethyl-, tripropyl-, and triisoamylamines, yellow oils, which are decomposed by hydrochloric acid with formation of the parent ester, and with triisobutylamine in benzene, a yellow solution which deposits a red oil not decomposed by dilute hydrochloric acid.

The triethylammonium salt of ethyl acetophenoneoxalate, $C_{12}H_{12}O_4 \cdot NEt_3$, forms a white, crystalline mass, m. p. 57°. This ester combines with other tertiary amines, forming oils.

Methyl dioxalylsuccinate combines with all tertiary amines, including triisobutylamine.

Phloroglucinol yields a methylammonium, m. p. 165—167°, ethylammonium, $(C_6H_6O_3)_2 \cdot NEt_3$, m. p. 103—104°, propylammonium, m. p. 87—91°, isoamylammonium, m. p. 97—100°, and triisobutylammonium, m. p. 103—107°, salt. This behaviour, in conjunction with the known reactions of phloroglucinol, is in agreement with the conception of it as a hydroxydiketotetrahydrobenzene.

Phloroglucinol diethyl ether combines with tertiary amines slowly in absence of a solvent, forming colourless *oils*, which are formed more rapidly by treatment of the ether with the tertiary amine in benzene and evaporation of the solution.

Ethyl phloroglucinoldicarboxylate forms a *triethylammonium* salt, $C_{12}H_{14}O_7 \cdot NEt_3$, m. p. 101° , which decomposes moderately quickly in a vacuum.

Enol-ketone Desmotropic Compounds.—The enolic modification of methyl mesityloxidoxalate ($K \rightleftharpoons E$) combines with triethylamine, forming a yellow, oily *salt*, which gradually decomposes in a vacuum, yielding the enolic ester. The ketonic modification does not react with tertiary amines.

The enolic modification of dibenzoylacetylmethane ($K \rightleftharpoons E$) reacts with trimethylamine in toluene solution at -15° , forming yellow, hexagonal prisms, m. p. $94-97^\circ$; this salt, which remains unchanged for some days at 0° in a sealed tube, but decomposes rapidly when exposed to air at the ordinary temperature, is formed also, but more slowly, by the action of the base on the ketonic modification of dibenzoylacetylmethane in toluene solution at -10° . Both modifications give a transient, yellow coloration, and, thereafter, a colourless, crystalline *product* when treated with the base in ethereal solution at -15° . The ketonic modification reacts with triethylamine alone or in toluene solution, forming a yellow *salt*, $C_{17}H_{14}O_3 \cdot NEt_3$, m. p. $86-90^\circ$; in ethereal solution, this is at first formed, but changes into colourless crystals. Tripropylamine also transforms the ketone, forming the *ammonium* salt of the enolic modification. On the other hand, whilst the enolic modification is indifferent to triisomyl- and triisobutylamines, these bases slowly enolise the ketone.

The enolic modification of tribenzoylmethane ($K \rightleftharpoons E$) forms yellow *salts* with trimethyl- and triethylamines; whilst the action of triisomylamine leads partly to the formation of a *salt*, partly to ketonisation of the enol, the latter action alone takes place in presence of triisobutylamine. The ketonic modification is indifferent to tertiary amines alone, or in presence of benzene or ether at the ordinary temperature.

The enolic modifications of ethyl benzylidenebisacetoacetate ($K \rightleftharpoons E$) are transformed by tertiary bases into the ketonic form, which is stable towards these reagents. G. Y.

Phenylcarbimide as Reagent for Determining the Constitution of Merotropic Compounds. ARTHUR MICHAEL and PHILIP H. COBB (*Annalen*, 1908, 363, 64-93).—Dieckmann, Hoppe, and Stein found (Abstr., 1905, i, 135) that the reactivity of phenylcarbimide is greatly increased by the presence of traces of an alkali, and concluded that if such traces are excluded the carbimide does not react with stable ketones, such as the acyclic 1 : 3-dicarbonyl compounds, or with hydroxymethylene derivatives, and that under these conditions phloroglucinol is not attacked, or is attacked only with great difficulty (compare Goldschmidt, Abstr., 1905, i, 340). Michael, on the other hand, found phloroglucinol to react readily with phenylcarbimide in

cold ethereal solution (Abstr., 1905, i, 195). The present authors have therefore again studied the action of phenylcarbimide on ketones, carrying out the experiments partly in glass tubes boiled out with water and acids, and partly in platinum apparatus, and taking all precautions as to the purity of the substances employed. It is found that at the ordinary temperature ethyl acetoacetate and ethyl phenylhydroxymethyleneacetate form *C*- and *O*-additive compounds respectively, whilst at 100° phloroglucinol readily forms the compound obtained by Dieckmann, Hoppe, and Stein only in presence of alkalis. An observation that a specimen of phenylcarbimide containing phenylcarbylamine is less reactive than the pure reagent may explain the differences in the results obtained by the different investigators.

Only certain ketones are capable of reacting with phenylcarbimide; dibenzoylmethane, for example, is indifferent to this reagent. The chemical potential necessary for the reaction $\text{CH}_2\text{R}\cdot\text{COR}' + \text{NPh}\cdot\text{CO} = \text{NPh}\cdot\text{CO}\cdot\text{CHR}\cdot\text{COR}'$ must depend on the nature of the substituting groups R and R'. The formation of the additive compound takes place directly, and not by way of an intermediate *O*-derivative, as is shown by the formation of an *additive* compound by ethyl β -diethylaminocrotonate,



On treatment with concentrated sulphuric acid, the additive compound yields diethylamine and the additive compound of phenylcarbimide and ethyl acetoacetate; hence addition can take place directly to an unsaturated methenyl group.

It has been found further that, whilst ethyl benzoylacetate reacts with phenylcarbimide, forming ethyl benzoylmalonanilate, ethyl methyl- and ethyl-acetoacetates are indifferent to the reagent even in presence of alkalis.

Whilst ethyl cyanoacetate does not react with phenylcarbimide, the sodiocyanoacetate readily forms an *additive* compound, which, on treatment with hydrochloric acid, yields ethyl cyanomalonanilate, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_2$. This crystallises in prisms, m. p. 145°, and is hydrolysed slowly by boiling alkalis, forming cyanoacetanilide.

α -Formylpropionanilide (Abstr., 1905, i, 195) separates from light petroleum in crystals, m. p. 95—96°.

A study of the rise in temperature caused by mixing fatty alcohols with phenylcarbimide gave the following results. The rise in temperature is quoted in degrees; the figures in brackets are the weights in grams of the alcohol and the phenylcarbimide brought into reaction.

Methyl alcohol (0.1:0.26), 37°; ethyl alcohol (0.14:0.29), 23°; *n*-propyl alcohol (0.1:0.3), 23°; (0.17:0.32), 28°; *isopropyl* alcohol (0.1:0.3), 12°; (0.17:0.32), 13°; *n*-butyl alcohol (0.185:0.3), 26.5°; (1.0:1.6), 47°; *isobutyl* alcohol (0.185:0.3), 22°; (1.0:1.6), 31°; *tert.*-butyl alcohol (0.185:0.3), 5°; (1.0:1.6), 4°. The *additive* compounds of the three butyl alcohols crystallise from light petroleum in needles, m. p. 63—64°, 86°, and 134—135° respectively.

The action of phenylcarbimide on ethyl lactate leads to the formation of considerable amounts of carbanilide.

Methyl salicylate does not react with phenylcarbimide at 160°. At 170° the mixture yields only carbanilide, and at 175°, triphenylisocyanurate. On the other hand, an *additive* compound, $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}$,

m. p. 117°, which is probably identical with Lambling's derivative (Abstr., 1902, i, 756), is formed in two to four days by the action of phenylcarbimide on methyl salicylate at the ordinary temperature in presence of traces of sodium acetate, propylamine, or tributylamine. In some experiments, there was obtained a product, m. p. 238—240° (Snape, Trans., 1885, 47, 770 ; 1886, 49, 254 ; Smolka and Friedreich, Abstr., 1890, 618). Ethyl salicylate reacts in the same manner as the methyl ester. The *additive* compound, $C_{16}H_{15}O_4N$, formed in two hours in presence of traces of sodium acetate, separates from carbon disulphide in crystals, m. p. 98—100°.

In presence of sodium acetate, the *isobutyl* ester and phenylcarbimide form triphenyl *isocyanurate*.

In contrast to the salicylates, methyl *m*- and *p*-hydroxybenzoates react with phenylcarbimide in the absence of a catalyst at the ordinary temperature. The *additive* compound of the *m*-ester, $C_{16}H_{15}O_4N$, separates from benzene in crystals, m. p. 115—116° ; the *additive* compound of the *p*-ester, m. p. 134—135°.

The authors have studied also the behaviour of phenylcarbimide towards phenols and anilines containing negative substituting groups or atoms (compare Gumpert, Abstr., 1885, 656 ; 1886, 342). It is found that the reaction is hindered more by a nitro-group in the ortho- than by a nitro-group in the para-position. *o*-Nitrophenol reacts with phenylcarbimide only at 150—170°, traces of an additive compound being formed. At the ordinary temperature, the carbimide slowly polymerises, and the urethane is not formed. *p*-Nitrophenol and phenylcarbimide, on the other hand, react slowly at the ordinary temperature, forming the *urethane*, $C_{13}H_{10}O_4N_2$, which crystallises in yellow prisms ; polymerism of the reagent does not take place.

Picric acid does not react with phenylcarbimide.

Both *o*- and *p*-chlorophenols react more readily than does *p*-nitrophenol ; *o*-chlorophenyl phenylcarbamate, $C_{13}H_{10}O_2NCl$, separates from benzene in crystals, m. p. 120—121°.

Quantitative experiments with the three nitroanilines show that the meta-compound reacts most easily, the ortho-compound least so. Similarly, the velocity of the formation of *o*-chlorodiphenylcarbamide, needles, m. p. 181—182°, from *o*-chloroaniline and phenylcarbimide can be followed by titration, but not that of the meta- or the para-compound, which takes place with too great rapidity.

The dihydroxybenzenes do not react with phenylcarbimide in ethereal solution at the ordinary temperature ; the mixture gradually forms small amounts of the polymeride of the carbimide. G. Y.

Acetyl Chloride and Acetic Anhydride as Reagents for Distinguishing between Enolic and Ketonic Modifications. ARTHUR MICHAEL and ARTHUR MURPHY, jun. (*Annalen*, 1908, 363, 94—106).—The formation of an acetate by the action of acetyl chloride on a carbinol, $R\cdot OH$, takes place in two stages, the first being the formation of an additive compound, $R\cdot O\cdot CMeCl\cdot OH$, and the second, the splitting off of hydrogen chloride. The ease with which the first stage, and therefore the whole reaction, takes place depends on the nature of the group R , and the reaction

may be entirely prevented if R is sufficiently negative. It is for this reason that the stable enolic compounds, ethyl acetylmalonate and benzoylacetate, are not acetylated by acetyl chloride or acetic anhydride, whilst benzoyldiacetylmethane remains unattacked by acetyl chloride even in pyridine solution. Similarly, the enolic forms of desmotropic compounds of the groups $K \rightleftharpoons E$ and $K \rightleftharpoons E$ are not acetylated by acetyl chloride, but are dissolved and ketonised by the reagent. On the other hand, a ketonic modification may be acetylated by acetyl chloride if the ketone carbonyl possesses sufficient chemical potential for the chloride to form the additive compound, $OAc \cdot CRCI \cdot C_nH_{2n+1}$, and if the conditions are favourable to the splitting off of hydrogen chloride from this, when the acetyl derivative of the enolic modification must be formed; hence acetylation of a merotropic compound by acetyl chloride or acetic anhydride cannot be looked on as evidence of the existence of the substance in the enolic form.

When acetic anhydride is employed, there is the further disadvantage that reaction takes place usually only at high temperatures (150—200°), when intramolecular transformation is still more probable, especially as it is difficult under such conditions to exclude sodium acetate, which Dieckmann, Hoppe, and Stein have shown (Abstr., 1905, i, 135) to act catalytically even in traces. This disadvantage is avoided by employing acetyl chloride at temperatures below 100°, but, although under these conditions enol-acetyl derivatives are not obtained from the ketonic modifications of di- and triacetylmethanes, its behaviour with certain other enolic and ketonic compounds shows that acetyl chloride cannot be considered as a trustworthy reagent for determining the constitution of a merotropic compound.

Enolic Compounds.—When heated with acetyl chloride in a reflux apparatus, ethyl acetylmalonate, benzoylacetate, dibenzoylacetate and *C*-acetylmalonanilate, *C*-diacetylacetanilide, benzoyldiacetylmethane, and triphenylvinol remain unchanged. Under the same conditions, ethyl α -hydroxymethylenepropionate and hydroxymethylenephénylacetate, and hydroxymethylenecamphor form acetyl derivatives. Benzoyldiacetylmethane and triphenylvinol are not acetylated by boiling acetic anhydride.

Ketonic Compounds.—Diacetylmethane, $\alpha\alpha$ -diacetylethane, acetylheptoylmethane, ethyl acetoacetate and diacetoacetate, methyl oxalacetate, *C*-dibenzoylacetanilide, ethyl diphenylacetoacetate, benzoylacetylmethane, dibenzoylmethane, ethyl benzoylacetate, ethyl methanetricarbmonoanilate, and ethyl benzoylsuccinate remain unchanged, or if attacked do not form acetyl derivatives when heated with acetyl chloride at 100°.

Enol-keto-desmotropism.—The enolic modification of methyl mesityloxidoxalate ($K \rightleftharpoons E$) is transformed by acetyl chloride at the ordinary temperature into the ketonic modification, which is obtained together with an oil, insoluble in sodium carbonate, when the enol is heated with acetyl chloride, traces of hydrogen chloride being evolved. Under the same conditions, the ketonic modification remains unchanged.

The ketonic modification of dibenzoylacetylmethane ($K \rightleftharpoons E$), m. p. 148°, is formed by the action of acetyl chloride in ethereal solution on the enolic modification, or on the ketonic modification, m. p. 107—110°.

The enolic modification of ethyl diacetylsuccinate ($K \rightleftharpoons E$) is transformed by acetyl chloride into a mixture of the β - and γ -ketonic forms; under the same conditions, the γ -ketone is transformed into the β -ketone, and hence prolonged action of acetyl chloride on the enolic modification leads to the formation of the β -ketone alone.

The ketonic modifications of tribenzoylmethane ($K \rightleftharpoons E$), *p*-bromotribenzoylmethane, and ethyl dibenzoylsuccinate are formed when the enolic modifications are heated with acetyl chloride. Under the same conditions, the ketonic modifications of the two methane derivatives remain unchanged, whilst the γ -ketonic form of the ester, m. p. 75°, is converted into the β -ketonic form, m. p. 128—130°.

G. Y.

Sugars. JAN. J. BLANKSMA AND W. ALBERDA VAN EKENSTEIN (*Chem. Weekblad*, 1908, 5, 777—781).—*l*-Gulose, *l*-idose, *d*-talose, and *l*-ribose have been isolated by combination with substituted phenylhydrazines, followed by decomposition of the hydrazones by benzaldehyde or formaldehyde. The sugars were obtained in the form of syrups which did not crystallise.

l-Gulose was prepared by reduction of *l*-gulonolactone with sodium amalgam (compare Fischer and Stabel, *Abstr.*, 1891, 667), the sodium hydroxide formed being neutralised periodically with sulphuric acid. After the reduction, the solution was concentrated, the sodium sulphate filtered off, and washed with alcohol to remove the syrup. Evaporation of the alcohol left a syrup containing somewhat less than half the weight of the lactone used. This substance separated out in part after a time, and the rest was removed by dissolving in water, neutralising with barium carbonate, filtering off the barium gulonate, and concentrating the filtrate. On treating the residual syrup with phenylhydrazine, *l*-gulosephenylhydrazone separated in yellow crystals, m. p. 136°. The product recrystallised from water has m. p. 143°. It was boiled in aqueous solution with the calculated quantity of benzaldehyde, the benzaldehydephenylhydrazone filtered off, and the slight excess of benzaldehyde removed by steam. On evaporation, the *l*-gulose remained as a light yellow syrup of sweet taste. It could not be obtained crystalline from either water, methyl alcohol, ethyl alcohol, mixtures of alcohol and water, or of alcohol and ether. When cooled with liquid air, it solidified to a hard, glass-like solid, $[\alpha]_D - 20.4^\circ$. Its power of reducing Fehling's solution is 71.5% of that of invert-sugar. These numbers are probably too low, as the syrup contained water. Fischer (*loc. cit.*) states that *l*-gulose is slightly dextrorotatory; that obtained by the authors' method is lævoro-rotatory.

The *methylguloside* was obtained from the syrup by the action of a concentrated solution of hydrochloric acid in absolute methyl alcohol,

removal of the hydrochloric acid by lead carbonate, and evaporation of the filtrate. It is a syrup, and has not been crystallised.

Benzylglucoside was prepared by a similar method from benzyl alcohol. After long standing, it crystallises, and on recrystallisation from methyl alcohol has m. p. 145° . The quantity was too small to admit of analysis.

l-Idose was obtained by a method analogous to that employed for *l*-gulose, starting from *l*-idonolactone. It is a clear syrup, with $[\alpha]_D + 7.5^{\circ}$, and a reducing power 43% of that of invert-sugar. It does not combine with substituted phenylhydrazine or benzoylhydrazine.

d-Talose was prepared from talonic acid, obtained by Fischer's method (Abstr., 1892, 299), which yields a mixture of unchanged galactonic acid and talonic acid. The two acids were converted into the corresponding phenylhydrazides, and these separated by repeated crystallisation from alcohol, talonylphenylhydrazide being the most soluble, and separating from the mother liquor in star-shaped or nodular, acicular masses. Talonic acid was obtained from its phenylhydrazide by boiling with baryta water, removing the phenylhydrazine with ether, and adding sulphuric acid (compare Fischer and Passmore, Abstr., 1890, 152). The acid was converted into its lactone by heating on the water-bath, and reduced to *d*-talose with sodium amalgam. The phenylmethylhydrazone was then prepared, and, after repeated crystallisation from methyl alcohol, had m. p. 154° . When boiled in aqueous solution with benzaldehyde, the hydrazone is converted into talose, which forms a colourless syrup, $[\alpha]_D + 13.95^{\circ}$; reducing power is 71.4% of that of invert-sugar.

l-Ribose was prepared similarly from ribonolactone, but could not be purified by conversion into its phenylhydrazone (compare Fischer and Piloty, Abstr., 1892, 439) or phenylmethylhydrazone, as these compounds are freely soluble in all solvents. The syrup has $[\alpha]_D + 14^{\circ}$, and a reducing power 55.5% of that of invert-sugar. A. J. W.

Presence of *i*-Dimethylinosite in the Latex of *Melaboeai* from Sumatra. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1908, 27, 257—259).—The liquid expressed from the coagulated latex of *Melaboeai* contains *i*-dimethylinosite, which can be isolated in the form of rectangular crystals, m. p. 206° (Girard, *Compt. rend.*, 1870, 67, 820, gives 195°); the tetra-acetyl derivative has m. p. 195° (Girard, *loc. cit.*, gives 193°). On treatment with hydriodic acid, it yields *i*-inosite, m. p. 222° (Maquenne, Abstr., 1887, 356, gives 217°), which forms a hexa-acetyl derivative, m. p. 217° (Maquenne, Abstr., 1887, 308, gives 212°). M. A. W.

Forms of Lactose. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, 30, 1767—1783).—In an earlier paper (Abstr., 1904, i, 974), it has been stated that lactose hydrate crystallises from aqueous solutions of the sugar at the ordinary temperature, whilst at temperatures above 95° the β -anhydrous form separates. The present investigation was undertaken with the object of determining the transition temperature between these forms of lactose, and as it was found that the work illustrated very fully the general conditions underlying transition

temperatures, the measurements were extended to several related phenomena.

All the results agreed quantitatively with the conclusions obtained previously, namely, that aqueous solutions of lactose contain two substances in equilibrium, and that the mutarotation of lactose results from the gradual establishment of equilibrium of the balanced equation $C_{12}H_{22}O_{11}, H_2O \rightleftharpoons H_2O + C_{12}H_{22}O_{11}$ (β -modification). It is shown that the hypotheses of hydration and stereoisomerisation which have been advanced to explain the mutarotation of sugars are summed up and reconciled by the following equation, in which the equilibrium of the first balanced reaction is established instantaneously, whilst that of the second is attained gradually, giving rise to the slow change of rotation: $\alpha\text{-form} + H_2O \rightleftharpoons \text{hydrated form} \rightleftharpoons H_2O + \beta\text{-form}$.

Determinations of the initial and final solubilities of lactose hydrate and β -anhydride between 0° and 100° show that the transition temperature between them is 93° , and this value is confirmed by vapour-pressure measurements. The specific rotatory power of the three forms of lactose has been determined at 15° and 25° , and the results show that the equilibrium in solution does not change perceptibly with the temperature in this interval. It has also been found that the equilibrium does not change with the concentration, since there is no slow change in the rotation of the solutions after dilution. Schmøger has found the rotatory power of the stable solution of lactose at 20° to be 55.3° per gram $C_{12}H_{22}O_{11}$. Accepting this value, the initial specific rotation of the hydrate is 86.0° , and that of the β -anhydride, 35.4° . The freezing points of lactose solutions, the vapour pressures of saturated solutions of lactose hydrate, and the aqueous vapour pressure of the solid hydrate in contact with the β -anhydride are also recorded. The heat of solution of the β -anhydride has been calculated from the solubility data, and found to agree with the value obtained by direct measurement (this vol., ii, 665). The heat of vaporisation of water from the hydrate has been calculated from the vapour pressures of the hydrate, and also from the heats of solution and transition of the two forms, and the two values agree satisfactorily. E. G.

Colloidal Properties of Starch and the Unity of its Constitution. EUGÈNE FOUARD (*Compt. rend.*, 1908, 147, 813—816. Compare this vol., i, 503).—The author has shown previously that a pseudo-solution of starch, when filtered through collodion, is divided into two portions, one consisting of a true solution, the other containing colloidal starch. The experiments described in the present paper confirm the conclusion that starch is a single chemical compound capable of undergoing complete and reversible physical transformation into the state of perfect solution. Thus, when the pseudo-solution is fractionally filtered through a collodion membrane, the successive fractions are found to have the same rotatory power. The residual fractions of the colloid show less tendency to coagulate than the earlier fractions, but this is found to be due to the fact that the traces of mineral phosphates, on the presence of which this phenomenon depends, are not evenly divided

between the true solution and the colloidal residue, the last fraction of which is almost neutral to methyl-orange or phenolphthalein.

The conclusion is drawn that the mode of aggregation of the elementary starch molecule is variable, and depends on the reaction of the surrounding plasma, which varies under different conditions. Thus, owing to different influences, such as the age of the cell-wall modifying the osmotic permeability of the membrane, different molecular aggregates of variable resistance are produced, and this gives rise to the concentric layers observed in the natural starch grain. W. O. W.

Action of Ammonium Persulphate Solution on Cellulose.
II. The Relation of the Cellulose Peroxide formed to the other Products of the Reaction and the Mechanism of the Process of Oxidation. Reaction of Oxycellulose with Nessler's Reagent. HUGO DITZ (*J. pr. Chem.*, 1908, [ii], 78, 343—364. Compare Abstr., 1907, i, 829).—As it has been stated that hydrogen peroxide is formed by the decomposition of ammonium persulphate, the action of hydrogen peroxide on cellulose was compared with that of the persulphate. Whilst the action of the latter is accompanied by evolution of much gas, only very little gas is evolved by the action of hydrogen peroxide, and cellulose peroxide is not formed. It is shown that the cellulose peroxide formed by the persulphate method does not contain sulphuric acid. When boiled with water, the peroxide yields a small amount of a flocculent substance, which may be oxycellulose; the acid (acid-cellulose?) present in the peroxide is insoluble in water. Cellulose peroxide does not evolve ammonia when boiled with lime water, but gives with Nessler's reagent a brown coloration, becoming grey in consequence of the reduction of the mercuric salt by the small amount of oxycellulose present in the peroxide. Oxycellulose contains probably an aldehyde group, as it behaves towards Nessler's reagent in the same manner as a very dilute solution of formaldehyde; it is suggested that the reducing properties of cellulose and hydrocellulose are dependent on the presence of small amounts of oxycellulose (compare Rosenthaler, Abstr., 1906, ii, 911).

The gases evolved by the action of ammonium or potassium persulphate on cellulose are now found to contain carbon dioxide as well as "active" oxygen; the latter is evolved from ammonium persulphate, also, by the action of zinc, tin, or antimony in presence of dilute sulphuric acid; copper, on the other hand, dissolves in ammonium persulphate in presence of dilute sulphuric acid without evolution of "active" oxygen or sulphur dioxide. When 100 c.c. of a 10% solution of ammonium persulphate are heated with filter paper and 5 c.c. of dilute sulphuric acid, and the gases evolved passed into a potassium iodide-starch solution, this becomes violet after eight minutes, and after fifteen minutes requires 0.3 c.c. of *N*/10 sodium thiosulphate solution for decolorisation. A slightly greater effect is produced by employing linen in place of filter paper. Under the same conditions, but in absence of cellulose, the potassium iodide-starch solution is only slightly coloured in eleven minutes, and after twenty-five minutes is decolorised by 0.05 c.c. of *N*/10 sodium thiosulphate. In absence of both cellulose and sulphuric acid, the gases evolved on heating ammonium

persulphate solution do not colour potassium iodide-starch solution in twenty-five minutes.

In conclusion, the mechanism of the oxidation of cellulose is discussed, and the formation of oxycellulose is compared with that of formaldehyde when methyl alcohol is heated with a persulphate. The formation of the peroxide may take place by addition of oxygen either directly to the cellulose molecule or secondarily to oxycellulose. G. Y.

Preparation of Sulphonic Esters of Cellulose. ACTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 200334).—Alkali-soluble cellulose, produced from bleached cotton by the action of zinc chloride and hydrochloric acid, is treated with toluene-*p*-sulphonyl chloride in the presence of 10% aqueous sodium hydroxide. The toluene-*p*-sulphonic ester of cellulose separates after twenty hours as a white, amorphous powder, insoluble in acid zinc chloride solution or in cuprammonium solution; it dissolves in hot glacial acetic acid, and its solution in epichlorohydrin, chloroform, or ethyl acetate on evaporation leaves a transparent pellicle. G. T. M.

Preparation of Alcohol from Substances containing Cellulose. THEO KOERNER (*Zeitsch. angew. Chem.*, 1908, 21, 2353—2359).—The author has endeavoured to ascertain whether the sugar obtained by hydrolysis from wood, etc., by dilute sulphuric acid was entirely derived from the cellulose, or in part from the lignous substances. Comparable experiments with sawdust, straw, and sulphite-cellulose show the amount of alcohol obtained to be proportional to the cellulose present.

It has been stated that sulphurous acid increases the yield of alcohol, but the author finds that such previous treatment actually decreases the amount of alcohol obtainable. As hydrocellulose is found to yield as much as 17·95% of alcohol, it was thought possible that by treating wood, sulphite-cellulose, or straw with oxidising agents before hydrolysis, a similarly increased yield of alcohol might be obtained. With dilute solutions of hydrogen peroxide, this has been realised, the yield of alcohol being materially increased, although in the case of chromic acid a marked decrease is observed. Similarly, the yield of alcohol is found to be decreased by a preliminary oxidation with a solution of potassium persulphate or ozone, the oxidation proceeding beyond the hydrocellulose stage. J. V. E.

Investigations on the Charring of Wood. II. PETER KLASON, GUST. VON HEIDENSTAM, and EVERT NORLIN (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 10, 1—17. Compare this vol., i, 717).—The charring of wood out of contact with air at a maximum temperature of 400° proceeds mainly according to the equation $2C_{42}H_{60}O_{28} = 3C_{16}H_{10}O_2$ (wood-charcoal) + $28H_2O + 5CO_2 + 3CO + C_{28}H_{32}O_9$. The velocity of this change depends on the temperature. Charring begins at about 270°, and increases greatly in rapidity at about 300°. This dry distillation of wood is an exothermic change, the heat of the reaction being about 6% of the heat of combustion; in the case of cellulose, the heat of the reaction is about 5% of that of combustion. The methyl alcohol obtained is formed entirely from the methoxy-groups of the lignin, and the amount obtained from birch or beech wood is about

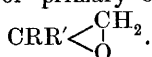
double that yielded by fir or pine. Acetic acid is formed from the cellulose, and also, to a greater extent, from the lignin; birch or beech gives about double as much of the acid as fir or pine. The calorific value of the combustible gases formed during dry distillation is about 3·8% of that of the wood itself; these gases contain neither hydrogen nor aromatic hydrocarbons. Wood charcoal, having the composition $C_{16}H_{10}O_2$, may be regarded as the product of the exothermic charring of wood.

T. H. P.

Modification of the Preparation of Methylamine from Bromoacetamide. MAURICE FRANÇOIS (*Compt. rend.*, 1908, 147, 680—682. Compare this vol., i, 768).—By a modification of the method of preparing methylamine from bromoacetamide described previously, the author is able to obtain a yield of 72% of the theoretical, instead of 35%. The solution of bromoacetamide is prepared by the interaction of acetamide and bromine in presence of water and calcium carbonate, thus avoiding possible loss of bromine through formation of hypobromites or bromates, as when potassium hydroxide is used. The resulting red solution is mixed with cold 30% aqueous sodium hydroxide, and placed in a narrow tube bent several times up and down, which is heated by boiling water. The products are distilled in a current of steam, ammonia is separated by yellow mercuric oxide, and the methylamine distilled off and converted into the hydrochloride.

J. C. C.

Preparation of Amino-alcohols. J. D. RIEDEL (D.R.-P. 199148).—The amino-alcohols, $OH \cdot CRR' \cdot CH_2 \cdot NR''R'''$, are obtained by the action of primary or secondary aliphatic amines on the alkylene oxides,



β-Methylbutylene *αβ*-oxide, $CMeEt \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array}$, b. p. 80°/760 mm., prepared

from *β*-methylbutylene chlorohydrin and sodium hydroxide, gives rise to *dimethylaminodimethylethylcarbinol*, $NMe_2 \cdot CH_2 \cdot CMeEt \cdot OH$, b. p. 57°/23 mm., when treated with dimethylamine in benzene solution at 125°. The *hydrochloride* of the *benzoyl* derivative of this base, m. p. 175°, may be employed as a local anæsthetic.

*iso*Butylene *αβ*-oxide, $CMe_2 \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array}$, b. p. 53°/760 mm., prepared from *isobutylene* chlorohydrin, furnishes with dimethylamine the base *dimethylaminotrimethylcarbinol*, $NMe_2 \cdot CH_2 \cdot CMe_2 \cdot OH$, b. p. 160°/48 mm.; the *hydrochloride* of the *benzoyl* derivative, m. p. 202°, crystallises from absolute alcohol.

αδ-Dimethylamylene *αβ*-oxide, $C_5H_{11} \cdot CMe \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array}$, b. p. 147°/760 mm.,

D 0·8416, obtained from *αδ*-dimethylamylene chlorohydrin by the action of aqueous sodium hydroxide, yields *dimethylaminodimethylisoamylcarbinol*, $C_5H_{11} \cdot CMe(OH) \cdot CH_2 \cdot NMe_2$, b. p. 98—99°/24 mm., on treatment with dimethylamine in benzene solution; the *hydrochloride* of the *benzoyl* derivative of this base separates in silky needles, m. p. 138°.

β-Phenylpropylene *αβ*-oxide, $\text{CMePh} \begin{smallmatrix} \text{CH}_2 \\ \diagup \text{O} \end{smallmatrix}$, b. p. 93°/33 mm.,

D 1·0436, obtained from phenylpropylene chlorohydrin, gives rise to *dimethylaminophenyldimethylcarbinol*, b. p. 135—136°/32 mm., *hydrochloride*, needles, m. p. 159—160°, *aurichloride*, m. p. 110°, *benzoyl* derivative, oily, furnishing a *hydrochloride*, prisms, m. p. 205—206°.

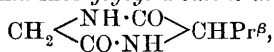
Methylaminophenyldimethylcarbinol, $\text{OH} \cdot \text{CMePh} \cdot \text{CH}_2 \cdot \text{NHMe}$, b. p. 135—138°/31 mm., *hydrochloride*, leaflets, m. p. 153°, *benzoyl* and *dibenzoyl* derivatives both melting at 122°, was obtained from *β*-phenylpropylene *αβ*-oxide and methylamine.

Methylaminodimethylethylcarbinol, $\text{OH} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NHMe}$, b. p. 80°/52 mm., *divaleryl* derivative, oil, b. p. 162°/26 mm., results from the interaction of *β*-methylbutylene *αβ*-oxide and methylamine.

G. T. M.

Synthesis of Polypeptides. XXVII. 3. Derivatives of Active Valine. EMIL FISCHER and HELMUTH SCHEIBLER (*Annalen*, 1908, 363, 136—167).—Only inactive dipeptides of valine have been prepared previously. A knowledge of the optically active forms appeared desirable, not only to permit of a comparison of the synthetical substances with the products of protein hydrolysis, but also for the study of Walden's transformation. Glycyl-*d*-valine, *d*-alanyl-*d*-valine, and *l*-leucyl-*d*-valine are readily prepared in the usual manner by coupling *d*-valine with the chlorides of the halogeno-fatty acids, and treating the products with aqueous ammonia, as are also *d*-*α*-bromoisovaleryl-glycine and *l*-*α*-bromoisovaleryl-*d*-valine by coupling *d*- and *l*-*α*-bromoisovaleryl chlorides with glycine and *d*-valine respectively. In order to avoid racemisation, these bromo-compounds must be converted into the dipeptides by means of anhydrous, liquid ammonia. On hydrolysis, *d*-valylglycine yields *d*-valine and glycine, whilst *l*-valyl-*d*-valine yields *dl*-valine. When treated with ammonia in methyl-alcoholic solution at 0°, the methyl ester of *l*-valyl-*d*-valine yields an inactive anhydride, termed *trans*-valine anhydride.

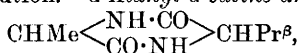
Chloroacetyl-d-valine, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHPr}^s \cdot \text{CO}_2\text{H}$, crystallises from water in prisms, m. p. 113—115° (corr.), or from alcohol in plates; $[\alpha]_D^{20} + 15 \cdot 8^\circ$. Glycyl-*d*-valine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHPr}^s \cdot \text{CO}_2\text{H}$, separates from aqueous alcohol in microscopic needles, m. p. about 254° (corr.), $[\alpha]_D^{20} - 19 \cdot 7^\circ$ in aqueous, $-10 \cdot 5^\circ$ in hydrochloric acid, and $-6 \cdot 9^\circ$ in sodium hydroxide, solution. The *hydrochloride* crystallises in needles or prisms; the *copper* salt separates from its deep blue aqueous solution partly in microscopic prisms and partly as a vitreous mass. The *hydrochloride* of the methyl ester, $\text{C}_8\text{H}_{16}\text{O}_3\text{N}_2 \cdot \text{HCl}$, prepared by treatment of glycyl-*d*-valine with hydrogen chloride in methyl-alcoholic solution and evaporation of the product at 25° under diminished pressure, crystallises in needles. This is converted by methyl-alcoholic ammonia into *glycyl-d-valine anhydride*,



which crystallises in needles, m. p. about 266° (corr.), $[\alpha]_D^{20} + 20 \cdot 8^\circ$ in

glacial acetic acid, $+32.7^\circ$ in aqueous, or $+41^\circ$ in alcoholic solution (Fischer, Abstr., 1907, i, 901).

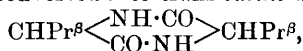
d- α -Bromopropionyl-*d*-valine, $\text{CHMeBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$, prepared from *d*- α -bromopropionyl chloride and *d*-valine, forms feathery crystals, m. p. 180° (corr.), $[\alpha]_D^{20} + 20.8^\circ$ to $+21^\circ$ in alcoholic solution. *d*-Alanlyl-*d*-valine, $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$, crystallises from dilute alcohol in microscopic needles, m. p. about 265° (corr.), $[\alpha]_D^{20} - 1.9^\circ$ in hydrochloric acid, -4.5° in *N*-sodium hydroxide, or -5.4° in aqueous solution. *d*-Alanlyl-*d*-valine anhydride,



is prepared by conversion of the dipeptide into its *methyl ester hydrochloride*, and treatment of this with ammonia in methyl-alcoholic solution; it crystallises in needles, m. p. about $268\text{--}270^\circ$ (corr.), $[\alpha]_D^{20} - 29.3^\circ$ in glacial acetic acid solution, and has less inclination than the preceding anhydride to separate from its solutions in the gelatinous state.

d-Bromoisohexoyl-*d*-valine, $\text{CH}_2\text{Pr}^\beta\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$, prepared from *d*- α -bromoisohexoyl chloride and *d*-valine, forms stout crystals, m. p. $150\text{--}151^\circ$, $[\alpha]_D^{20} + 24.3^\circ$ in alcoholic solution. *l*-Leucyl-*d*-valine, $\text{NH}_2\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$, crystallises from aqueous alcohol in spears or prisms containing water of crystallisation, which is lost in a vacuum over sulphuric acid, m. p. about 282° (corr.; slight decomp.) when quickly heated, $[\alpha]_D^{20} + 18.0^\circ$ in aqueous solution. The anhydride, $\text{C}_{11}\text{H}_{20}\text{O}_2\text{N}_2$, formed by way of the *methyl ester*, crystallises in microscopic needles, m. p. about 282° , $[\alpha]_D^{20} - 46.5^\circ$ to -50.2° in glacial acetic acid solution.

l- α -Bromoisovaleryl-*d*-valine, $\text{CHPr}^\beta\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$, prepared from *l*- α -bromoisovaleryl chloride and *d*-valine, crystallises in needles, m. p. $163\text{--}165^\circ$ (corr.), $[\alpha]_D^{20} - 22.7^\circ$ in absolute alcohol. *l*-Valyl-*d*-valine, $\text{C}_{10}\text{H}_{20}\text{O}_3\text{N}_2\cdot 1\frac{1}{2}\text{H}_2\text{O}$, crystallises in needles, and loses the water of crystallisation at $95^\circ/12\text{--}15\text{ mm.}$ over phosphoric oxide, m. p. about 308° (corr.), $[\alpha]_D^{20} - 70.6^\circ$ to -74.0° . The *hydrochloride* forms quadratic crystals, and is readily soluble in water. The *hydrochloride* of the methyl ester, formed in the usual manner, crystallises in needles, and on treatment with ammonia in methyl-alcoholic solution is converted into *trans-valine anhydride*,



which crystallises in prisms, m. p. $316\text{--}318^\circ$ (corr.), and is optically inactive.

d-Valylglycine, $\text{NH}_2\cdot\text{CHPr}^\beta\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared from *d*- α -bromoisovaleryl-glycine (Fischer and Scheibler, this vol., i, 858) by the action of liquid ammonia at 25° , crystallises from aqueous alcoholic-etheral solution in short prisms, m. p. about 272° (corr.), $[\alpha]_D^{20} + 89.8^\circ$ to $+93.6^\circ$ in aqueous solution, or $[\alpha]_D^{20} + 39.4^\circ$ in 10% hydrochloric acid. A by-product of the formation of this dipeptide crystallises on evaporation of the alcoholic-etheral mother liquor in prisms, and has an acid reaction and taste.

G. Y.

Distillation of Creatinine. R. ENGELAND (*Zeitsch. physiol. Chem.*, 1908, 57, 65—66).—The following compounds have been isolated from

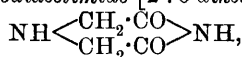
the products obtained by the destructive distillation of creatinine hydrochloride: ammonia, dimethylamine, and pyrrole. J. J. S.

Glycocholic Acid. MAURICE PIETTRE (*Compt. rend.*, 1908, 147, 810—813).—A convenient method is described for isolating glycocholic acid from pig's bile. The product amounts to 60—75% of the total weight of glycocholic acid present, and is quite free from taurocholic acid; its composition agrees with the formula $C_{27}H_{45}O_6N$. The pure acid has m. p. 150° , and $[\alpha]_D + 21^\circ 54'$ in alcoholic solution.

Alkali hydroxides have no action on glycocholic acid under ordinary conditions, but under pressure, complicated changes, exceeding the limits of simple hydrolysis, occur. The toxic properties of sodium glycocholate have been determined; with the higher animals, the lethal dose varies according to the method of administration. W. O. W.

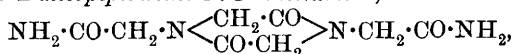
Iminodiacetic Acid and some Derivatives. W. J. A. JONGKEES (*Rec. trav. chim.*, 1908, 27, 287—326).—The derivatives of iminodiacetic acid, $NH(CH_2 \cdot CO_2H)_2$ (diglycollamidic acid, iminoacetic acid), described in the original can be divided into three groups: (I) derivatives containing the imino-group; (II) derivatives in which the hydrogen of the imino-group is replaced by acyl radicles, (III) hydantoin derivatives.

(I). The *hydrochloride* of iminodiacetic acid, $HCl \cdot NH(CH_2 \cdot CO_2H)_2$, obtained by the action of hydrogen chloride on the acid in the presence of alcohol, decomposes at 255° , and is unchanged by the action of such dehydrating agents as thionyl chloride or phosphorus pentachloride; the *ethyl ester*, $HCl \cdot NH(CH_2 \cdot CO_2Et)_2 \cdot H_2O$, has m. p. 74° , and, on treatment with alcoholic ammonia, yields *ethyl hydrogen iminodiacetate*, $NH(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO_2Et$, m. p. 175 — 176° ; the *hydrochloride*, $HCl \cdot NH(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO_2Et$, has m. p. 143° ; the *methyl ester*, $HCl \cdot NH(CH_2 \cdot CO_2Me)_2$, has m. p. 183° , and yields *methyl iminodiacetate*, $NH(CH_2 \cdot CO_2Me)_2$, b. p. $126^\circ/33$ mm. or $123.5^\circ/16$ mm., $D_{16.5}^{16.5} 1.1675$, from which the diamide, $NH(CH_2 \cdot CO \cdot NH_2)_2$, m. p. 143° (Heintz, *Annalen*, 1868, 148, 178), and the *monamide (iminoacetamic acid)*, $NH(CH_2 \cdot CO_2H \cdot CH_2 \cdot CO \cdot NH_2)$, m. p. 210° , are obtained by the action of ammonia; the *hydrochlorides* have m. p. 255° and 210° respectively; and the *compound*, $NH_3 \cdot HCl \cdot NH(CH_2 \cdot CO \cdot NH_2)_2$, obtained by treating the hydrochloride of methyl iminodiacetate with methylalcoholic ammonia, forms beautiful crystals, that soften at 145° , but do not melt at 190° . *Iminodiacetimide* [2:6-diketopiperazine],

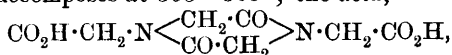


obtained by heating under 15 mm. pressure the ammonium salt, the monamide, or the diamide of the acid, forms white needles, m. p. 200 — 205° .

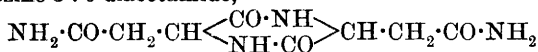
(II). 2:5-Diketopiperazine-1:4-diacetamide,



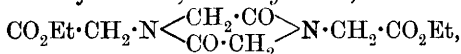
is obtained as a secondary product in the preparation of iminodiacetimide; it decomposes at 303 — 305° ; the *acid*,



forms crystals, m. p. 280—290°, and, unlike the isomeride, 2:5-diketopiperazine-3:6-diacetamide,

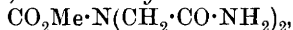


(Fischer, Abstr., 1905, i, 32), is stable towards boiling methyl-alcoholic potassium hydroxide; the *ethyl* ester,



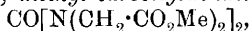
has m. p. 79—80°. *Acetylminodiacetonitrile*, $\text{Nac}(\text{CH}_2 \cdot \text{CN})_2$, obtained by the action of acetic anhydride on iminodiacetonitrile, is a viscid oil, b. p. 227°/16 mm.; *methyl acetylminodiacetate*, $\text{Nac}(\text{CH}_2 \cdot \text{CO}_2\text{Me})_2$, similarly prepared, has b. p. 184—185°/15 mm., m. p. 83·5—84°; *acetylminodiacetamide*, $\text{Nac}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, has m. p. 203°, and yields the *hydrochloride*, $\text{HCl} \cdot \text{Nac}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$.

Carbmethoxyiminodiacetonitrile, $\text{CO}_2\text{Me} \cdot \text{N}(\text{CH}_2 \cdot \text{CN})_2$, prepared from methyl chloroformate and iminodiacetonitrile, has m. p. 63—64°, b. p. 189°/15 mm.; *methyl carbmethoxyiminodiacetate*, $\text{CO}_2\text{Me} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{Me})_2$, has b. p. 167°/15 mm.; *carbmethoxyiminodiacetamide*,

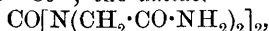


has m. p. 212°; *carbmethoxyiminodiacetic acid*, $\text{CO}_2\text{Me} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, has m. p. 123°, and the blue *copper* salt, $\text{C}_6\text{H}_7\text{O}_6\text{NCu} \cdot \text{H}_2\text{O}$, and the *barium* salt, $\text{C}_6\text{H}_7\text{O}_6\text{NBa} \cdot \text{H}_2\text{O}$, have been prepared.

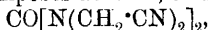
Methyl chloroformyliminodiacetate, $\text{COCl} \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{Me})_2$, obtained by the action of carbonyl chloride (1 mol.) on methyl iminodiacetate (2 mols.), has m. p. 74°; *methyl carbonyldi-iminodiacetate*,



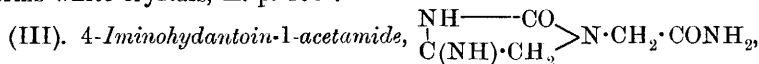
from carbonyl chloride (1 mol.) and methyl iminodiacetate (4 mols.), forms needles, m. p. 88—89°; the *amide*,



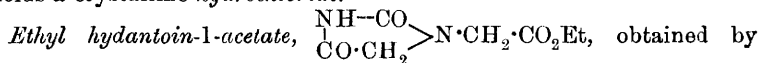
darkens at 230° and decomposes at 250°, and the *nitrile*,



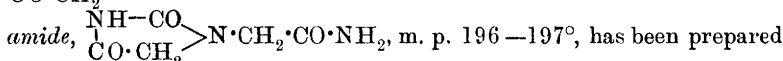
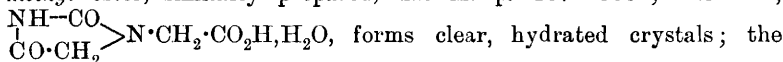
forms white crystals, m. p. 155°.



obtained by the action of alcoholic ammonia on carbmethoxyiminodiacetonitrile, forms colourless needles, which decompose at 245°, and yields a crystalline *hydrochloride*.



hydrolysis of the preceding compound with hot hydrochloric acid and subsequent esterification, forms beautiful needles, m. p. 84—85°; the *methyl* ester, similarly prepared, has m. p. 107—108°; the *acid*,

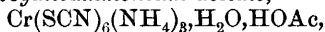


m. p. 196—197°, has been prepared (1) by the action of alcoholic ammonia on methyl chloroformyliminodiacetate; (2) as a secondary product in the hydrolysis of imino-hydantoin-1-acetamide, and (3) by the action of ammonia on the *ethyl* ester.

M. A. W.

Hexathiocyano-salts of Molybdenum. JOHANNA MAAS and JULIUS SAND (*Ber.*, 1908, 41, 3367—3376. Compare this vol., i, 397, 513).—A reply to the criticism of Rosenheim and Garfunkel (this vol., i, 614). The authors have carefully re-analysed the potassium, ammonium, and zinc amino-salts, and confirm their previous results.

The *chromihexathiocyanoammonium acetate*,



prepared from the chloride, $\text{CrCl}_3 \cdot (\text{H}_2\text{O})_4 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$, ammonium thiocyanate, and acetic acid, crystallises in reddish-violet, rhombic needles, isomorphous with the corresponding molybdenum salt. W. R.

Preparation of Additive Compounds of Chloral with Amides. NATHAN SULZBERGER (D.R.-P. 198715).—Chloral combines additively with the amides of the higher fatty acids. *Chloral palmitinamide*, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{CO} \cdot [\text{CH}_2]_{14} \cdot \text{CH}_3$, an oleaginous, white, crystalline powder, m. p. 110° , is produced by mixing its generators and warming at 100° . *Chloral α -bromopalmitin anilide*, prepared in a similar manner, is a colourless, crystalline powder with a greasy feel.

G. T. M.

Action of Phosphorus Pentachloride on Halogenated Acid Amides. WILHELM STEINKOPF (*Ber.*, 1908, 41, 3571—3595).—Although in regard to their rates of formation and stability the halogen-substituted acetonitriles and acetamides closely resemble nitroacetamide and -acetonitrile, it is found that they do not yield the corresponding acetimide chlorides when treated with thionyl chloride, whereas, as shown by Steinkopf and Bohrmann (this vol., i, 327), the action of thionyl chloride on nitroacetamides leads to the formation of nitroacetimide chlorides. The author has studied therefore the action of phosphorus pentachloride on dichloro- and dibromoacetonitriles.

Wallach found (this Journ., 1877, ii, 182) that, whilst the action of phosphorus pentachloride on acetamide leads to the formation of the amide chloride, which readily loses hydrogen chloride, forming the imide chloride, di- and tri-chloroacetamides yield products which may have the formulæ (1) $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NCl} \cdot \text{POCl}_2$ and $\text{CCl}_3 \cdot \text{CO} \cdot \text{NCl} \cdot \text{POCl}_2$ or (2) $\text{CHCl}_2 \cdot \text{CCl} : \text{N} \cdot \text{POCl}_2$ and $\text{CCl}_3 \cdot \text{CCl} : \text{N} \cdot \text{POCl}_2$ respectively. It is found that now that the formation of such phosphorus compounds is a general reaction of the α -halogenated acetamides. The formulæ (2) are to be preferred, as the action of moisture on these compounds leads to the displacement of a chlorine atom by a hydroxyl group, and the formation of a product, $\text{CHCl}_2 \cdot \text{C}(\text{OH}) : \text{N} \cdot \text{POCl}_2$, or its tautomeric form, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl}_2$, is more probable than that of a product, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{N}(\text{OH}) \cdot \text{POCl}_2$.

[With CZESLAU BENEDEK.]—The liquid product, obtained by the action of phosphorus pentachloride on chloroacetamide in absence of moisture (Wallach, *loc. cit.*), gives, on analysis, figures agreeing with the formula $\text{CH}_2\text{Cl} \cdot \text{CCl} : \text{N} \cdot \text{POCl}_2$; it decomposes on distillation in a vacuum, and, on exposure to moisture, evolves hydrogen chloride and yields small amounts of crystalline chloroacetylphosphamic chloride, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl}_2$.

Dichloroacetylphosphamic chloride, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl}_2$, formed by the action of moist air on $\alpha\beta\beta$ -trichloroethylidenephosphamic chloride (Wallach, *loc. cit.*), crystallises in white plates, m. p. $112-113^\circ$. When treated with sodium ethoxide in alcoholic solution, it forms the *ethyl* ester, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{PO}(\text{OEt})_2$, which crystallises in white needles, m. p. $72-73^\circ$, is soluble in dilute sodium hydroxide or ammonia, forms a yellow *precipitate* with platinum tetrachloride in ammoniacal solution, and can be titrated with *N*/10 potassium hydroxide. The *dianilide*, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{PO}(\text{NHPh})_2$, prepared by heating the oxydichloride with aniline in ethereal solution, or by the successive action of an excess of aniline and of water on $\alpha\beta\beta$ -trichloroethylidenephosphamic chloride, crystallises from alcohol in white needles, m. p. $219-220^\circ$. The *bisphenylhydrazide*, $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{PO}(\text{NH} \cdot \text{NHPh})_2$, forms white crystals, m. p. 190° (decomp.).

Trichloroacetylphosphamic chloride, $\text{CCl}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl}_2$, prepared by evaporating the light petroleum solution of the imide chloride-phosphorus oxydichloride (Wallach, *loc. cit.*) in contact with moist air, crystallises in white needles, m. p. $146-148^\circ$, and when treated with water yields phosphoric acid and trichloroacetamide. The *methyl* ester, $\text{CCl}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{PO}(\text{OMe})_2$, crystallises in white leaflets, m. p. $105-107^\circ$, and dissolves in dilute alkalis; the *potassium* salt, $\text{C}_4\text{H}_6\text{O}_4\text{NCl}_3\text{PK}$, m. p. about 135° , is hygroscopic. The *ethyl* ester, $\text{C}_6\text{H}_{11}\text{O}_4\text{NCl}_3\text{P}$, forms crystalline aggregates, m. p. $47-48^\circ$. The *dianilide*, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3\text{Cl}_3\text{P}$, white needles, m. p. $194-195^\circ$. The *bisphenylhydrazide*, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_5\text{Cl}_3\text{P}$, m. p. $237-238^\circ$ (decomp.).

The product of the action of phosphorus pentachloride on bromoacetamide is unstable and has not been isolated.

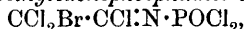
[With H. GRÜNUPF.]—*Tribromochloroethylidenephosphamic chloride*, $\text{CBr}_3 \cdot \text{CCl} \cdot \text{N} \cdot \text{POCl}_2$, formed from phosphorus pentachloride and tribromoacetamide at $90-110^\circ$, is obtained as a liquid, which gradually crystallises. *Tribromoacetylphosphamic chloride*, $\text{CBr}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl}_2$, formed by exposing the preceding substance to air, separates from benzene in crystals, m. p. $105-106^\circ$, and decomposes on further exposure to moisture. When treated with sodium methoxide in methyl-alcoholic solution, it forms *methyl dibromomethoxyacetylphosphamate*,



which separates from water in white crystals, m. p. $92-93^\circ$. The corresponding *ethoxy-ethyl* ester, $\text{C}_8\text{H}_{16}\text{O}_5\text{NBr}_2\text{P}$, forms long needles, m. p. 91° .

[With G. KIRCHHOFF.]— $\alpha\beta$ -*Dichloro- β -bromoethylidenephosphamic chloride*, $\text{CHClBr} \cdot \text{CCl} \cdot \text{N} \cdot \text{POCl}_2$, prepared from chlorobromoacetyl compound, is obtained as a yellow liquid. The *amide*, formed by the action of moisture on this, could not be purified, and was converted directly into the *ethyl* ester, $\text{CHClBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{PO}(\text{OEt})_2$, colourless crystals, m. p. $67-68^\circ$.

$\alpha\beta\beta$ -*Trichloro- β -bromoethylidenephosphamic chloride*,

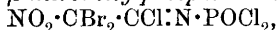


prepared from dichlorobromoacetamide, forms crystals, m. p. 68° . The *chloride*, $\text{CCl}_2\text{Br} \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl}_2$, forms colourless crystals, m. p. 147° ;

the *methyl* ester of this, $C_4H_7O_4NCl_2BrP$, separates from water in crystals, m. p. 107° ; the *ethyl* ester, m. p. $76-77^\circ$.

Dichloronitroacetamide, $NO_2 \cdot CCl_2 \cdot CO \cdot NH_2$, prepared by the action of chlorine on ammonio-nitroacetamide, is obtained as a white, crystalline precipitate, m. p. $94-95^\circ$. The $\alpha\beta$ -trichloro- β -nitrophosphamic chloride, $NO_2 \cdot CCl_2 \cdot CCl \cdot N \cdot POCl_2$, forms white crystals, m. p. $55-60^\circ$. *Dichloronitroacetylphosphamic chloride*, $C_2HO_4N_2Cl_4P$, separates from benzene in crystals, m. p. 165° (decomp.); the *ethyl* ester, $C_6H_{11}O_6N_2Cl_2P$, long needles, m. p. 56° .

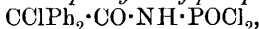
α -Chloro- $\beta\beta$ -dibromo- β -nitroacetylphosphamic chloride,



forms white crystals, m. p. about 65° . *Dibromonitroacetylphosphamic chloride*, $C_2HO_4N_2Cl_2Br_2P$, white crystals, m. p. $187-188^\circ$ (decomp.).

[With C. BENEDEK.]— α -Chloro- β -bromophenylethylidenephosphamic chloride, $CHBrPh \cdot CCl \cdot N \cdot POCl_2$, was analysed. The derivatives are unstable.

α -Chlorodiphenylacetamide has m. p. $111-113^\circ$ (115° : Bickel, Abstr., 1889, 999). *Chlorodiphenylacetylphosphamic chloride*,

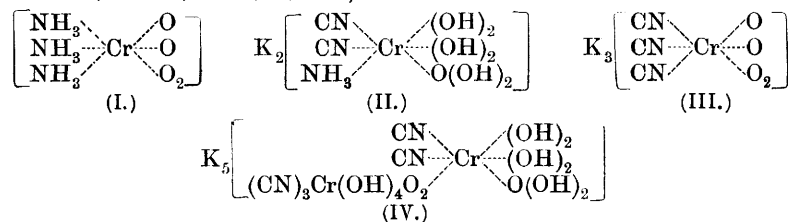


forms crystals resembling ammonium chloride, m. p. $122-123^\circ$. The *methyl* ester, $C_{16}H_{17}O_4NClP$, white crystals, m. p. $104-106^\circ$.

$\alpha\beta$ -Trichloropropylidenephosphamic chloride, $CMeCl_2 \cdot CCl \cdot N \cdot POCl_2$, prepared from di- α -chloropropionamide and phosphorus pentachloride at $85-95^\circ$, crystallises from light petroleum in white needles, m. p. 80° . Di- α -chloropropionylphosphamic chloride, $C_3H_4O_2NCl_5P$, snow-white needles, m. p. $127-128^\circ$.

Other nitro-amides, such as nitroacetamide and nitromalonamide, also react with phosphorus pentachloride, but the products are too unstable to permit of their isolation. G. Y.

Higher Oxidation Products of Chromium. IV. Chromium Tetroxide Compounds. ERNST H. RIESENFELD [and, in part, ALFRED WESCH] (*Ber.*, 1908, 41, 3536—3552. Compare Abstr., 1906, ii, 92; this vol., ii, 951; Riesenfeld and Wohlers, Abstr., 1907, ii, 357).—The mol. wt. of Wiede's triamminechromium tetroxide (Abstr., 1898, ii, 28) has been determined by the cryoscopic method, and the values obtained found to agree with the formula $(NH_3)_3CrO_4$ (compare Werner, Abstr., 1906, ii, 760). The structural formula I has been

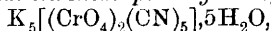


assigned to this compound; in support of this formula, it has been found possible to prepare the dicyanomonomamine derivative, II, inter-

mediate between the tricyano-compound, III, of Wiede (*loc. cit.*) and the triamminechromium tetroxide. A compound has also been prepared having the formula IV, in which one of the positions in the complex is occupied by a group similar in composition to the rest of the complex radicle. This is probably the first complex salt of this nature to be prepared.

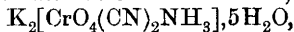
The complex in II and IV is represented as containing water, since compound II crystallises with water, which is removed together with ammonia when the substance is kept over calcium chloride, and compound IV crystallises with water, only part of which is eliminated over phosphoric oxide. One mol. of the triammine, when decomposed by acid or alkali, yields 2—3 equivalents of hydrogen peroxide, that is, only the O_2 group in the complex forms hydrogen peroxide, and is thus in all probability a bivalent group. It is therefore highly probable that the chromium in the tetroxide derivatives is sexavalent.

Potassium dichromium tetroxide pentacyanide,



is formed by treating an aqueous solution of potassium cyanide and chromic acid, cooled in an ice-salt freezing mixture, with hydrogen peroxide; it crystallises in dark reddish-brown prisms. Molecular-weight determinations by the cryoscopic method and electrical conductivity measurements show that the salt when completely dissociated in aqueous solution is ionised, thus: $K_5[(CrO_4)_2(CN)_5] = 5K^+ + [(CrO_4)_2CN]^- + 4CN^-$. It is converted by aqueous ammonia into

potassium dicyanononamminechromium tetroxide,



crystallising in long, slender, yellowish-brown needles. The complex of this salt is dissociated in dilute aqueous solution. It slowly evolves hydrogen cyanide and ammonia when kept, and decomposes with slight explosion when heated rapidly.

W. H. G.

Preparation of the Cyanides and Cyanamides of the Alkali and Alkaline Earth Metals. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 200986).—All nitrogen compounds of titanium, such as the nitride or the carbonitrides, readily give rise to cyanides or cyanamides when heated with carbon and the oxides, carbonates, sulphates, or other salts of the alkali and alkaline earth metals. The reaction occurs either in the presence or absence of a fusible medium, such as fusion mixture or a fusible chloride. The carbon may be introduced in the form of soot or pitch, or it may be obtained from a decomposable hydrocarbon. The titanium is left in a form capable of recombining with carbon, and thus the process is continuous. The alkali metals give rise to cyanides only; barium yields a mixture of cyanide and cyanamide, whereas calcium cyanamide is the sole product when lime is employed.

G. T. M.

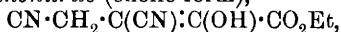
Preparation of Aminodicyanodiamidine. TEMISTOCLE JONA (*Gazzetta*, 1908, 38, ii, 480—484).—Thiele and Uhlfelder's method of preparing aminodicyanodiamidine by nitrating dicyanodiamidine and subsequently reducing (*Abstr.*, 1899, i, 119) gives low yields. As much as 80% of the theoretical quantity can be obtained by reducing nitrodicyanodiamidine by means of hydrochloric acid (D 1.19) and

zinc dust at a temperature not higher than 45° . When aminodicyanodiamidine dihydrochloride is heated with *p*-aminobenzaldehyde in a solution faintly acid by hydrochloric acid, it yields a red *compound*, crystallising from alcohol in long filaments and softening at 300° without showing signs of melting; the constitution of this compound is being investigated. T. H. P.

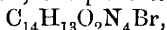
Desmotropy and Fluorescence of Ethyl Oxalosuccinonitrile. WILHELM WISLICENUS and PAUL BERG (*Ber.*, 1908, 41, 3757—3768).—Ethyl oxalate (1 mol.) and succinonitrile (1 mol.) condense under the influence of sodium ethoxide, yielding the sodium derivative of ethyl oxalosuccinonitrile, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$. Attempts to bring about condensation with a second molecule of ethyl oxalate were unsuccessful, although succinonitrile condenses with 2 mols. of methyl oxalate; the methyl analogue of the ethyl compound mentioned above could not, however, be prepared. Ethyl oxalosuccinonitrile exists in two tautomeric forms; the enolic form is obtained by treating the sodium derivative with acid, and passes into the ketonic form when warmed in aqueous solution. The ketonic form dissolves in alcohol, forming a bluish-violet, fluorescent solution. This is the first fluorescent substance of the aliphatic series to be prepared, and is consequently of some importance in connexion with the question of the relationship between chemical constitution and fluorescence.

The chemical behaviour of the ketone is represented by the formula $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ with but one exception, namely, its behaviour towards phenylhydrazine; although the enolic form yields a normal phenylhydrazone, the ketonic form gives rise to only small quantities of indefinite substances.

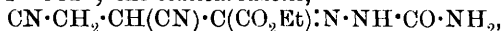
α -Ethyl oxalosuccinonitrile (enolic form),



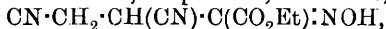
crystallises in colourless, pointed leaflets, m. p. $102-103^{\circ}$. The alcoholic solution is not fluorescent, and gives a dark cherry-red coloration with ferric chloride; the *copper* salt, $(\text{C}_8\text{H}_7\text{O}_3\text{N}_2)_2\text{Cu}$, forms emerald-green, rhombic leaflets, m. p. $118-121^{\circ}$ (decomp.). It yields with phenylcarbimide at the ordinary temperature the *additive* product, $\text{CN}\cdot\text{CH}_2\cdot\text{C}(\text{CN})\cdot\text{C}(\text{O}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{Et}$, small, flat needles, decomposing at 200° ; with ammonia in ethereal solution, the *ammonium* salt, $\text{C}_8\text{H}_{11}\text{O}_3\text{N}_3$, long leaflets, decomposing at $145-150^{\circ}$; with phenylhydrazine in alcoholic solution, the *phenylhydrazone*, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_4$, colourless needles, m. p. $150-151^{\circ}$; the *p*-bromophenylhydrazone,



has m. p. $181-182^{\circ}$; the *semicarbazone*,



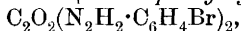
forms long, colourless needles, m. p. 162° ; the *oxime*,



crystallises in long needles, m. p. 110° .

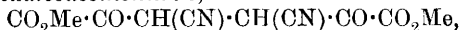
β -Ethyl oxalosuccinonitrile (ketonic form) crystallises in pale yellow, microscopic needles, m. p. $154-155^{\circ}$; it is reconverted into the α -form by an alcoholic solution of sodium ethoxide. It does not react with ammonia, *p*-bromophenylhydrazine, semicarbazide hydrochloride, hydroxylamine, or phenylcarbimide at the ordinary tempera-

ture, and yields with phenylhydrazine very small quantities of a substance, which crystallises in small, golden-yellow needles, decomposing at 122—125°. It reacts with phenylcarbimide at 100°, yielding the additive product described above, and with *p*-bromophenylhydrazine at 100°, forming *oxalic acid di-p-bromophenylhydrazide*,



colourless scales, m. p. 240° (decomp.).

Dimethyl dioxalosuccinonitrile,



crystallises in yellow, glistening, hexagonal leaflets, m. p. 185°. It does not give a coloration with ferric chloride, but with copper acetate forms a *copper salt*, $(\text{C}_{10}\text{H}_7\text{O}_6\text{N}_2)_2\text{Cu}$, crystallising in yellowish-green, microscopic needles.

W. H. G.

Negative Substituted Amino-oximes. III. Brominated Amino-oximes. WILHELM STEINKOPF and H. GRÜNUPP (*Ber.*, 1908, 41, 3569—3571).—The authors have prepared the mono-, di-, and tri-bromoethenylamino-oximes, and have found that, whilst the mono- and di-bromo-compounds resemble in their stability the chloro- and iodo-substituted ethenylamino-oximes, the tribromo-compound is comparatively unstable. The brominated ethenylamino-oximes are prepared by the action of hydroxylamine on the corresponding brominated acetonitriles in the same manner as are the chloro- and iodo-compounds. They give characteristic brown to brownish-red colorations with ferric chloride, and form hydrochlorides when treated with hydrogen chloride in ethereal solution.

Bromoethenylamino-oxime, $\text{CH}_2\text{Br} \cdot \text{C}(\text{NOH}) \cdot \text{NH}_2$, crystallises in yellowish-white leaflets, m. p. 95—96°, yields a dirty-green precipitate with alkaline copper sulphate solution, and reduces boiling alkaline mercuric chloride.

Dibromoethenylamino-oxime, $\text{CHBr}_2 \cdot \text{C}(\text{NOH}) \cdot \text{NH}_2$, crystallises in white needles, m. p. 120°, forms a dirty-green precipitate with alkaline copper sulphate, and reduces mercuric chloride in boiling alkaline solution. The *hydrochloride*, white powder, m. p. 163—165° (decomp.).

Tribromoethenylamino-oxime, $\text{CBr}_3 \cdot \text{C}(\text{NOH}) \cdot \text{NH}_2$, m. p. 126°, gradually decomposes at the ordinary temperature.

G. Y.

Silicoiodoform. OTTO RUFF [in part, EMIL GEISEL] (*Ber.*, 1908, 41, 3738—3744).—Silicoiodoform may be obtained in fairly large quantities by the action of hydrogen iodide on siliconitrogen hydride, SiNH , suspended in cold carbon disulphide, or more readily by treating trianilinosilicon hydride, $\text{SiH}(\text{NHPh})_3$, with hydrogen iodide in benzene.

Silicoiodoform decomposes slowly above 150°, liberating hydrogen and probably a volatile iodosilicon hydride. The b. p. of silicoiodoform is about 220°/760 mm., but on continued boiling the temperature slowly rises to about 300°; the residue left after distillation is chiefly silicon tetraiodide. Silicoiodoform boils without decomposition under a pressure of 14, 22, 67, and 122 mm. at 106°, 111°, 132°, and 155° respectively; it has D^{23}_D 3.286.

Trianilinosilicon hydride (trianilinosilicane), $\text{SiH}(\text{NHPh})_3$, prepared

by the interaction of aniline and silicochloroform in benzene, crystallises in slender, white needles, and begins to decompose at 114° . It is converted by hydrogen chloride, bromide, or iodide into the corresponding trihalogenated silicane, and by water into silicoformic acid and aniline.

Siliconitrogen hydride, SiNH , is obtained together with siliconamide by the interaction of silicochloroform vapour and ammonia diluted with hydrogen at about -10° , as a white powder. W. H. G.

Silico-acids and their Derivatives. WILHELM MELZER (*Ber.*, 1908, 41, 3390—3395).—Silicon tetrachloride reacts with organo-magnesium halides, yielding compounds of the type RSiCl_3 (compare Kipping, *Trans.*, 1907, 91, 209), alkyltrichlorosilanes. These react with water, yielding the silico-acids, $\text{R}\cdot\text{SiO}_2\text{H}$, and with anhydrous alcohol, yielding the ortho-esters, $\text{R}\cdot\text{Si}(\text{OEt})_3$. In the preparation of the chlorides, it is essential that all traces of moisture should be removed.

Propyltrichlorosilicane, $\text{C}_3\text{H}_7\cdot\text{SiCl}_3$, is a clear, colourless liquid, b. p. $123-125^{\circ}$; it has a penetrating odour, and fumes in contact with the air.

Silicobutyric acid, $\text{C}_3\text{H}_7\cdot\text{SiO}_2\text{H}$, forms a hard, solid mass, which can be ground to a powder. It is infusible.

Ethyl orthosilicobutyrate, $\text{C}_3\text{H}_7\cdot\text{Si}(\text{OEt})_3$, is a colourless liquid with an aromatic odour, and has b. p. $177-179^{\circ}$ and D 0.8945.

isoAmyltrichlorosilicane, $\text{C}_5\text{H}_{11}\cdot\text{SiCl}_3$, is a colourless liquid, b. p. $46^{\circ}/9$ mm., D 1.066.

Ethyl orthosilicohexoate, $\text{C}_5\text{H}_{11}\cdot\text{Si}(\text{OEt})_3$, has b. p. $195-200^{\circ}$ and D 0.9318.

Silicohexoic acid, $\text{C}_5\text{H}_{11}\cdot\text{SiO}_2\text{H}$, forms a hard, brittle solid, soluble in ether, benzene, or chloroform, and has not a definite m. p.

Benzyltrichlorosilicane, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{SiCl}_3$, has b. p. $94-96^{\circ}/11$ mm. and D 1.2834. The ortho-ester, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{Si}(\text{OEt})_3$, has b. p. $245-250^{\circ}$ and D 0.9864. *Silicophenylacetic acid*, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{SiO}_2\text{H}$, separates from ether as a clear, vitreous solid, m. p. $65-66^{\circ}$.

α -*Naphthyltrichlorosilicane*, $\text{C}_{10}\text{H}_7\cdot\text{SiCl}_3$, is a viscid liquid with a penetrating odour, and has b. p. $165-170^{\circ}/22$ mm. and D 1.3760. The ortho-ester, $\text{C}_{10}\text{H}_7\cdot\text{Si}(\text{OEt})_3$, has b. p. $220-230^{\circ}/18$ mm., and the acid, $\text{C}_{10}\text{H}_7\cdot\text{SiO}_2\text{H}$, has m. p. $125-130^{\circ}$ (compare Khotinsky and Seregenkoff, this vol., i, 1032). J. J. S.

Velocity of Decomposition of the Ozonides of Certain Cyclic Hydrocarbons. CARL D. HARRIES and HANS VON SPLAWA NEYMANN (*Ber.*, 1908, 41, 3552—3558).—In the communication of Harries and Neresheimer (*Abstr.*, 1906, i, 833), it is incorrectly stated that a sparingly soluble ozonide of cyclohexene is obtained by passing ozone into a solution of the hydrocarbon in chloroform. This ozonide is formed when carbon tetrachloride is the solvent, whilst when chloroform or hexane is the solvent employed, an ozonide is obtained which may be crystallised from alcohol. The two ozonides have approximately the same composition, and behave similarly when decomposed by water.

The decomposition of the ozonides of cyclopentene and cyclohexene

by water has been studied quantitatively (compare Harries and Tank, this vol., i, 517); it is found that under similar conditions *cyclopentene* ozonide is decomposed in one hour to about the same extent as *cyclohexene* ozonide in two and a-half hours.

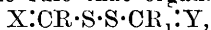
α -*cycloHexene ozonide*, $C_6H_{10}O_3$, obtained by passing ozone into a solution of the unsaturated hydrocarbon in hexane, crystallises in stellate groups of small, white needles, m. p. 75° ; it decomposes at 90° .

β -*cycloHexene ozonide* is formed together with the α -ozonide by acting on a solution of the hydrocarbon in carbon tetrachloride with ozone; it is a sparingly soluble, solid substance, m. p. 115 — 120° (decomp.), and when analysed gives values which lie between those required for $C_6H_{10}O_3$ and $C_6H_{10}O_4$.

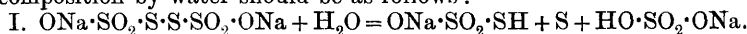
Both ozonides are decomposed by boiling water, yielding adipic acid (about 44%), adipic dialdehyde, *cyclopentenealdehyde*, and adipic semialdehyde (about 13%). *Adipic semialdehyde* (δ -*aldehydovaleric acid*), $CHO \cdot [CH_2]_4 \cdot CO_2H$, forms colourless crystals, m. p. 124 — 125° ; the *p*-nitrophenylhydrazone crystallises in yellow needles, m. p. 134° .

W. H. G.

Lowest Oxides of Hydrogen Sulphide. EMIL FROMM (*Ber.*, 1908, 41, 3397—3425).—[With ADOLF ROESICKE.]—In previous communications (*Abstr.*, 1906, i, 656; 1907, i, 982; this vol., i, 700), the author has stated the rule that organic disulphides of the type



containing neighbouring double linkings, are decomposed by water or alkalis, sulphur being eliminated. An attempt has been made to apply the rule to the elucidation of the constitution of sodium tetrathionate. If this salt be represented as $ONa \cdot SO_2 \cdot S \cdot S \cdot SO_2 \cdot ONa$, its decomposition by water should be as follows:



The amounts of sulphur and of sodium sulphate (compare Gutmann, *Abstr.*, 1907, ii, 862) obtained when sodium tetrathionate and water are repeatedly evaporated to dryness approximate to the quantities required by the preceding equations. Experiments, in which the prevention of the secondary reaction is attempted by the addition of ammonium hydroxide or sodium hydrogen carbonate, do not give satisfactory results. In the decomposition of sodium tetrathionate by water or alkalis, it seems impossible to stop secondary reactions, but there appears to be no doubt that sulphur is always a product of the primary reaction.

Aromatic disulphides are exceptions to the foregoing rule; by treatment with an alkali, they are decomposed without elimination of sulphur. The author regards the decomposition as occurring initially, thus: $Ph \cdot S \cdot S \cdot Ph + H_2O = Ph \cdot SH + Ph \cdot S \cdot OH$, but the evidence for this view is by no means conclusive. When phenyl disulphide, alcoholic sodium hydroxide, and benzyl chloride are heated in a reflux apparatus, *phenyl benzyl sulphide*, $Ph \cdot S \cdot CH_2Ph$, m. p. 42° , and phenylbenzylsulphone are obtained, without doubt by the action of the benzyl chloride on the initially formed phenyl mercaptan and benzenesulphinic acid respectively (compare Schiller and Otto, this *Journ.*, 1877, 463). Since, however, benzoic acid is also formed from the benzyl chloride

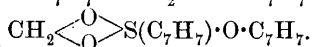
when 4:4'-dinitrodiphenyl disulphide is used in the place of phenyl disulphide (this vol., i, 631), some oxidising agent must be produced in the reaction; this fact furnishes the chief evidence for the author's view quoted above. The hypothetical phenyl derivative of sulphur hydrate, $\text{Ph}\cdot\text{S}\cdot\text{OH}$, being unstable in alkaline solution, changes to phenyl mercaptan and benzenesulphinic acid, somewhat like benzaldehyde in the Cannizzaro reaction. By the decomposition of sodium ethyl thiosulphate by alcoholic sodium hydroxide, Gutmann (Abstr., 1907, i, 671; this vol., i, 497) obtained a solution which oxidised arsenites to arsenates, and probably contained the ethyl derivative, $\text{Et}\cdot\text{S}\cdot\text{OH}$. By treating this solution with benzyl chloride, the author obtains ethyl mercaptan, benzyl ethyl sulphide, benzylethylsulphone, and benzyl disulphide; the formation of these substances is regarded as furnishing additional evidence for the existence of the ethyl derivative of sulphur hydrate. The fission of *p*-tolyl disulphoxide by sodium hydroxide in the presence of benzyl chloride yields *p*-toluenesulphinic acid, *p*-tolyl disulphide, and *p*-tolylbenzylsulphone, the formation of which is due to the action of the benzyl chloride on the sulphinic acid (compare Otto and Rossing, Abstr., 1886, 711; Remsen and Turner, Abstr., 1901, i, 270; Fromm and Palma, Abstr., 1906, i, 819).

[With O. GAUPP.]—Derivatives of sulphonylic acid, H_2SO_2 , have been obtained by several investigators (compare Bazlen, Abstr., 1905, ii, 240; Reinking, Dehuel, and Labhardt, *ibid.*, i, 261). By the interaction of zinc dust and sulphuryl chloride in dry ether, Fromm and Palma (Abstr., 1906, i, 819) obtained a solution of zinc sulphonylate, which yielded dibenzylsulphone by heating with benzyl chloride and 10% sodium hydroxide. A more searching examination of the reaction has shown the presence of a small amount of benzylsulphonic acid, so that the formation of zinc hyposulphite in the first reaction is not excluded, as previously mentioned. Since, however, sodium or zinc hyposulphite is insoluble in dry ether, or in ether containing water, alcohol, or zinc chloride, the formation of the sulphonic acid cannot be due to a hyposulphite; its production is explained thus: (I) $\text{Zn} + \text{SO}_2\text{Cl}_2 = \text{ZnCl}_2 + \text{SO}_2$. (II) $\text{SO}_2 + 2\text{NaOH} + \text{CH}_2\text{PhCl} = \text{NaCl} + \text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Na} + \text{H}_2\text{O}$. Magnesium, copper, iron, or sodium have no action on sulphuryl chloride in dry ether, but sodium amalgam reacts vigorously, the product yielding with benzyl chloride and sodium hydroxide, benzylsulphonic acid, the formation of which is again attributed to the liberation of sulphur dioxide.

Aldehydes or ketones react with sodium hyposulphite in the presence of sodium hydroxide in accordance with the equation: $\text{RR}'\text{CO} + \text{Na}_2\text{S}_2\text{O}_4 + \text{NaOH} = \text{RR}'\text{C}(\text{OH})\cdot\text{SO}_2\text{Na} + \text{Na}_2\text{SO}_3$ (compare Meister, Lucius & Brüning, Eng. Pat., 1903, 5867; *Chem. Zentr.*, 1906, i, 423; Bazlen, *loc. cit.*). The substance, $\text{RR}'\text{C}(\text{OH})\cdot\text{SO}_2\text{Na}$, may be a hydroxysulphinic acid, an ester of sodium hydrogen sulphonylate, or a derivative of orthosulphonylic acid (compare Bazlen, *loc. cit.*). To ascertain which representation is correct, the behaviour of Rongalite C (sodium formaldehydesulphonylate), $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_2\text{Na}$, has been studied. The reduction of rongalite by tin and hydrochloric acid, or by hydrogen sulphide in the presence of hydrochloric acid, does not give much information, since the production of the substance obtained, trithio-

formaldehyde, is explicable by each formula. Oxidation by potassium permanganate, or by chlorine or bromine water, causes complete decomposition. Better results are obtained by adding an alcoholic solution of benzyl chloride to rongalite and aqueous sodium hydroxide, and heating for three hours, whereby dibenzylsulphone, sodium benzylsulphonate in small amount, and *dibenzylrongalite*, $C_{15}H_{16}O_3S$, m. p. $80-81^\circ$, are obtained; in the absence of the alkali, only the sulphone is formed. The formation of the sulphone in the presence or the absence of sodium hydroxide is evidence for the sulphoxylate formula of rongalite: (I) $OH \cdot CH_2 \cdot O \cdot SO \cdot Na + NaOH + 2C_7H_7Cl = SO_2(C_7H_7)_2 + 2NaCl + CH_2O + H_2O$. (II) $OH \cdot CH_2 \cdot O \cdot SO \cdot Na + 2C_7H_7Cl = SO_2(C_7H_7)_2 + NaCl + HCl + CH_2O$.

Dibenzylrongalite is not formed in a secondary reaction between dibenzylsulphone, sodium hydroxide, and rongalite, neither does it yield the sulphone by heating with sodium hydroxide in the presence or the absence of benzyl chloride. Its formation is not due to a reaction between dibenzylsulphone and formaldehyde, for these two substances, heated with 10% sodium hydroxide, form *diformaldibenzylsulphone*, $C_{16}H_{16}O_3S$, m. p. 188° , which from its behaviour receives the constitution $O \begin{smallmatrix} \text{CH}_2 \cdot \text{CHPh} \\ \text{CH}_2 \cdot \text{CHPh} \end{smallmatrix} SO_2$, and is not obtained from dibenzylrongalite. Treated with hydrogen chloride in glacial acetic acid, dibenzylrongalite yields benzyl chloride (hence one benzyl group is attached to oxygen) and *formaldibenzyldisulphoxide*, $C_{15}H_{14}O_2S_2$, m. p. 108° ; the latter is also obtained from dibenzyl disulphoxide, $C_{14}H_{14}O_2S_2$, m. p. 108° , formaldehyde, and hydrogen chloride. Dibenzylrongalite is decomposed by bromine in chloroform in sunlight, yielding benzyl bromide, *benzylsulphonyl bromide*, $C_7H_7 \cdot SO_2Br$, m. p. 79° , and *p*-bromobenzylsulphonic acid. Reviewing the preceding decompositions, the author concludes that rongalite is a sulphoxylate, $OH \cdot CH_2 \cdot O \cdot SO \cdot Na$ or $CH_2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} SNa \cdot OH$, and that dibenzylrongalite has the constitution $C_7H_7 \cdot O \cdot CH_2 \cdot O \cdot SO \cdot C_7H_7$ or



Sodium acetonesulphoxylate is more stable than rongalite, for a substance analogous to dibenzylrongalite is not obtained when its solution is heated with benzyl chloride and sodium hydroxide. Since, also, sodium benzaldehydesulphoxylate (Bazlen, *loc. cit.*) is unchanged when heated at 120° with benzyl chloride and aqueous sodium hydroxide, the author ascribes to these two sulphoxylates the formulæ of hydroxysulphinates: $OH \cdot CMe_2 \cdot SO_2Na$ and $OH \cdot CHPh \cdot SO_2Na$.

C. S.

Preparation of Sulphinic Acids. EMIL KNOEVENAGEL and JAMES KENNER (*Ber.*, 1908, 41, 3315—3322).—The authors find that aromatic sulphinic acids can be readily prepared in a yield of about 80% by the action (first studied by Friedel and Crafts, *Abstr.*, 1890, 241) of sulphur dioxide and aluminium chloride on aromatic hydrocarbons or their halogen derivatives at a low temperature. The reaction is started by passing dry hydrogen chloride through the

mixture, and the compound of aluminium chloride and aromatic sulphinic acid is decomposed by alkalis. Phenol ethers also yield sulphinic acids very readily, and the use of hydrogen chloride is not necessary, but sulfoxides and sulphonium compounds are also produced. The reaction is probably accompanied by the intermediate formation of the compound $\text{AlCl}_2 \cdot \text{SO}_2\text{Cl}$.

Sulphinic acids were prepared from benzene, *p*-toluene, *o*-, *m*-, and *p*-xylene, mesitylene (m. p. 100° . Holtmeyer, *Zeitsch. Chem.*, 1867, 686, gives $98-99^\circ$), ψ -cumene, *p*-cymene, naphthalene (*o*-acid), *p*-chlorobenzene (m. p. $98-99^\circ$. Oberländer, *Diss.*, Heidelberg, gives 5° lower), and *p*-bromobenzene.

Anisole yields anisolesulphinic acid (m. p. 73° . Kreuder, *Diss.*, Heidelberg, gives $97-98^\circ$) together with di-*p*-anisyl sulfoxide and trianisylsulphonium chloride (isolated as platinichloride). From phenetole a mixture of the sulfoxide and sulphonium compound was obtained. J. C. C.

Sulphinic Anhydrides. EMIL KNOEVENAGEL and LEO POLACK (*Ber.*, 1908, 41, 3323—3331).—When aromatic sulphinic acids are treated in the cold with acetic anhydride and a drop of concentrated sulphuric acid, or a few drops of a 0.1% solution of ferric chloride in acetic acid or acetic anhydride, the corresponding sulphinic anhydrides are produced.

Benzenesulphinic anhydride, $\text{O}(\text{SO} \cdot \text{C}_6\text{H}_5)_2$ (probably previously obtained by Otto and Ostrop, *Annalen*, 1866, 141, 374, as an oil; compare also Otto and Gruber, *ibid.*, 1868, 145, 11), is a white, crystalline substance, m. p. $66-67^\circ$. When preserved in a closed vessel or over concentrated sulphuric acid in a vacuum desiccator, it decomposes with the formation of benzene disulphoxide, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{S} \cdot \text{C}_6\text{H}_5$, and benzenesulphonic acid, together with compounds of high m. p. The latter are not formed when the substance is kept in a vacuum desiccator over soda-lime, and the above decomposition proceeds more slowly.

Toluene-p-sulphinic anhydride, $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO} \cdot \text{O} \cdot \text{SO} \cdot \text{C}_6\text{H}_4\text{Me}$, has m. p. 75° ; it decomposes after a time into *p*-toluene disulphoxide and a mixture of toluene-sulphinic and -sulphonic acids.

p-Xylenesulphinic anhydride, $\text{O}(\text{SO} \cdot \text{C}_6\text{H}_3\text{Me}_2)_2$, has m. p. $68-69^\circ$. In a vacuum desiccator it decomposes into *p*-xylenesulphonic acid and *p*-xylene disulphoxide, white tablets, m. p. $70-72^\circ$. The same products are formed when *p*-xylenesulphonic acid is heated in a sealed tube at $120-130^\circ$.

ψ -Cumenesulphinic anhydride, $\text{O}(\text{SO} \cdot \text{C}_6\text{H}_2\text{Me}_3)_2$, has m. p. $92-93^\circ$. Mesitylenesulphinic anhydride has m. p. $118-121^\circ$. *p*-Cymenesulphinic anhydride was obtained as an oil, which was probably a mixture of isomerides. *p*-Bromobenzenesulphinic anhydride begins to melt at $79-81^\circ$, and is completely molten at $108-109^\circ$. Even after ten minutes the m. p. is raised to 140° , and after a longer time the substance is converted into *p*-bromobenzene disulphoxide, m. p. 155.5° , which is also formed on heating *p*-bromobenzenesulphinic acid in a sealed tube at $120-130^\circ$. *p*-Iodobenzenesulphinic anhydride, when freshly prepared, begins to melt at $75-80^\circ$, and is completely molten

above 100°. After half an hour the m. p. is 160° (decomp.), and *p*-iodobenzene disulphoxide is probably present.

When benzene- or *p*-toluene-sulphinic anhydride is mixed with ammonium carbonate, the ammonium salt of the corresponding sulphonic acid is formed, together with the corresponding disulphoxide. The latter anhydride gives with dry ammonia, ammonium toluene-*p*-sulphonate, together with the corresponding disulphoxide and a trace of the sulphinic acid. When the experiment is carried on after the vessel containing the toluene-*p*-sulphinic anhydride has been filled with dry hydrogen, a small amount of *p*-toluenesulphonamide is formed. Benzenesulphonic anhydride gives with diethylamine the diethylamine salt of benzenesulphinic acid; with aniline, di-*p*-aminophenyl sulphoxide; with *p*-toluidine, the corresponding salt of benzenesulphinic acid, and with phenol, hydroxydiphenyl sulphide. J. C. C.

Action of Arsenites and Cyanides on Thiosulphonates.

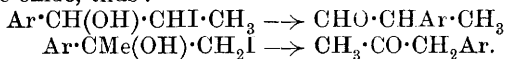
AUGUST GUTMANN (*Ber.*, 1908, 41, 3351—3356).—Sodium toluene-*p*-thiosulphonate is reduced by potassium cyanide or sodium arsenite in sodium hydroxide solution to the *p*-sulphinate, with attendant formation of thiocyanate or thioarsenate at 100°: $C_6H_4Me \cdot S_2O_2Na + Na_3AsO_3 = C_6H_4Me \cdot SO_2Na + Na_3AsO_3S$.

A solution of the toluene-*p*-thiosulphonate, boiled with 10 mols. of sodium hydroxide in 15% solution, becomes lemon-yellow, and on evaporation deposits sulphinate. The yellow solution gives with hydrochloric acid, sulphur and sulphinate, but no hydrogen sulphide; with an alkaline zinc solution, no zinc sulphide, and with arsenite or cyanide, decolorisation at once results. The conclusion is drawn that the yellow colour is due to NaOSH, the *sodium hydropersulphide* reacting thus with cyanide: $NaOSH + KCN = KCNS + NaOH$.

Sodium sulphide also gives a deep yellow solution, which is likewise decolorised by cyanide or arsenite, and is held to contain NaSSH.

W. R.

Transposition of Phenyl. Migration of the Naphthyl Group in Iodohydrins of the Naphthalene Series. MARC TIFFENEAU and DAUDEL (*Compt. rend.*, 1908, 147, 678—680).—The authors find that, exactly as in the cases previously observed with the phenyl group (compare this vol., i, 165, 166), the naphthyl nucleus in derivatives containing the ethylene linking migrates under the influence of iodine and mercuric oxide, thus:



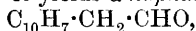
a-Allylnaphthalene, $C_{10}H_7 \cdot CH_2 \cdot CH : CH_2$, prepared by the interaction of allyl bromide and magnesium *a*-naphthyl bromide, has b. p. 265—267°; with mercuric oxide and iodine in aqueous ethereal solution, the *iodohydrin*, $C_{10}H_7 \cdot CH_2 \cdot CH(OH) \cdot CH_2I$, is obtained, which loses its iodine when treated with silver nitrate, but the aldehydic compound is not formed.

a-Naphthylpropylene, $C_{10}H_7 \cdot CH : CH \cdot CH_3$, produced by boiling *a*-allyl-naphthalene with alcoholic potassium hydroxide, has b. p. 147—149°/15 mm., and 275—278° under the ordinary pressure, accompanied by

partial polymerisation. When treated with mercuric oxide and iodine, it is directly transformed into α -1-naphthylpropaldehyde, b. p. 170—171°/14 mm., D_4^{20} 1.118 (Darzens, this vol., i, 91), which, on oxidation, yields α -1-naphthylpropionic acid, m. p. 145°.

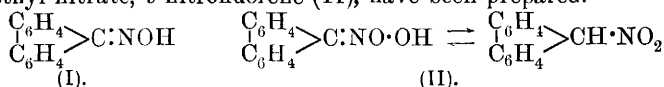
β -1-Naphthylpropylene, $C_{10}H_7 \cdot CMe \cdot CH_2$, with iodine and mercuric oxide, gives α -naphthylacetone, $C_{10}H_7 \cdot CH_2 \cdot CO \cdot CH_3$, the semicarbazone of which has m. p. 205°.

α -Naphthylethylene, $C_{10}H_7 \cdot CH : CH_2$, prepared by the interaction of acetaldehyde and magnesium α -naphthyl bromide, is the chief constituent of the fraction of the products, b. p. 135—138°/15 mm.; with iodine and mercuric oxide, it yields α -naphthylacetaldehyde,



b. p. 163—166°/13 mm. The semicarbazone has m. p. 208°. On oxidation, the aldehyde yields α -naphthylacetic acid. J. C. C.

Condensation of Fluorene with Alkyl Nitrites and Nitrates by means of Potassium Ethoxide. WILHELM WISLICENUS and MARTIN WALDMÜLLER (*Ber.*, 1908, 41, 3334—3340).—Although fluorene does not react with amyl nitrite (Thiele and Henle, *Abstr.*, 1906, i, 571) or ethyl nitrate (Wieland, *Diss.*, Munich, 1901) in presence of sodium ethoxide, the authors find that the condensation proceeds smoothly when potassium ethoxide is used. From fluorene and amyl nitrite, fluorenoneoxime (I), and from fluorene and ethyl nitrate, 9-nitrofluorene (II), have been prepared.



The two desmotropic forms of the latter have been obtained; the *aci*-form is comparatively very stable. For the condensation, an alcoholic-ethereal solution of potassium ethoxide is used.

The potassium compound of fluorenoneoxime, $C(C_6H_4)_2 \cdot NOK$, is stable in dry air, and decomposes between 210° and 220°. With water it yields fluorenoneoxime.

The potassium compound of 9-isonitrofluorene (9-*aci*-nitrofluorene) results from the condensation of fluorene and ethyl nitrate in presence of potassium ethoxide. It forms small, yellow needles, and a dilute solution of it gives a dark green coloration with ferric chloride. The corresponding ammonium salt, small, yellow crystals, decomposing at 146—148°, sodium salt, glistening, yellow leaflets, and silver salt are described. 9-isoNitrofluorene (9-*aci*-nitrofluorene), prepared from the sodium salt, forms small, greenish-yellow needles, m. p. 132—135°; it dissolves in potassium hydroxide. 9-Nitrofluorene, formed when an alcoholic solution of the *aci*-compound is kept or is warmed for a short time, crystallises in small, colourless, glistening tablets, m. p. 181—182° (decomp.). It is insoluble in potassium hydroxide, but is dissolved by sodium or potassium ethoxide, regenerating the *aci*-form. An ethereal solution of the *aci*-form gives with dry ammonia an immediate precipitate of the ammonium salt, but the true nitro-compound does not react with ammonia under the same conditions. Phenylcarbimide is without action on the nitro-derivative, whilst with the *aci*-form a vigorous reaction ensues,

accompanied by evolution of gas. Both forms of nitrofluorene yield fluorenone when carefully heated. When a solution of the potassium compound of the *aci*-form is exposed to the air, or if air is passed through the solution, fluorenone and potassium nitrite are formed; the reaction proceeds more quickly with an absolute alcoholic solution. 9-Bromo-9-nitrofluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CBr} \cdot \text{NO}_2$, prepared by adding bromine water to an aqueous solution of potassium *aci*-nitrofluorene, forms small, yellow, glistening needles, m. p. 107–108° (decomp.). On heating, bromine and nitrogen dioxide are evolved and fluorenone is formed. J. C. C.

Hydrofluorides of Some, in Part very Weak, Organic Bases. RUDOLF F. WEINLAND and F. REISCHLE (*Ber.*, 1908, 41, 3671–3674. Compare Weinland and Lewkowitz, *Abstr.*, 1905, i, 518).—The following hydrofluorides have been prepared: From triphenylamine (with concentrated alcoholic hydrofluoric acid), $\text{NPh}_3 \cdot \text{HF}$, bright green powder; from diphenylamine, with aqueous hydrofluoric acid, $\text{NHPH}_2 \cdot 2\text{HF}$, small, colourless crystals; with alcoholic hydrofluoric acid, $\text{NHPH}_2 \cdot 3\text{HF}$, colourless leaflets; from azobenzene, $\text{N}_2\text{Ph}_2 \cdot \text{HF}$, long, orange-red, glistening needles; from dimethylpyrone, with aqueous hydrofluoric acid, $\text{C}_7\text{H}_8\text{O}_2 \cdot 3\text{HF} \cdot \frac{1}{2}\text{H}_2\text{O}$, large, colourless prisms, and with alcoholic hydrofluoric acid, $\text{C}_7\text{H}_8\text{O}_2 \cdot 3\frac{1}{2}\text{HF} \cdot \frac{1}{2}\text{H}_2\text{O}$, leaflets. J. C. C.

Studies in Nitration. V. Melting Points of Mixtures of *o*- and *p*-Nitroanilines. J. BISHOP TINGLE and H. F. ROLKER (*J. Amer. Chem. Soc.*, 1908, 30, 1764–1767. Compare *Abstr.*, 1907, i, 120; this vol., i, 408, 778, 893).—In an earlier paper (this vol., i, 408), the melting points of mixtures of *o*- and *m*-, and of *m*- and *p*-nitroanilines were recorded, and it was stated that the curve for mixtures of the ortho- and para-compounds was very irregular. The experiments on *o*- and *p*-nitroaniline have now been repeated, in which the difference in composition between consecutive mixtures was 2%. Curves have been constructed showing the melting points of the original mixtures and the melting points after the fused mixtures had been cooled quickly and then re-melted. It is suggested that the variations in these two series of melting points are due to polymorphism, a substance on melting changing into another form with a different m. p.

The solubility of the nitroanilines in alcohol has been determined. At 15°, 100 c.c. of 95% alcohol dissolve 15.848 grams of *o*-, 4.960 grams of *m*-, and 4.030 grams of *p*-nitroaniline. E. G.

***o*-Chloroacetanilide and Some Halogenphenylglycines.** CARL G. SCHWALBE, W. SCHULZ, and HERMANN JOCHHEIM (*Ber.*, 1908, 41, 3790–3796).—It is known that the presence of negative groups makes the displacement of a halogen in a benzene derivative more easily effected. It was therefore anticipated that oxindole would be formed on heating *o*-*o*-dichloroacetanilide with copper powder, and that indigotin would result from the fusion of *o*-chlorophenylglycine with sodamide.

The halogen is, however, too firmly held, and only a 0.4% yield of indigotin was obtained, and oxindole could only be detected.

o-*ω*-Dichloroacetanilide, $C_8H_4Cl \cdot NH \cdot CO \cdot CH_2Cl$, prepared either from chloroacetic acid, *o*-chloroaniline, and phosphorus trichloride (compare Janson, Abstr., 1907, i, 312), or from chloroacetyl chloride and *o*-chloroaniline, crystallises from light petroleum in woolly needles, m. p. 67°.

o-Chlorophenylglycine, $C_8H_7O_2NCl$, obtained from *o*-chloroaniline by heating with alcoholic potash, formaldehyde, and potassium cyanide (Abstr., 1904, i, 153), crystallises in white leaflets, m. p. 171°. The *amide*, $C_8H_9ON_2Cl$, forms white, glistening needles, m. p. 142°; the *ethyl ester*, $C_{10}H_{12}O_2NCl$, is a colourless oil, b. p. 288—291°; *acetyl-o-chlorophenylglycine*, $C_{10}H_{10}O_3NCl$, forms white crystals, decomp. 210°; its *ethyl ester*, $C_{12}H_{14}O_3NCl$, is a colourless liquid, b. p. 205°/20 mm. The *m*- and *p*-chlorophenylglycines have m. p.'s 93° and 141° respectively; 2 : 4-dichlorophenylglycine, $C_8H_6O_2NCl_2$, crystallises from water; m. p. 127°. The *o*- and *p*-bromophenylglycines, $C_8H_7O_2NBr$, have m. p.'s 157° and 150°. W. R.

Preparation of Aromatic Glycines. GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 199624).—Aromatic glycines have hitherto been prepared by the interaction of monohalogenated acetic acids and aromatic amines. It has now been found that the former may be replaced by the dihalogenated vinyl ethers, the latter being supposed to change in the following manner: $C_2HCl_2 \cdot OEt + H_2O = HCl + CH_2Cl \cdot CO_2Et$. Accordingly, 1 mol. of the dihalogenated vinyl ether is allowed to react with 3 mols. of the aromatic base in aqueous or dilute alcoholic solution, but the excess of base may be replaced by some acid-fixing agent, such as calcium, magnesium, or barium carbonate. Ethyl dichloro- or dibromo-vinyl ether and aniline give rise to a mixture of ethyl phenylglycinate (90%) and phenylglycinanilide (10%). G. T. M.

Diphenylamine Derivatives. FRITZ ULLMANN and REINER DAHMEN (*Ber.*, 1908, 41, 3744—3755).—While attempting to prepare 4-nitrodiphenylamine-2-sulphonic acid by Fischer's method (Abstr., 1892, 331) with the object of obtaining from it the corresponding sulphone by elimination of water, it was found, on boiling the aqueous solution of the acid with a small quantity of sulphuric acid, that the sulpho-group was removed, with the formation of *p*-nitrodiphenylamine. Further investigation has shown that aminodiphenylamine-2-sulphonic acids behave in a similar manner; it has therefore been found possible by this method to prepare the following derivatives of diphenylamine: *p*-nitro-, *p*-amino-, 4-nitro-4'-amino-, 4-nitro-3'-amino-, and 4-nitro-2'-amino-diphenylamine, 4-nitrophenyl-2'-tolylamine, 4-nitrophenyl-4'-tolylamine, and 4-aminophenyl-4'-tolylamine.

The sodium salts of the *o*-sulphonic acids were obtained by the interaction of the base with sodium 2-chloro-5-nitrobenzenesulphonate; in the case of aniline and *o*-toluidine, the condensation was brought about by heating in the presence of calcium carbonate and glycerol; with *p*-toluidine and the three phenylenediamines, the components were simply heated together in aqueous solution with calcium carbonate.

Sodium 4-nitrophenyl-2'-tolylamine-2-sulphonate, $C_{13}H_{11}O_5N_2SNa$, crystallises in yellow needles. *4-Nitrophenyl-2'-tolylamine*, $C_{13}H_{12}O_2N_2$, forms glistening, dark yellow leaflets, m. p. 115° , and is reduced to *4-aminophenyl-2'-tolylamine*, $C_{13}H_{14}N_2$, white leaflets, m. p. 58.5° , the sulphate of which forms white needles. The *p*-amino-compound may also be obtained from *4-aminophenyl-2'-tolylamine-2-sulphonic acid*, $C_{13}H_{14}O_3N_2S$, which crystallises in small, colourless needles.

Sodium 4-nitrophenyl-4'-tolylamine-2-sulphonate, $C_{13}H_{11}O_5N_2SNa$, forms orange-red needles with a blue reflex. *4-Nitro-4'-aminodiphenylamine* has m. p. 207° : Bandrowski gives m. p. 211° (Abstr., 1901, i, 48); the *hydrochloride*, $C_{12}H_{11}O_2N_3 \cdot HCl$, forms dark steel-blue, glittering needles.

4-Nitro-4'-aminodiphenylamine-2-sulphonic acid, $C_{12}H_{11}O_5N_3S$, crystallises in yellowish-brown needles.

4-Nitrophenyl-4'-tolylamine, $C_{13}H_{12}O_2N_2$, crystallises in glistening, yellow needles, m. p. 136° . *4-Aminophenyl-4'-tolylamine-2-sulphonic acid*, $C_{13}H_{14}O_3N_2S$, forms small, white needles; the *sodium salt* crystallises in colourless leaflets.

4-Nitro-3'-aminodiphenylamine-2-sulphonic acid, $C_{12}H_{11}O_5N_3S$, forms brownish-yellow needles. *4-Nitro-3'-aminodiphenylamine*, $C_{12}H_{11}O_2N_3$, crystallises in glistening, brownish-yellow leaflets, m. p. 156° ; the *hydrochloride* forms large, deep yellow needles with a blue reflex.

4-Nitro-2'-aminodiphenylamine-2-sulphonic acid, $C_{12}H_{11}O_5N_3S$, crystallises in yellow needles. It is converted when boiled with dilute sulphuric acid into *4-nitro-2'-aminodiphenylamine* (14%) and *4-nitrophenol-2-sulphonic acid*. W. H. G.

Phenyl-, Naphthyl-, and Menthyl-carbimides. C. VALLÉE (Ann. Chim. Phys., 1908, [viii], 15, 331—432).—The author has made an exhaustive examination of the reactions between certain aryl-carbimides and (1) organic acids (compare Abstr., 1905, i, 771), (2) phenol and some of its substituted derivatives, (3) esters of hydroxy-acids, (4) amino-acids, and of the condensation of *s*-diphenyl-carbamide with certain acyl tartaric anhydrides. The following compounds are described for the first time: *aniline benzenesulphinic acid*, $PhSO_2H \cdot NH_2Ph$, m. p. 132° ; *aniline hydroxybenzylphosphinite*, $OH \cdot CHPh \cdot PHO \cdot OH \cdot NH_2Ph$, m. p. 99° ; *aniline dihydroxydibenzylphosphinate*, $PO(CHPh \cdot OH)_2 \cdot OH \cdot NH_2Ph$, m. p. 190° ; the *diphenylurethane* of *ethyl dihydroxydibenzylphosphinate*, $C_{30}H_{29}O_6N_2P$, m. p. 203° ; *phenylurethane* of *tribromophenol*, $C_6H_2Br_3 \cdot O \cdot CO \cdot NHPh$, m. p. 168° ; *menthylurethane* of *trimethylcarbinol*, $CMe_3 \cdot O \cdot CO \cdot NH \cdot C_{10}H_{19}$, m. p. 112° , $[\alpha]_D - 55.33^\circ$ in toluene; the *menthylurethane* derivative of *ethyl lactate* yields the *lactam*, $CHMe \cdot CHO \cdot CO \cdot N \cdot C_{10}H_{19}$, m. p. 77.5° .

The phenylurethanes of substituted phenols, or of the esters of hydroxy-acids, are readily prepared by heating phenylcarbimide with

the hydroxy-compound in the presence of a small quantity of sodium; the phenylurethane of methyl tartrate crystallises in the monoclinic system [$a : b : c = 1.0544 : 1 : 0.4566$; $\beta = 103^\circ$].

The influence of (a) the solvent, (b) the molecular weight and the position of the substituting radicles, and (c) the ethylenic linking in the radicles on the specific rotation of the numerous optically active urethanes prepared in the course of the work is fully discussed in the paper.

M. A. W.

Preparation of Compounds of *p*-Aminophenol, *p*-Methylaminophenol, and *p*-Phenylenediamine with Sulphurous Acid. SOCIÉTÉ ANONYME DES PLAQUES ET PAPIERS PHOTOGRAPHIQUES A. LUMIÈRE ET SES FILS (D.R.-P. 198497).—Crystalline additive compounds of sulphurous acid with *p*-aminophenol, *p*-methylaminophenol, and *p*-phenylenediamine may be produced either by passing sulphur dioxide into a hot aqueous solution or suspension of these bases, or by treating them with 40% aqueous sodium hydrogen sulphite. The salts of the bases may be employed for this reaction, providing that a mixture of sulphite and hydrogen sulphite is employed.

The compound, $10\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \cdot \text{H}_2\text{SO}_3$, from *p*-aminophenol, white leaflets, m. p. 184° , is only sparingly soluble in cold water.

The compound, $6\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \cdot \text{H}_2\text{SO}_3$, from *p*-methylaminophenol, forms small, colourless, odourless crystals, decomposing at 87° .

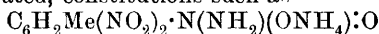
The compound, $9\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_3$, from *p*-phenylenediamine, colourless crystals, m. p. 137° , has a faint odour of sulphur dioxide; it is readily soluble in cold water. These products find employment as photographic developers.

G. T. M.

Abnormal Salts. ANTONI KORCZYŃSKI (*Bull. Acad. Sci. Cracow*, 1908, 633—644).—Finely-powdered phenols and acids have been submitted to the action of dry ammonia. At the ordinary temperature, 1 mol. of ammonia is absorbed by *o*-nitrophenol, 1-nitro-2-naphthol, *o*-nitro-*p*-cresol, dibromo-*o*-nitrophenol, *o*- and *p*-nitrophenolmercurihydroxides, benzoic, cinnamic, *o*- and *m*-nitrobenzoic, 3:5-dinitrobenzoic, *o*- and *p*-chlorobenzoic, and *p*-bromobenzoic acids. *p*-Nitrophenol, 2:4-dinitrophenol, and 3:5-dinitrophenol absorb $1\frac{1}{2}\text{NH}_3$. Two molecules of ammonia are absorbed by *p*-bromo-*o*-nitrophenol, 2:6-dinitrophenol, 3:5-dinitro-*p*-cresol, 5-bromo-3-nitro-*p*-cresol, 4-bromo-2:6-dinitrophenol, picric acid, tribromophenol, trichlorophenol, *p*-nitrobenzoic and 2:4-dinitrobenzoic acids at the ordinary temperature; by *o*-nitro-*p*-cresol, *o*-nitrophenolmercurihydroxide, and *p*-nitrophenolmercurihydroxide at -10° , and by dibromo-*o*-nitrophenol, *m*- and *p*-nitrobenzoic acids, and *o*-chlorobenzoic acid at -15° . The sodium or potassium salts of the preceding compounds do not absorb ammonia.

Trinitrobenzoic acid absorbs 4NH_3 at 0° , yielding a black substance, which loses 2NH_3 at 25° . Trinitrobenzene and trinitrotoluene at -10 to -15° absorb 2NH_3 , forming reddish-brown, crystalline

substances. For these substances, from which the original compounds cannot be regenerated, constitutions such as



are proposed (compare Hantzsch and Kissel, Abstr., 1900, i, 89).

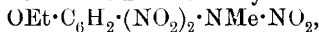
C. S.

New Method of Formation of Ethers of Glycerol with Phenols. PETAR SCHIVKOVITCH (*Monatsh.*, 1908, 29, 951—958).—Brunner obtained a substance, $\text{C}_9\text{H}_{12}\text{O}_4$, during the preparation of quinoldicarboxylic acid by the action of carbon dioxide on quinol in the presence of a hydrogen carbonate and glycerol (Abstr., 1907, i, 319). This substance is probably an ether of glycerol with quinol, but, as it is formed in only very small quantities, it could not be thoroughly investigated. The author has therefore studied the interaction of glycerol with various phenols at 200—210°, and finds that mono-ethers of glycerol are formed.

Phenyl glycerol ether (compare Lindemann, Abstr., 1891, 1198) is formed by heating phenol, glycerol, and sodium acetate together in an atmosphere of hydrogen at 200—210° for twelve to twenty hours. The following derivatives of glycerol are prepared in a similar manner: *o*-tolyl ether, $\text{C}_8\text{H}_5(\text{OH})_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{Me}$, glistening needles, m. p. 66°; *m*-tolyl ether, $\text{C}_{10}\text{H}_{14}\text{O}_3$, white needles, m. p. 65°; *p*-tolyl ether, white needles, m. p. 73—74°; *α*-naphthyl ether, $\text{C}_{13}\text{H}_{14}\text{O}_3$, white scales, m. p. 91—92°; *β*-naphthyl ether, $\text{C}_{13}\text{H}_{14}\text{O}_3$, white scales, m. p. 109—110°.

W. H. G.

Preparation of 3-Nitro-2-cyano-1-methoxybenzene, 3-Nitro-2-cyano-1-ethoxybenzene, 4-Nitro-2-cyano-1-methoxybenzene, and 4-Nitro-2-cyano-1-ethoxybenzene. JAN J. BLANKSMA (*Chem. Weekblad*, 1908, 5, 789—795).—The preparation of nitrocyanoderivatives of phenetole and anisole is described. 3-Nitro-2-cyanophenetole (compare Lobry de Bruyn, Abstr., 1885, 656) is prepared from 2 : 3-dinitrophenetole (this vol., i, 157) by the action of alcoholic ammonia, which yields 2-amino-3-nitrophenetole. The amino-group is replaced by the cyano-group by the Sandmeyer reaction. When boiled with acetic anhydride, 3-nitro-2-aminophenetole yields the corresponding acetyl derivative, which crystallises from light petroleum, m. p. 64°. When heated at 120° in alcoholic solution with methylamine, 2 : 3-dinitrophenetole yields 3-nitro-2-methylaminophenetole, m. p. 59°, which crystallises from alcohol. Nitric acid, D 1.52, transforms the last compound into 3 : 5-dinitro-2-nitromethylaminophenetole,

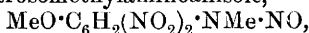


which forms colourless crystals from alcohol, m. p. 79—80° (not 69°, as previously stated, Abstr., 1905, i, 431).

2 : 3-Dinitroanisole was treated analogously to the corresponding dinitrophenetole with alcoholic ammonia, and yielded 3-nitro-*o*-anisidine, $\text{C}_6\text{H}_3(\text{OMe})(\text{NH}_2)(\text{NO}_2)$, yellow crystals from alcohol or benzene, m. p. 76° (compare Bantlin, Abstr., 1879, 237). The corresponding acetyl derivative was obtained by the action of acetic anhydride; it has m. p. 128°. The acetylation is much facilitated by addition of a drop of concentrated sulphuric acid to the mixture. The acetylation of

3:5-dinitro-*o*-anisidine, $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{NH}_2$, was similarly effected. The compound formed has m. p. 202° .

Exchange of the NH_2 group for CN by Sandmeyer's method converts 3-nitro-*o*-anisidine into 3-nitro-2-cyanoanisole, colourless leaflets, m. p. 171° (de Bruyn, *loc. cit.*). When heated in alcoholic solution with methylamine at 120° , 2:3-dinitroanisole yields 3-nitro-2-methylaminoanisole in the form of dark red needles, readily soluble in alcohol, m. p. 58° . Nitric acid, D 1.52, converts this compound into 3:5-dinitro-2-nitrosomethylaminoanisole,



m. p. 118° .

Reduction of 2:4-dinitrophenetole with ammonium sulphide or sodium disulphide yields 4-nitro-*o*-phenetidine, which by Sandmeyer's reaction is converted into 4-nitro-2-cyanophenetole. It crystallises from boiling water in colourless crystals, m. p. 101° . It is very slightly soluble in cold, but more so in boiling water, and readily soluble in boiling alcohol. With a mixture of nitric acid and sulphuric acid, it yields 4:6-dinitro-2-cyanophenetole, m. p. 72° (Abstr., 1902, i, 281).

4-Nitro-*o*-anisidine yields analogously 4-nitro-2-cyanoanisole, colourless crystals from boiling water, m. p. 126° , slightly soluble in cold, readily in boiling alcohol. On treatment with a mixture of nitric acid and sulphuric acid, it is converted into 4:6-dinitro-2-cyanoanisole, which separates from dilute alcohol in colourless crystals, m. p. 71° .

On nitration of 2:3-dinitro-anisole (or -phenetole) and 3-nitro-2-cyano-anisole (or -phenetole), the NO_2 group takes up the para-position with reference to the alkyloxy-group; with 4-nitro-2-cyano-anisole (or -phenetole), it takes up the ortho-position. A. J. W.

Nitration of 5-Nitro-1:3-dimethoxybenzene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1908, 27, 251—256).—When 5-nitro-1:3-dimethoxybenzene (Vermeulen, Abstr., 1906, i, 256) is treated with nitric acid (D 1.52) in the presence of sulphuric acid, 4:5:6-trinitro-1:3-dimethoxybenzene, $\text{C}_6\text{H}(\text{OMe})_2(\text{NO}_2)_3$, m. p. 193° (*Rec. trav. chim.*, 1908, 27, 39), is obtained, together with a small quantity of a compound, m. p. 110° , which has not yet been identified.

The constitution of the trinitro-derivative was determined by converting it by means of alcoholic ammonia into 2:6-dinitro-3:5-dimethoxyaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}(\text{OMe})_2(\text{NO}_2)_2$, m. p. 223° ; this yielded 4:6-dinitro-1:3-dimethoxybenzene, m. p. 155° (Abstr., 1902, i, 715), on diazotisation and subsequent treatment with alcohol (this vol., i, 157), and 4:6-dinitroresorcinol, m. p. 210° , was obtained from the latter compound by hydrolysis. The following compounds obtained from 4:5:6-trinitro-1:3-dimethoxybenzene are described:

2:6-Dinitro-3:5-dimethoxymethylaniline, $\text{NHMe} \cdot \text{C}_6\text{H}(\text{OMe})_2(\text{NO}_2)_2$, m. p. 191° ; 2:6-dinitro-1-methylnitroamino-3:5-dimethoxybenzene, $\text{NO}_2 \cdot \text{NMe} \cdot \text{C}_6\text{H}(\text{OMe})_2(\text{NO}_2)_2$, m. p. 176° , and 2:6-dinitro-3:5-dimethoxydiphenylamine, $\text{NHPh} \cdot \text{C}_6\text{H}(\text{OMe})_2(\text{NO}_2)_2$, m. p. 190° .

4:5-Dinitro-1:3-dimethoxybenzene, m. p. 131° , is obtained when 5-nitro-1:3-dimethoxybenzene is treated with nitric acid, D 1.45,

and this is converted into the trinitro-compound described above on further nitration with nitric acid (D 1.52). M. A. W.

Aloesol, a Complex Phenol prepared from Certain Aloes. EUGÈNE LÉGER (*Compt. rend.*, 1908, 147, 806—808. Compare this vol., i, 40).—The compound $C_{11}H_4O_3Cl_4$, obtained previously by the author in the chlorination of Cape or Uganda aloes, is not tetrachloromethoxynaphthaquinone, as the author at first supposed, but a derivative of a new phenol, aloesol. *Tetrachloroaloesol* separates from acetic acid in colourless needles, m. p. 268.9° (corr.). This dissolves in alkalis, giving a yellow solution, from which the original compound is precipitated by the addition of excess of alkali. The *acetyl* derivative, $C_{11}H_3O_3Cl_4Ac$, crystallises in pale yellow prisms, m. p. 125° (corr.).

Dichlorotetrahydroaloesol, $C_{11}H_8O_3Cl_2$, prepared by the action of zinc and acetic acid on tetrachloroaloesol, forms colourless, microscopic needles, m. p. 275° (corr.), and in its behaviour towards alkalis resembles tetrachloroaloesol. The *barium* compound, $(C_{11}H_7O_3Cl_2)_2Ba$, forms long, colourless needles. The *acetyl* derivative occurs in colourless, prismatic needles, m. p. 150 — 151° (corr.). A yellow modification, however, is formed when acetic anhydride is employed, and this furnishes, on hydrolysis, a yellow modification of dichlorotetrahydroaloesol having the same m. p. as the colourless variety.

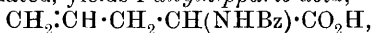
The presence of a benzene ring in tetrachloroaloesol is indicated by the fact that nitric acid decomposes it with formation of oxalic acid and tetrachloroquinone. W. O. W.

Preparation of a Compound having the Composition of Nitrosobenzyl Alcohol. KALLE & Co. (D.R.-P. 199317).—The monomercury derivative of *o*-nitrotoluene (compare Abstr., 1907, i, 908) when treated with cold concentrated hydrochloric acid gives rise to an unstable compound, isolated by extraction with ether or distillation in steam, and having the composition of an *o*-nitrosobenzyl alcohol, $NO \cdot C_6H_4 \cdot CH_2 \cdot OH$; this product gives with mercuric chloride an additive compound crystallising from benzene in white needles. When 6% hydrochloric acid is employed in this reaction, the anhydride, anthranil, is obtained. G. T. M.

***o*-, *m*-, and *p*-Tolylethyl Alcohols.** K. KLING (*Bull. Acad. Sci. Cracow*, 1908, 632—633).—By the energetic electrolytic reduction of *o*-, *m*-, and *p*-tolylacetic acids, the corresponding alcohols have been obtained. *o*-Tolylethyl alcohol, $C_7H_7 \cdot CH_2 \cdot CH_2 \cdot OH$, has b. p. 243 — 243.5° (corr.), D_4^{20} 1.0159, and n_D 1.5214. The *meta*-isomeride has b. p. 242.5 — 243° (corr.), D_4^{20} 1.0127, and n_D 1.5231, and the *para*-compound has b. p. 244.5 — 245° (corr.), D_4^{20} 1.0177, and n_D 1.5271. C. S.

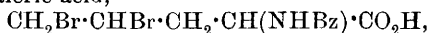
Isolation of Cholesterol from Fats. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, 57, 515—519).—Gliken adversely criticises a method he incorrectly attributes to the author. References are given to an improved method, published in the author's *Festschrift*, and a brief account of it is again published. W. D. H.

Allylhippuric Acid. A Convenient Material for the Preparation of $\gamma\delta$ -Disubstituted α -Amino-*n*-valeric Acids. SÖREN P. L. SÖRENSEN (*Ber.*, 1908, 41, 3387—3390. Compare *Abstr.*, 1905, i, 749; also Fischer and Krämer, this vol., i, 858).—When ethyl allylphthaliminomalonate is hydrolysed with sodium hydroxide and then evaporated with hydrochloric acid, allylglycine is formed, and this, when benzoylated, yields *r*-allylhippuric acid,

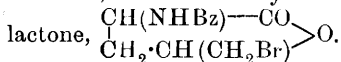


which crystallises from benzene in rectangular plates, m. p. 107—107.5°. The racemic acid can be resolved by means of brucine or quinidine; with the former base, the salt of the *l*-acid crystallises first, and with the latter base, the salt of the *d*-acid.

The active acids combine with bromine, yielding $\gamma\delta$ -dibromo- α -benzoylaminovaleric acid,



as an oil, and this readily loses hydrogen bromide, forming a crystalline lactone,



It is suggested that this should be used for the syntheses of α -amino- $\gamma\delta$ -dihydroxy- and other $\gamma\delta$ -substituted valeric acids. J. J. S.

***o*-Bromophenyl- and α -Bromophenyl-acetamides.** WILHELM STEINKOFF and CZESLAU BENEDEK (*Ber.*, 1908, 41, 3595—3598).—Attempts to prepare nitrated phenylacetamides for the purpose of comparison with nitroacetamide have been unsuccessful. In the course of the work, the authors have prepared two brominated phenylacetamides. These are now described.

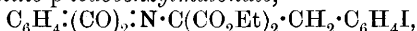
***o*-Bromophenylacetamide**, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared by the action of bromine on phenylacetamide suspended in water, separates in white crystals, m. p. 181°, and on treatment with sodium nitrite in sulphuric acid solution yields *o*-bromophenylacetic acid.

α -Bromophenylacetamide, $\text{CHBrPh}\cdot\text{CO}\cdot\text{NH}_2$, prepared by treating α -bromophenylacetyl chloride in benzene solution with a current of dry ammonia, forms white crystals, m. p. 143—144°, and on hydrolysis with nitrous acid yields α -bromophenylacetic acid, m. p. 87°.

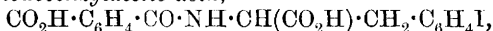
G. Y.

Halogen Amino-acids: *p*-Iodophenylalanine. HENRY L. WHEELER and SAMUEL H. CLAPP (*Amer. Chem. J.*, 1908, 40, 458—468. Compare this vol., i, 897).—In continuation of their work, the authors have synthesised *p*-iodophenylalanine.

Ethyl phthalimino-*p*-iodobenzylmalonate,



prepared by heating *p*-iodobenzyl bromide with ethyl sodiophthaliminomalonate, forms flat, colourless prisms or six-sided plates, m. p. 112°. On alkaline hydrolysis and subsequent acidification, it gives *phthalamic p*-iodobenzylacetic acid,

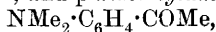


in needles, m. p. 179°; it, on acidification with hydrochloric acid, the precipitate is digested with the acid for two hours, *p*-iodophenylalanine, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{I}$, is produced, forming thin scales,

m. p. 270° (decomp.). The *hydrochloride*, thin, flat, colourless plates, decomposing at 248° , and *silver* and *copper* salts are described. The *phenylcarbimide* forms aggregates of flat prisms or plates, m. p. $178-179^{\circ}$ (decomp.). The *hydantoin*, $C_{16}H_{13}O_2N_2$, prepared from this by boiling with 20% hydrochloric acid, forms flat, rhombohedral crystals, m. p. $195-196^{\circ}$. The *ethyl* ester of *p*-iodophenylalanine is a colourless, viscid oil, b. p. $223-226^{\circ}/25$ mm., of which the *picrate* forms flat, yellow plates or tablets, m. p. $200-203^{\circ}$. J. C. C.

***p*-Dimethylaminocinnamic Acid.** LOTTE WEIL (*Monatsh.*, 1908, 29, 895-908).—The object of this investigation was to ascertain if a methylamino- or dimethylamino-group influences the replacement of α -halogen atoms by methoxy- or ethoxy-groups in the same manner as alkyloxy-groups (compare Hertzka, Abstr., 1905, i, 291; Werner, Abstr., 1906, i, 180; Goldschmidt, Abstr., 1907, i, 241). β -Bromo-*p*-dimethylaminocinnamic acid was therefore prepared, and was found to be quite stable towards boiling alcohol and aqueous potassium hydroxide, so that a *p*-dimethylamino-group does not exert the same influence on an α -halogen atom as a *p*-methoxy-group. The *p*-dimethylamino-group was found, however, to have a great influence on the alkylcarboxy-group, for methyl *p*-dimethylaminocinnamate cannot, like methyl cinnamate, be converted by ammonia into the corresponding amide.

p-Dimethylaminocinnamic acid, $NMe_2 \cdot C_6H_4 \cdot CH:CH \cdot CO_2H$, may be prepared by Perkin's method provided potassium acetate is used in the place of the sodium salt; it crystallises in glistening, yellow leaflets, m. p. 216° (decomp.); the *silver* salt is yellow. The *ethyl* ester, $C_{13}H_{17}O_2N$, is most readily obtained by the action of sodium on a mixture of ethyl acetate and *p*-dimethylaminobenzaldehyde; it crystallises in golden-yellow leaflets, m. p. $74-75^{\circ}$, b. p. $205-208^{\circ}/19$ mm.; the *picrate*, $C_{13}H_{17}O_2N \cdot C_6H_3O_7N_3$, forms red crystals, m. p. $130-132^{\circ}$. The *methyl* ester, $C_{12}H_{15}O_2N$, forms pale yellow crystals, m. p. $134-136^{\circ}$; it is converted by bromine in chloroform into a bromo-derivative, which forms colourless crystals, m. p. $164-168^{\circ}$ (decomp.), and is either *methyl $\alpha\beta$ -dibromo-*p*-dimethylamino- β -phenylpropionate*, $NMe_2 \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot CO_2Me$, or *methyl β -bromo-*p*-dimethylaminocinnamate hydrobromide*, $NMe_2 \cdot C_6H_4 \cdot CBr:CH \cdot CO_2Me, HBr$. The substance just described is converted by boiling water, alcohol, or aqueous potassium hydroxide into *methyl β -bromo-*p*-dimethylaminocinnamate*, $NMe_2 \cdot C_6H_4 \cdot CBr:CH \cdot CO_2Me$, an exceedingly stable compound crystallising in glistening, yellow leaflets, m. p. 96° ; it is not affected by aqueous potassium hydroxide, but is converted by alcoholic potassium hydroxide into *β -bromo-*p*-dimethylaminocinnamic acid*, $C_{11}H_{12}O_2NBr$, yellow crystals, m. p. 165° , and *p*-dimethylaminoacetophenone,



crystallising in long needles, m. p. 103° . The latter compound may also be obtained by treating *p*-aminoacetophenone with methyl sulphate; the *phenylhydrazone* forms pale yellow crystals, m. p. about 150° . The substance, m. p. 59° , described by Klingel (Abstr., 1886, 61) is not *p*-dimethylaminoacetophenone, as stated by this author.

p-Dimethylamino- β -phenylpropionic acid, $NMe_2 \cdot C_6H_4 \cdot C_2H_4 \cdot CO_2H$, is obtained as its sodium salt by treating ethyl *p*-dimethylamino-

cinnamate in alcohol with sodium ; it crystallises in colourless leaflets, m. p. 104°.

p-Dimethylaminobenzaldehyde-*p*-bromophenylhydrazone, $C_{15}H_{16}N_3Br$, crystallises in brown, felted needles, m. p. 181°.

p-Aminoacetophenonephenylhydrazone has m. p. 112°. W. H. G.

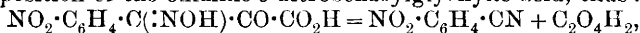
Action of Nascent Hypiodous Acid on Unsaturated Acids.

J. BOUGAULT (*Ann. Chim. Phys.*, 1908, [viii], 15, 296—312).—A detailed account of work already published (compare this vol., i, 179, 269, 340, 791). The action of iodine in the presence of sodium carbonate or hydrogen carbonate on certain $\beta\gamma$ -unsaturated acids is quantitative, and can be employed for the volumetric estimation of hydropiperic and phenylisocrotonic acids. M. A. W.

Preparation of Arylthioglycollic [Arylthiolacetic] Acids.

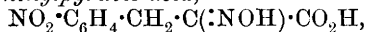
KALLE & Co. (D.R.-P. 201231 and 201232. Compare this vol., i, 672).—The condensation of a diazonium salt with a thioglycollic acid occurs more readily and at lower temperatures (20—25°) in the presence of "molecular copper." A good yield of *o*-carboxyphenylthiolacetic acid is obtained by condensing diazotised anthranilic acid with thioglycollic acid in warm alkaline solution ; the intermediate product is precipitated by acids, dissolved in aqueous sodium carbonate, and the solution heated to boiling until all the nitrogen is expelled, when the final product is obtained by cooling and acidifying. G. T. M.

Some Oximes of the *o*-Nitrotoluene Series and their Changes. ARNOLD REISSERT (*Ber.*, 1908, 41, 3810—3816).—On boiling with water, the oxime of *o*-nitrophenylglyoxylic acid yields *o*-nitrobenzonitrile and carbon dioxide, and this oxime was supposed to be formed as an intermediate product in the conversion of *o*-nitrophenylpyruvic acid oxime by nitrous acid into the *o*-nitrobenzonitrile (*Abstr.*, 1897, i, 417). Further inquiry has, however, shown that by slowly adding a sodium nitrite solution at the bottom of a dilute hydrochloric acid solution of the *o*-nitrophenylpyruvic acid at 60° and afterwards heating to 100°, a 90% yield of *o*-nitrobenzonitrile and oxalic acid is obtained. The oxalic acid can only be produced by the decomposition of the oximino-*o*-nitrobenzoylglyoxylic acid, thus :



and the assumption of the intermediate formation of the nitrophenylglyoxylic acid is incorrect.

Oximino-o-nitrophenylpyruvic acid,



obtained from the acid and hydroxylamine, crystallises in almost colourless needles, m. p. 161° (decomp.), and is hydrolysed by mineral acids into its components. When boiled with water, it is slowly converted into *o*-nitrophenylacetonitrile. A small quantity of *o*-nitrophenylacetamide, $C_8H_8O_3N_2$, colourless crystals, m. p. 160—161°, was also isolated ; it was also obtained by heating ethyl *o*-nitrophenylacetate with alcoholic ammonia under pressure at 100°. The nitrophenylacetonitrile is formed by heating the oxime of nitrophenylpyruvic acid at 140—145°.

The liability of these oximes to change into nitriles depends on the presence of negative contiguous groups, CO_2H and $\cdot\text{CO}\cdot\text{CO}_2\text{H}$, as *o*-nitrobenzaldoxime is more stable. The conversion of this oxime into *o*-nitrobenzonitrile or its amide is accomplished if small quantities of alkaline substances, like borax, potassium cyanide, or sodium carbonate, are added to the water and the mixture heated for some hours.

W. R.

Preparation of *o*-Carboxyphenylthioglycollic [α -Carboxyphenylthiolacetic] Acid. KALLE & Co. (D.R.-P. 199249).—*o*-Carboxyphenylthiolacetic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, yellow crystals, m. p. 213° , was obtained by the interaction of the sodium salts of *o*-thiolbenzoic and chloroacetic acids in aqueous solution; it finds employment in the production of dyes and pharmaceutical products.

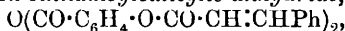
G. T. M.

Preparation of the Anhydrides of Acylsalicylic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 201325 and 201326).—The therapeutic employment of the acylsalicylic acids is attended with two disadvantages—their distinctly acid taste and their appreciably irritating action on the sensitive mucous lining of the stomach. Their anhydrides, which have now been prepared, are free from these disagreeable properties.

Acetylsalicylic [*o*-acetoxybenzoic] *anhydride*, $\text{O}(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OAc})_2$, white crystals, m. p. 85° , is obtained by condensing acetylsalicylic acid in benzene solution with thionyl chloride, carbonyl chloride, trichloromethyl formate, or hexachlorodimethyl carbonate in the presence of pyridine.

Acetylsalicylyl [*o*-acetoxybenzoyl] *chloride*, colourless crystals, m. p. $43\text{--}44^\circ$, b. p. $135^\circ/12\text{ mm.}$, from phosphorus pentachloride and acetylsalicylic acid, when warmed with this acid (1 mol.) and dimethylaniline in toluene solution, or when heated with sodium acetylsalicylate, also gives rise to the same anhydride.

The *ethyl carbonate* compound, $\text{O}(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Et})_2$, clusters of needles, m. p. 74° , was obtained from the corresponding acid by the action of sulphuryl chloride and pyridine in benzene solution. *Benzoylsalicylic anhydride*, m. p. $106\text{--}107^\circ$, was prepared from the corresponding acid by means of carbonyl chloride and quinoline in benzene solution, and *cinnamoylsalicylic anhydride*,



m. p. $114\text{--}116^\circ$, was obtained from cinnamoylsalicylic acid (Proc., 1906, 22, 317) by the action of carbonyl chloride and antipyrine in benzene solution.

Other condensing agents, such as acetyl chloride, phosphoryl chloride, and phosphorus tribromide and trichloride, may be employed in the production of these anhydrides.

G. T. M.

Rule in Benzoylation of Aromatic Hydroxy-acids and their Esters. LASSAR COHN and JOSEF LÖWENSTEIN (Ber., 1908, 41, 3360—3367).—It has been found that the hydroxyl cannot be benzoylated in a hydroxy-compound containing a carboxyl or a

sulphonic group in any position in the ring by the Schotten-Baumann method, but that its esters give benzoates. The following benzoates have been prepared.

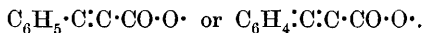
Benzoylsalicylic [*o*-benzoyloxybenzoic] acid, $C_{14}H_{10}O_4$, obtained in small yield by stirring together dipotassium salicylate and benzoyl chloride in light petroleum, crystallises from dilute alcohol; m. p. 132° . It is easily hydrolysed by alkali. The greater portion of the product of the reaction is insoluble in water, and when distilled gives benzoic acid and its phenyl ester. Methyl benzoylsalicylate (benzosalin: D.R.-P. 169247) is obtained in quantitative yield by the Schotten-Baumann method; m. p. 92° , b. p. $350-358^\circ$ (decomp.), $270-280^\circ/120$ mm. *Ethyl p*-benzoyloxybenzoate, $C_{16}H_{14}O_4$, has m. p. 94° , b. p. $358-360^\circ$; the ester of *m*-hydroxybenzoic acid is hydrolysed under the conditions of the experiment, and no benzoyl derivative was obtained.

Ethyl β -benzoyloxynaphthoate, $C_{20}H_{16}O_4$, has m. p. 98° and b. p. $342-345^\circ$. The α -hydroxy- β -naphthoic acid (Abstr., 1888, 60) is considered to be the 2-hydroxynaphthalene-1-carboxylic acid because it is not esterified by hydrogen chloride and alcohol. The *ethyl* ester, $C_{18}H_{12}O_3$, has m. p. 46° , and gives the *benzoate*, $C_{20}H_{16}O_4$, m. p. 51° .

Crude ethyl phenol-*p*-sulphonate, obtained by the action of ethyl iodide on the silver salt, gives the *benzoate*, $C_{15}H_{14}O_5S$, W. R. m. p. 62° .

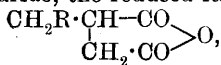
Simultaneous Formation of Isomeric Substitution Products of Benzene. ARNOLD F. HOLLEMAN. XI. Nitration of Phthalic and *iso*Phthalic Acids. J. HUISINGA (*Rec. trav. chim.*, 1908, 27, 260-286).—A detailed account of work already published (Abstr., 1907, i, 136). The percentage solubilities of 3-nitrophthalic, anhydrous 5-nitroisophthalic, hydrated 5-nitroisophthalic, 4-nitroisophthalic, and 2-nitroisophthalic acids at 25° are 2.048, 0.220, 0.157, 0.967, and 0.216 respectively. M. A. W.

Colour Reactions during the Hydrolysis of Acid Anhydrides. HANS STOBBE (*Ber.*, 1908, 41, 3720-3725).—In the hydrolysis of certain colourless anhydrides to the colourless salts of the corresponding dibasic acids by means of alkali hydroxides, the author has noticed the appearance of an evanescent coloration. The actual colour depends on the particular anhydride, and may be yellow, red, violet, or blue. It is shown that the production of a coloration is characteristic of anhydrides containing either of the following groupings:



Examples of compounds which give such colorations are phenylitaconic anhydride, the two stereoisomeric phenylmethylytaconic anhydrides, diphenylitaconic anhydride, γ -diphenyleneitaconic anhydride, and the anhydrides of 1-phenyl-1:2-dihydronaphthalene-2:3-dicarboxylic acid and the corresponding 1:4-diphenyl-2:3-dicarboxylic acid.

Dimethylytaconic anhydride, the reduced itaconic anhydrides,



and the anhydrides of tetrahydronaphthalenedicarboxylic acids do not give colorations.

Experiments have been made by mixing together absolute alcoholic sodium hydroxide with solutions of the anhydrides in various solvents, and determining the time during which the coloration persisted. It was found that in the presence of acetone the colour was retained for a much longer time, especially when the volume of acetone used was relatively large. In all experiments, 1 c.c. of *N*/10 sodium hydroxide and 0.0003 gram of anhydride were used.

In the case of the two stereoisomeric phenylmethylitaconic anhydrides, the colorations were so fugitive that even with acetone the solutions became quite colourless after a few seconds.

Alcohols have a similar effect to ketones, but benzene, chloroform, and carbon tetrachloride have little effect. Alcoholic solutions of other bases have also been used.

J. J. S.

Synthesis of Trimethylhomogallic Acid (Methyliridic Acid).

FERDINAND MAUTHNER (*Ber.*, 1908, 41, 3662—3665).—3:4:5-Trimethoxybenzaldehyde (this vol., i, 348), hippuric acid, anhydrous sodium acetate, and acetic anhydride, when heated on the water-bath for

one and a-half hours, yield the substance, $C_6H_2(OMe)_3 \cdot CH : C \begin{smallmatrix} CO \\ \diagup \\ NBz \end{smallmatrix}$,

m. p. 165—166°, which is hydrolysed by dilute sodium hydroxide, ammonia, benzoic acid, and 3:4:5-trimethoxyphenylpyruvic acid, $C_6H_2(OMe)_3 \cdot CH_2 \cdot CO \cdot CO_2H$, m. p. 167—168°, being formed. The last-mentioned acid forms an *oxime*, $C_{12}H_{15}O_6N$, m. p. 155—156°, and with *o*-phenylenediamine hydrochloride, yields a *trimethoxybenzylquinoxalone*, $C_{18}H_{18}O_4N_2$, m. p. 196—197°, and is converted by hydrogen peroxide in alkaline solution into trimethylhomogallic [3:4:5-trimethoxyphenylacetic] acid, $C_6H_2(OMe)_3 \cdot CH_2 \cdot CO_2H$.

C. S.

[Preparation of Triphenylmethane Colouring Matters from Diortho-substituted Benzaldehydes]. ANILINFARBEN- & EXTRACT-FABRIKEN VORMALS. J. R. GEIGY IN BASEL (D.R.-P. 199943).—The diortho-substituted benzaldehydes, when condensed with *o*-cresotic acid, give rise to triphenylmethane colouring matters, which have valuable tinctorial properties, being faster to light and alkalis, and dyeing wool in acid-bath in deeper shades, than those from the mono-ortho-substituted benzaldehydes. The following new aldehydes are described:

2:6-Dichlorobenzaldehyde, colourless needles, m. p. 70—71°; 2:6-dichloro-3-nitrobenzaldehyde, colourless leaflets, m. p. 76—77°; 2:6-dichlorobenzaldehyde-3-sulphonic acid; 2-chlorobenzaldehyde-6-sulphonic acid; benzaldehyde-2:6-disulphonic acid, and 6-chlorobenzaldehyde-2:4-disulphonic acid; the sodium salts of all these acids, excepting the last, are salted out in colourless needles; 2:3:6- and 2:4:6-trichlorobenzaldehydes form colourless needles, melting at 86—87° and 58—59° respectively.

G. T. M.

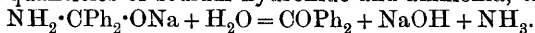
Condensation of *cyclo*Pentanone with Benzaldehyde. MAX KAUFFMANN (*Ber.*, 1908, 41, 3726—3727).—In the preparation of dibenzylidenecyclopentanone (Vörlander and Hobohm, *Abstr.*, 1896, i,

603), it is necessary that the alkali hydroxide solution used should not be too dilute. The author finds that very dilute alkali solutions, or solutions of weak alkalis, such as ammonia, trimethylamine, or sodium carbonate, bring about condensations, but that the products formed are quite different from the sparingly soluble dibenzylidenecyclopentanone. Some of these products are oily, others have comparatively low m. p.'s; some are colourless, whereas others are yellow. J. J. S.

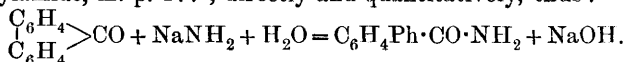
Preparation of Colouring Matters of the Thioindigo-Red Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 198509).—*Bis-o-thioacetophenone*, $S_2(C_6H_4 \cdot COMe)_2$, a substance analogous to indigo-red, is produced by passing air through a solution of *o*-thioacetophenone in aqueous sodium hydroxide. Other oxidising agents, such as alkali ferricyanides, persulphates, perborates, or percarbonates, may be employed. This red colouring matter is also obtained by heating *o*-thioacetophenone with crystallised sodium sulphide; this operation gives rise to the leuco-derivative, which is oxidised as before by aerial oxidation in alkaline solution.

G. T. M.

Products of the Action of Sodamide on Ketones. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1908, 147, 824—826. Compare Abstr., 1906, i, 441).—When a benzene or toluene solution of benzophenone is heated to boiling with sodamide, in some cases an abundant white precipitate is formed, with or without the previous production of an intense blue coloration, whilst in other cases the sodamide slowly dissolves with or without the subsequent separation of a deposit. The production of the blue colour is probably due to the action of free sodium contained in the sodamide (compare Schorigin, this vol., i, 866). The more nearly anhydrous the solution the slower the precipitate is in forming. By collecting the precipitate, drying, and treating with water, benzamide, mixed with a little benzoic acid, is formed. When decomposed with dilute ammonia, benzamide only is formed. The reactions can be represented thus: $COPh_2 + NaNH_2 = NH_2 \cdot CPh_2 \cdot ONa$; $NH_2 \cdot CPh_2 \cdot ONa + H_2O = NH_2 \cdot COPh + C_6H_6 + NaHO$. If freshly-prepared sodamide free from sodium is used, and the solvent is absolutely anhydrous, no deposit is formed in the hot solution, but the substance separates after a time as an abundant crystalline crust of the composition $NH_2 \cdot CPh_2 \cdot ONa$, which, when treated with water, regenerates the whole of the benzophenone, and gives theoretical quantities of sodium hydroxide and ammonia, thus:



Under the same conditions, phenyl *p*-tolyl ketone gives an almost equimolecular mixture of benzamide and toluoylamide, whilst phenyl anisyl ketone yields rather more anisamide than benzamide. Fluorenone, when treated in toluene solution with sodamide, gives diphenyl-*o*-carboxylamide, m. p. 177°, directly and quantitatively, thus:



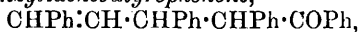
E. H.

Action of Alcoholic Potassium Hydroxide Solution on Ketones. P. J. MONTAGNE (*Rev. trav. chim.*, 1908, 27, 327—359. Compare Abstr., 1907, i, 854).—Zagumenny (Abstr., 1877, 459) has shown that benzhydrol is produced when benzophenone is heated at 160° with alcoholic potassium hydroxide. The author finds the same reduction occurs when the ketone is boiled for two days with a 20% alcoholic solution of potassium hydroxide, and that substituted derivatives of benzophenone, when similarly treated, are either reduced similarly or are decomposed, yielding benzoic acid and the substituted benzene. Thus 4-chloro-, 4-bromo-, 4-methyl-, or 4-phenyl-benzophenone yields the corresponding substituted benzhydrol, whilst 2:4:6-trichlorobenzophenone yields trichlorobenzene and benzoic acid; 2:4:6-tribromobenzophenone yields 4-bromobenzhydrol; 2:4:6-trimethylbenzophenone remains unaltered, and phenyl α -naphthyl ketone yields phenyl- α -naphthylcarbinol.

The following new compound was prepared in the course of the work: 2:4:6-tribromobenzophenone, $C_6H_2Br_3 \cdot COPh$, obtained by heating benzoyl chloride, 1:3:5-tribromobenzene, and aluminium chloride at 150—160°, forms colourless, shining, triclinic crystals [F. M. JAEGER, $a:b:c = 1.3939:1:1.1065$; $\alpha = 130^\circ 36'$, $\beta = 122^\circ 59'$, $\gamma = 58^\circ 58'$], $D^{15} 2.034$, m. p. 147°, b. p. 405°/765 mm. The same compound was also prepared from 2:4:6-tribromobenzoyl chloride (Sudborough, *Trans.*, 1895, 67, 596) and benzene in the presence of aluminium chloride. The crystallographic measurements by F. M. Jaeger of the following compounds are recorded: 2-bromobenzophenone forms large, colourless, monoclinic prisms [$a:b:c = 0.5045:1:0.9322$; $\beta = 83^\circ 24.5'$], $D^{14} 1.517$; phenylindoxazen forms colourless, rhombic crystals [$a:b:c = 0.7905:1:1.2600$], $D^{15} 1.295$; 2:4:6-tribromobenzonitrile crystallises in the monoclinic system [$a:b:c = 1.2113:1:1.1025$; $\beta = 44^\circ 23.75'$]; 2:4:6-tribromobenzamide crystallises from alcohol in long needles, which, in contact with the mother liquor, change into monoclinic prisms [$a:b:c = 2.1655:1:1.1092$; $\beta = 83^\circ 45'$]; 2:4:6-tribromobenzoyl chloride forms colourless, triclinic prisms [$a:b:c = 1.9341:1:1.0041$; $\alpha = 89^\circ 54.6'$, $\beta = 108^\circ 43.75'$, $\gamma = 84^\circ 21'$].

M. A. W.

Reactions of Organic Magnesium Compounds with Cinnamylidene Esters. II. Reactions with Methyl α -Phenylcinnamylideneacetate. MARIE REIMER and GRACE POTTER REYNOLDS (*Amer. Chem. J.*, 1908, 40, 428—444. Compare Abstr., 1907, i, 852).—It was shown previously that the compounds produced by the action of organic magnesium compounds on methyl cinnamylidenemalonate are formed by 1:4-addition, and the authors have now extended the reaction to the case of methyl α -phenylcinnamylideneacetate. The reaction proceeds with much greater difficulty than in the previous cases examined, and the resulting compounds are not esters, formed by 1:4-addition, but ketones or tertiary alcohols, formed by replacement of the methoxyl group and subsequent addition of a second molecule of reagent in the 1:4- or 1:2-position, according to the nature of the magnesium compound.

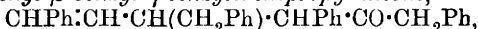
αβ-Diphenyl-γ-benzylidenebutyrophenone,

prepared by the action of magnesium phenyl bromide (3 mols.) on methyl α-phenylcinnamylideneacetate (1 mol.) in boiling ethereal solution, crystallises in slender, soft, white needles, m. p. 191·5—192·5°. When oxidised with permanganate, it yields *β-benzoyl-αβ-diphenylpropionic acid*, $\text{CHPhBz}:\text{CHPh}:\text{CO}_2\text{H}$, which crystallises with 1EtOH in small, shining needles, m. p. 211—212°; the *methyl ester* forms shining, white needles, m. p. 159°.

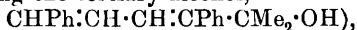
αβ-Diphenyl-γ-benzylidenebutyrophenone reacts with magnesium phenyl bromide, yielding a tertiary alcohol which could not be isolated in the pure state; on oxidation, it gives *αβγγ-tetraphenylbutyrolactone*, $\text{CHPh}-\text{CO} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{O}$, crystallising in slender needles, m. p. 221—221·5°, and, on distillation under diminished pressure, it yields a yellow oil, from which separates a *compound*, $\text{C}_{22}\text{H}_{18}\text{O}$, probably phenylbenzylidenepropiophenone, crystallising in needles, m. p. 134—135°.

Bromo-αβ-diphenyl-γ-benzylidenebutyrophenone,

or, less probably, $\text{CHPh}:\text{CBr}:\text{CHPh}:\text{CHPh}:\text{COPh}$, forms white needles, m. p. 186—187°.

Benzyl α-phenyl-β-benzyl-γ-benzylidenepropyl ketone,

prepared by the interaction of magnesium benzyl bromide and methyl α-phenylcinnamylideneacetate, forms slender, white needles, m. p. 150°. Magnesium *o*-tolyl or naphthyl bromides do not react with the ester, but magnesium methyl iodide in excess furnishes an oil (probably containing the tertiary alcohol,

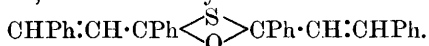


which, on distillation under reduced pressure, loses water and yields a *hydrocarbon*, $\text{CHPh}:\text{CH}:\text{CH}:\text{CPh}:\text{CMe}:\text{CH}_2$, white crystals, m. p. 97—98°, b. p. 140—150°/25 mm. J. C. C.

Thio-derivatives of Ketones. VI. EMIL FROMM (*Ber.*, 1908, 41, 3644—3661).—Whilst two isomeric forms of trithioaldehydes are known in accordance with stereochemical views, attempts to obtain stereoisomerides of trithioketones, derived from ketones of the type $\text{R}:\text{CO}:\text{R}'$, have hitherto been unsuccessful (compare Fromm and Baumann, *Abstr.*, 1895, i, 362; Fromm and Ziersch, *Abstr.*, 1906, i, 930; Fromm and Höller, *Abstr.*, 1907, i, 710).

[With W. LAMBRECHT.]—The authors have now succeeded in obtaining two stereoisomeric, half-sulphurised thioketones by the action of ammonia and hydrogen sulphide on an alcoholic solution of benzylideneacetophenone. The one or the other isomeride is obtained according as the ammonia or the hydrogen sulphide is introduced first into the alcoholic solution. If the solution is saturated with hydrogen sulphide, cooled to 0°, treated with a large excess of ammonia, and left overnight, a quantitative yield of *β-duplobenzylideneacetophenone sulphide* [*monothioduplobenzylideneacetophenone*], $\text{C}_{30}\text{H}_{24}\text{OS}$, m. p. 181°, is obtained as an amorphous, white powder. The *α-isomeride*, m. p. 96°,

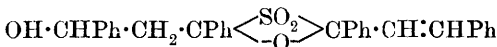
is obtained when an alcoholic solution of benzylideneacetophenone is saturated with ammonia, cooled, and treated with hydrogen sulphide. The two substances show the same reactions. For example, dry distillation causes the formation of benzylideneacetophenone and unexamined products containing sulphur; reduction by zinc dust and glacial acetic acid yields benzylacetophenone, whilst the action of phenylhydrazine in boiling glacial acetic acid results in the formation of hydrogen sulphide and triphenylpyrazoline. These reactions, which show that the skeleton of benzylideneacetophenone is still existent in the two isomerides, are in harmony with the formula



It is a matter of doubt whether the stereoisomerism is connected with the ethylenic linkings or is conditioned by the disposition of the groups about the plane of the heterocyclic ring. Since, however, the more fusible α -duplobenzylideneacetophenone sulphide is transformed into the β -isomeride by the rapid evaporation of its solution in chloroform containing iodine, the latter view is the more favoured, the α -isomeride having the *cis*-configuration.

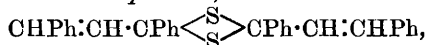
If a chloroform solution of either isomeride is treated with bromine in chloroform, and alcohol is then added, sulphur is eliminated, the solution becomes decolorised, and Rupe and Schneider's β -bromo- ω -benzylacetophenone (Abstr., 1895, i, 361) is precipitated. In the absence of the alcohol, decolorisation occurs more slowly, hydrogen bromide is evolved, and a *tribromide*, $\text{C}_{30}\text{H}_{25}\text{OBr}_3\text{S}$, m. p. 147° , is obtained. The α - or the β -isomeride with excess of iodine in chloroform yields a *substance*, $\text{C}_{30}\text{H}_{28}\text{O}_3\text{S}$, m. p. 191° .

When chloroform solutions of the α - and β -isomerides are oxidised by potassium permanganate and dilute sulphuric acid, stereoisomeric oxidation products are obtained. This result is noteworthy, since stereoisomeric trithioaldehydes yield the same oxidation product. The *substance*, $\text{C}_{30}\text{H}_{26}\text{O}_4\text{S}$, m. p. 216° , obtained by the oxidation of β -duplobenzylideneacetophenone sulphide, forms small, white prisms, whilst the oxidation product of the α -isomeride, m. p. 198° , crystallises in needles and is transformed by iodine into its isomeride. Little has been settled regarding the constitution of these oxidation products; they are stable to phenylhydrazine, or benzoyl chloride and sodium hydroxide, or hydrogen chloride in cold glacial acetic acid. They yield benzylideneacetophenone by treatment with hot acetic anhydride and sodium acetate. The formula



is proposed, but is contrary to the fact that the oxidation products cannot be acetylated or benzoylated.

Duplobenzylidenethioacetophenone,



m. p. 191° , is obtained in a bad yield when hydrogen chloride, followed by an excess of hydrogen sulphide, is led into an alcoholic solution of benzylideneacetophenone at 0° ; it is decomposed by

phenylhydrazine, yielding hydrogen sulphide and a substance which is probably triphenylpyrazoline.

[With JAMES L. MCKEE.]—With the hope of preparing another compound possessing the peculiar additive properties of duplobenzylidenethioacetone (Fromm and Höller, *loc. cit.*), the authors have examined the reaction between dibenzylidenacetone and hydrogen sulphide in acid and in ammoniacal solution. Complex compounds are obtained which do not show any marked additive powers, and for which constitutional formulæ are suggested.

Duplodibenzylidenacetoneoxytriamine, $C_{34}H_{35}ON_3$, decomposing at 97° , is an amorphous, yellowish-brown substance obtained by the action of ammonia on an alcoholic suspension of dibenzylidenacetone. It readily loses ammonia when its ethereal solution is treated with hydrogen chloride, whereby the *hydrochloride*, $C_{34}H_{32}ON_2 \cdot 2HCl$, decomp. 185° , is precipitated, from which ammonium hydroxide liberates *duplodibenzylidenacetoneoxydiamine*, $C_{34}H_{32}ON_2$, which decomposes at 137° . When an alcoholic suspension of dibenzylidenacetone is treated with ammonia, cooled, and then treated with hydrogen sulphide, a yellowish-white precipitate of *duplodibenzylidenethioacetonediamine*, $C_{34}H_{34}N_2S_2$, is obtained, which readily loses hydrogen sulphide and takes up water, yielding *duplodibenzylidenethioacetonediamine*, $C_{34}H_{34}ON_2S$, which decomposes at 103 – 119° , and is best purified through the *hydrochloride*, $C_{34}H_{34}ON_2S \cdot 2HCl$. *Duplodibenzylidenacetoneoxytrisulphide*, $C_{34}H_{32}OS_3$, m. p. 110 – 127° (decomp.), is obtained by saturating an alcoholic suspension of dibenzylidenacetone with hydrogen sulphide, adding a slight excess of alcoholic ammonia, and again passing an excess of hydrogen sulphide. If the solution is saturated with ammonia and submitted to the prolonged action of hydrogen sulphide, *duplodibenzylidenacetonepentasulphide*, $C_{34}H_{32}S_5$, m. p. 201° , is obtained, which crystallises in colourless needles, and is oxidised by potassium permanganate and sulphuric acid in the presence of a little benzene to *duplodibenzylidenacetoneheptaoytetrasulphide*, $C_{34}H_{32}O_7S_4$, decomp. 160 – 161° , and *duplodibenzylidenacetonehexaoxytetrasulphide*, $C_{34}H_{32}O_6S_4$, decomp. 130° .

The action of hydrogen chloride, followed by hydrogen sulphide, on an alcoholic suspension of dibenzylidenacetone yields a *substance*, $2C_{17}H_{14}O \cdot 3H_2S$, decomp. 150° , or *triplodibenzylidenacetonetetrasulphide*, $C_{51}H_{50}S_4$, m. p. 99 – 100° .

Speranski's thiomenthene, $C_{20}H_{34}S$, m. p. 50° (Abstr., 1907, i, 627), is precipitated when hydrogen sulphide is passed into a 10% alcoholic solution of menthone saturated with hydrogen chloride.

C. S.

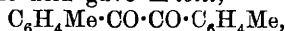
Study of the Benzoin Condensation. THOR EKECRANTZ and ALFR. AHLQVIST (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 13, 1–26).—The benzoin condensation is not general with aromatic aldehydes, the possibility of the reaction depending on the nature of the substituent groups present. The presence of amino-, hydroxy-, or

nitro-groups, or of large side-chains, in the aldehyde molecule hinders the reaction, whilst the presence of the substituent group in the meta-position is most favourable to the condensation. With aldehydes containing alkyl- or alkyloxy-groups, the reaction, in general, soon results in an equilibrium between condensation product and unchanged aldehyde. As a secondary reaction, occurs the formation of the acid corresponding with the aldehyde. With nitro-substituted benzaldehydes, large quantities of the acids are formed instead of benzoin, and in the case of *m*- and *p*-nitrobenzaldehydes the ethyl esters of the acids are also formed. With volatile acids, the corresponding cyanohydrins are often formed. Since, in the authors' condensation experiments, the alcohol corresponding with the aldehyde, and formed by the simultaneous oxidation and reduction of the aldehyde, was in no case detected, it is assumed that this alcohol takes part in various reactions, resulting in the formation of resin, which always arises in smaller or larger amount in the reaction between potassium cyanide and substituted aromatic aldehydes. Without invalidating Bredig and Stern's hypothesis that the benzoin condensation is due to catalysis by cyanogen ions (*Zeitsch. Elektrochem.*, 1904, 10, 582—587), the explanation of the varying behaviour of aromatic aldehydes when treated with potassium cyanide may be found in the acid character of the aldehydes (compare Euler, Abstr., 1906, i, 140). In the case of all aldehydes with which the degree of dissociation is greater than with hydrogen cyanide, for example, the nitrobenzaldehydes, aldehyde salt will be obtained in relatively large quantity, hydrogen cyanide, which is only slightly dissociated, being formed at the same time. Since potassium cyanide in aqueous solution is not only electrolytically dissociated, but also hydrolysed, according to the equation: $\text{KCN} + \text{H}_2\text{O} = \text{KHO} + \text{HCN}$, the formation of the acid corresponding with the aldehyde may be simply explained as follows: (1) under the influence of dilute alkali a hydrogen atom migrates from one aldehyde molecule to another, giving, for example, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}(\text{OH})\cdot$ and $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot$; (2) these residues take up respectively the hydrogen and hydroxyl formed by hydrolysis, giving $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$. When these acids are formed in large quantities, they give rise to their strongly dissociated potassium salts, which cause a diminution of the cyanogen ions and so prevent the benzoin condensation from taking place. The condensation can therefore only occur with aldehydes which only exhibit a slight tendency to form salts, such as benzaldehyde and its alkyl and alkyloxy-derivatives and halogen derivatives of benzaldehyde and furfuraldehyde. In cases where the substituent group does not alter appreciably the degree of dissociation of the aldehyde, the condensation is considerably retarded by the presence of a side-chain.

In their experiments on the benzoin reaction, the authors dissolved 10—20 grams of aldehyde in four times the quantity of 66% alcohol and heated the mixture, together with an amount of potassium cyanide equal to 10—15% of that of the aldehyde, either (1) in a reflux apparatus on the water-bath for one hour, or (2) in a sealed tube at 60°.

With benzaldehyde, benzoin, benzoic acid, and mandelonitrile were formed.

Of the three tolualdehydes, the para-compound is the slowest to react and the meta-compound the most ready. From *p*-tolualdehyde, *p*-toluic acid is obtained along with the *p*-toluoin. *o*-Toluoin, $C_{16}H_{16}O_2$, crystallises from aqueous alcohol in silky needles, m. p. 79° . *m*-Toluoin could only be obtained as a syrup, oxidation of which with chromic oxide in acetic acid gave *m*-tolil,



which crystallises from alcohol in yellow needles, m. p. 103° .

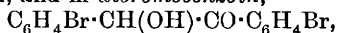
Cuminaldehyde yields cuminoïn and cuminic acid. With salicylic aldehyde, no benzoin condensation occurs, the aldehyde undergoing profound decomposition with formation of resin (compare Zincke, *Annalen*, 1883, 216, 316). *p*-Hydroxybenzaldehyde and vanillin remain almost entirely unchanged, whilst anisaldehyde yields anisoïn and anisic acid. Experiments made with 3-methoxy-4-benzyloxybenzaldehyde in order to ascertain the influence of side-chains on the reaction, showed that this compound yields no benzoin.

Benzanisoin, $OH \cdot CHPh \cdot CO \cdot C_6H_4 \cdot OMe$, which was prepared by the action of potassium cyanide on a mixture of benzaldehyde and anisaldehyde in 80% alcohol, and is analogous to Fischer's benzo-furoïn (Abstr., 1880, 798), crystallises from aqueous alcohol in colourless needles, m. p. $105-106^\circ$, and dissolves in most organic solvents.

Cuminanisoin, $C_6H_4Pr^s \cdot CH(OH) \cdot CO \cdot C_6H_4 \cdot OMe$, separates from aqueous alcohol in crystals, m. p. $81-82^\circ$, and is readily soluble in the ordinary organic solvents.

m-Chlorobenzaldehyde yields small quantities of *m*-dichlorobenzoin, together with *m*-chlorobenzoic acid.

m-Bromobenzaldehyde yields *m*-bromobenzaldehyde cyanohydrin, *m*-bromobenzoic acid, and *m*-dibromobenzoin,



which crystallises from aqueous alcohol in pale yellow needles, m. p. $123-124^\circ$, and dissolves readily in the ordinary organic solvents.

From *m*-aminobenzaldehyde, no definite product could be obtained.

T. H. P.

Preparation of Derivatives of Benzanthrone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 200335).—The alkyl derivatives of anthraquinone and α -aminoanthraquinone can be employed in the production of derivatives of benzanthrone (compare Abstr., 1907, i, 324, 943). β -Methylantranol, produced by the reduction of β -methylanthraquinone with tin and hydrochloric acid, when heated at $140-150^\circ$ with glycerol and concentrated sulphuric acid gives rise to *methylbenzanthrone*, yellow needles, m. p. 199° .

Dimethylbenzanthrone, yellow needles, m. p. 165° , is similarly obtained from 1 : 3-dimethylantraquinone (m. p. $159-163^\circ$), the latter being first converted into the corresponding oxantranol. G. T. M.

Constitution and Colour. II. FRIEDRICH KEHRMANN (*Ber.*, 1908, 41, 3396. Compare this vol., i, 699).—A criticism of K. H. Meyer's views on the halochromism of quinones (this vol., i, 731). J. J. S.

Preparation of Chloroacylaminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 199758).—The aminoanthraquinones when chlorinated or brominated give rise to polyhalogenated derivatives, but when chlorine or chlorine evolving agents react with the acylaminoanthraquinones, the monochloro-derivatives are produced containing the halogen in the ortho- or para-position with regard to the amino-group.

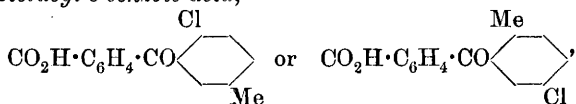
4-Chloroacetyl-1-aminoanthraquinone, yellow crystals, m. p. 203—204°, obtained by passing chlorine into a glacial acetic acid solution of acetyl-1-aminoanthraquinone and sodium acetate at 80°, gives, on hydrolysis with sulphuric acid, 4-chloro-1-aminoanthraquinone, red needles, m. p. 179—180°. 4:8-Dichloro-1:5-diacetyldiaminoanthraquinone, brown crystals, m. p. above 300°, and 4:8-dichloro-1:5-diaminoanthraquinone, red needles with green reflex, were similarly obtained.

1:5-Anthraquinonyldiurethane, from 1:5-anthraquinone and ethyl chlorocarbonate, when chlorinated in glacial acetic acid gives rise to 4:8-dichloro-1:5-anthraquinonyldiurethane, brown crystals. The preparation of 1-chloro-2-acetylaminoanthraquinone, yellow leaflets or needles, m. p. 240—241°, 1-chloro-2-aminoanthraquinone, reddish-brown crystals, m. p. 234—236°, and 1-chloro-2-anthraquinonyldiurethane, yellow leaflets m. p. 189—191°, is carried out in a similar manner. G. T. M.

Friedel and Crafts' Reaction. GUSTAV HELLER and KURT SCHÜLKE (*Ber.*, 1908, 41, 3627—3638).—The authors find that in the condensation of phthalic anhydride and benzene in presence of aluminium chloride, a reaction previously studied by Heller (*Zeitsch. angew. Chem.*, 1906, 19, 669), exactly 1 mol. of aluminium chloride, Al_2Cl_6 , is required for the condensation of 1 mol. of phthalic anhydride, and suggest that an intermediate compound is formed, thus: $\text{C}_8\text{H}_4\text{O}_3 + \text{Al}_2\text{Cl}_6 + \text{C}_6\text{H}_6 \rightarrow \text{C}_8\text{H}_4\text{O}_3 \cdot \text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_6 \rightarrow \text{C}_{14}\text{H}_9\text{O}_3 \cdot \text{Al}_2\text{Cl}_5 + \text{HCl}$. This reaction has also been extended to the case of other hydrocarbons and some of their derivatives. From benzene and toluene, almost quantitative yields of *o*-benzoylbenzoic and *p*-toluoyl-*o*-benzoic acids were obtained. When the latter is heated on the water-bath with fuming sulphuric acid (20% SO_3), β -methylanthraquinone is obtained in almost colourless needles (Limpricht and Wiegand, *Abstr.*, 1900, i, 498, state that the crystals are usually yellow).

A 97% yield of α -naphthoyl-*o*-benzoic acid is obtained from naphthalene when benzene is used as solvent, and the acid is condensed to naphthanthraquinone by warming with 10 parts of concentrated sulphuric acid at 45—50° (compare Elbs, *Abstr.*, 1886, 1037). This yields a monosulphonic acid on treatment with fuming sulphuric acid (20% SO_3). Anthracylbenzoic acid is formed from anthracene, benzene being used as a solvent, but it could not be isolated in the pure state.

p-Chlorotoluoyl-*o*-benzoic acid,



prepared from *p* chlorotoluene, crystallises in aggregates of slender needles, m. p. 164—165°. When warmed with fuming sulphuric acid,

it condenses to 4-chloro-1-methylantraquinone, which forms long, slender, yellow needles, m. p. 164° ; on oxidation with permanganate, the acid yields *p*-chlorocarboxybenzoyl-*o*-benzoic acid, $C_{15}H_9O_5Cl$, a crystalline powder, m. p. $234-236^{\circ}$.

When 4-chloro-1-methylantraquinone is heated under pressure with 66% nitric acid to 195° , it yields 4-chloroantraquinone-1-carboxylic acid, crystallising in bundles of yellow needles, m. p. $228-229^{\circ}$.

o-Chlorotoluoyl-*o*-benzoic acid, the exact constitution of which was not determined, is prepared from *o*-chlorotoluene; it forms crystalline aggregates, m. p. $182-183^{\circ}$, and on warming with fuming sulphuric acid gives chloromethylantraquinone (Me:Cl = 1:2 or 2:3), which forms glistening needles, m. p. 213° . By oxidising *o*-chlorotoluoyl-*o*-benzoic acid with permanganate, *o*-chlorocarboxybenzoyl-*o*-benzoic acid, $C_{15}H_9O_5Cl \cdot H_2O$, is produced. This forms long rhombohedra, and loses H_2O above 110° , sinters at 184° , and melts at 188° .

When the chloromethylantraquinone just described is heated under pressure with 66% nitric acid at 210° , β -chloroantraquinone-carboxylic acid ($CO_2H:Cl = 1:2$ or $2:3$) is formed. This crystallises in slender, pale yellow, bushy needles, m. p. 280° ; the sodium salt forms almost colourless needles. On heating above its m. p., the acid loses carbon dioxide, and 2-chloroantraquinone is left. J. C. C.

The Colour and Affinity for Mordants of Anthraquinone Derivatives. GUSTAV HELLER (*Ber.*, 1908, 41, 3639—3640).— β -Chloroantraquinonecarboxylic acid and 4-chloroantraquinone-1-carboxylic acid (preceding abstract), like the other simple derivatives of anthraquinone, are pale yellow. The alkaline solutions, however are almost colourless, and the sodium salts are even paler than the acids. The substances have no affinity for mordants, and it may generally be stated that the affinity for mordants of anthraquinone derivatives is proportional to the intensity of colour of the sodium salts. J. C. C.

Phenanthrene Series. XXIV. Morpholquinone from Phenanthrene. JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1908, 41, 3696—3703).—Morpholquinone, 3:4-dihydroxyphenanthraquinone, may be obtained from 3-hydroxyphenanthraquinone (Werner, *Abstr.*, 1902, i, 440) by the following stages: nitration, reduction, diazotisation, and boiling with water. A modification of Werner's method of diazotising 3-aminophenanthraquinone is described. Nitric acid reacts with 3-hydroxyphenanthraquinone, yielding a mixture of the isomeric 2- and 4-nitro-derivatives, both of which dissolve readily in sodium carbonate solution. One of these crystallises from glacial acetic acid in yellow needles, and is identical with Werner's product. It has been found possible to obtain a *dinitro*-derivative by the action of nitric acid on 3-hydroxyphenanthraquinone. It crystallises in yellow needles, m. p. $227-228^{\circ}$, and reacts with *o*-phenylenediamine, yielding a *phenanthraphenazine*, m. p. 249° . The morpholquinone is obtained, together with other products, when the mixture of mononitro-derivatives is reduced with tin and hydrochloric acid, the resulting mixture of amino-compounds diazotised, and the diazo-solution boiled.

Morpholquinone can also be prepared from the mother liquors from 3-nitrophenanthraquinone, obtained when 9 : 10-diaminophenanthrene is treated with acetic anhydride and nitric acid (see following abstract). The mother liquor is evaporated, reduced and diazotised, and the resulting diazo-solution boiled. J. J. S.

Phenanthrene Series. XXIII. 3-Nitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1908, 41, 3679—3695. Compare Werner, *Abstr.*, 1904, i, 863; Schmidt and Kämpf, *Abstr.*, 1902, i, 757, 797).—Starting with 3-nitrophenanthraquinone, it has been found possible to prepare morpholquinone (compare preceding abstract). A convenient method for the preparation of the 3-nitro-derivative has been worked out, and numerous derivatives have been prepared.

In the case of 3-nitrophenanthraquinonedioxime, it has been found that the replacement of the hydrogen atoms of the oximino-groups by methyl or acetyl produces a weakening in colour (*Abstr.*, 1907, i, 630, 1054), and the same change is observed during anhydride formation (this vol., i, 16).

A modification of Pschorr's method (*Abstr.*, 1902, i, 672) for the preparation of 9 : 10-diaminophenanthrene hydrochloride is described. This salt is best nitrated by first acetylating by boiling with a mixture of acetic anhydride, acetic acid, and the theoretical amount of sodium acetate, and then stirring and heating with concentrated nitric acid in the presence of acetic acid, acetic anhydride, and a small amount (1 gram) of copper. The yield of pure 3-nitrophenanthraquinone is only some 20% of the theoretical.

3-Nitrophenanthraquinone monoimine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{C}_6\text{H}_4) \text{C}(\text{NH}) \text{CO}$,

obtained by shaking 3-nitrophenanthraquinone with alcoholic ammonia for five hours, crystallises from benzene in green prisms with a brassy lustre, and decomposes at 203°. Its benzene solution with hydrogen chloride yields a red *hydrochloride*. When boiled with acetic acid, it is converted back into the quinone.

3-Nitrophenanthraquinone semicarbazone, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_4$, is extremely unstable, and has m. p. 254° (decomp.). The dioxime, $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_3$, crystallises from alcohol in yellowish-red needles, m. p. 200° (decomp.). In the preparation of oximes of nitro-derivatives, it has been found advisable to use granular witherite to neutralise the liberated hydrogen chloride.

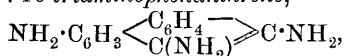
The *diacetyl* derivative of the dioxime, $\text{C}_{18}\text{H}_{13}\text{O}_6\text{N}_3$, crystallises from benzene in pale yellow plates, m. p. 183° (decomp.). The anhydride

of the dioxime, **3-nitrophenanthrafurazan,** $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{C}_6\text{H}_4) \text{C}(\text{N}) \text{N} \text{O}$, is

obtained when the dioxime is shaken with benzoyl chloride and sodium hydroxide solution. It crystallises from alcohol in yellow needles, m. p. 230—231°.

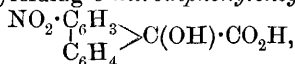
The *dimethyl ether* of the dioxime, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$, obtained by the action of methyl sulphate and concentrated sodium hydroxide solution on a benzene solution of the oxime, crystallises from alcohol in pale yellow needles, m. p. 190—192°.

When reduced with an alcoholic solution of stannous chloride, the dioxime yields 3 : 9 : 10-*triaminophenanthrene*,



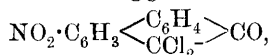
which is transformed into a *hexa-acetyl* derivative, $\text{C}_{26}\text{H}_{25}\text{O}_6\text{N}_3$, m. p. 307° , when heated with acetic anhydride and sodium acetate.

Warm 10% potassium hydroxide solution reacts with 3-nitro-phenanthraquinone, yielding 3-nitrodiphenyleneglycollic acid,



m. p. $239-240^\circ$, and 3-nitrofluorenone, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C} \end{array} \right\rangle \text{CO}$, which crystallises from alcohol in yellowish-brown needles, m. p. $209-210^\circ$. The *oxime*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C} \end{array} \right\rangle \text{C} \cdot \text{N} \cdot \text{OH}$, also forms yellowish-brown needles, m. p. 240° .

Phosphorus pentachloride reacts with 3-nitrophenanthraquinone, yielding equal quantities of 9 : 9-dichloro-3-nitro- and 10 : 10-dichloro-3-nitro-phenanthrones, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \right\rangle \text{CCl}_2$ and



which can be separated by means of benzene; the α -compound separates in pale yellow plates, m. p. $191-193^\circ$. The isomeric β -compound has m. p. $143-145^\circ$. When reduced with tin and hydrochloric acid, these two compounds yield the corresponding *chloroaminohydroxyphenanthrenes*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}(\text{OH}) \end{array} \right\rangle \text{CCl}$ and $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CCl} \end{array} \right\rangle \text{C} \cdot \text{OH}$, which have been isolated in the form of their hydrochlorides. All attempts to nitrate these chlorohydroxy-compounds proved unsuccessful.

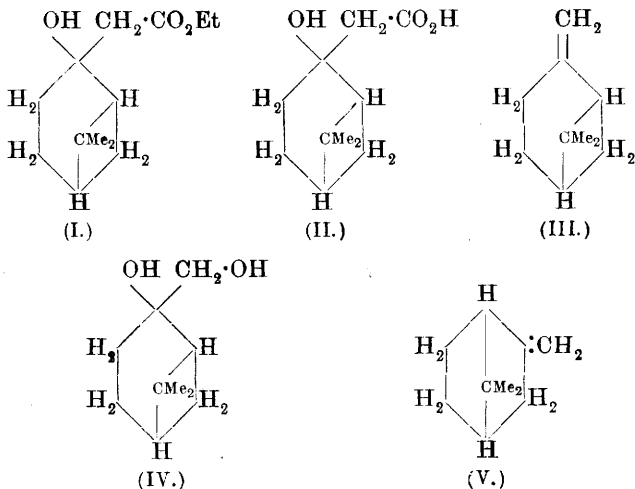
3-Aminophenanthraquinone (Werner, Abstr., 1902, i, 441) yields a *monoxime*, $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$, which crystallises in small, reddish-brown prisms, m. p. 247° (decomp.).

Attempts to obtain nitro-derivatives of the amine proved unsuccessful. With a mixture of acetic acid, acetic anhydride, and nitric acid, the base yields 3-aminodinitrodiphenic acid, $\text{C}_{14}\text{H}_8\text{O}_8\text{N}_3$, which crystallises from water in colourless plates, m. p. $200-201^\circ$ (decomp.).

J. J. S.

Terpenes and Ethereal Oils. XCVII. Synthesis of Fenchene, β -Pinene, Camphene, and Camphor from Nopinone. OTTO WALLACH (*Annalen*, 1908, 363, 1-19. Compare this vol., i, 813).—A previous attempt to prepare β -pinene from nopinone led to the synthesis of a hydrocarbon isomeric with the desired product (Abstr., 1907, i, 1058). Further experiments, however, have now resulted, not only in the synthesis of β -pinene, but also in the discovery of a remarkable intramolecular transformation. The interaction of nopinone, ethyl bromoacetate, and zinc leads to the formation of a hydroxy-ester (I). This was heated directly with potassium hydrogen

sulphate, and the resulting unsaturated ester hydrolysed. The terpene, obtained on distillation of the unsaturated acid, is now found to be identical with *Ld*-fenchene (V), which is obtained together with *Ll*-fenchene from *l*-fenchone in the same manner as *Dd*- and *Dl*-fenchenes are formed from *d*-fenchone (Abstr., 1899, i, 65; this vol., i, 809).



Ld-Fenchene, on oxidation, yields hydroxyfenchenic acid, m. p. 154°, and on hydration *isofenchyl* alcohol (Abstr., 1907, i, 1058), m. p. 62—63°, b. p. 202—204°, which on oxidation is converted into *iso*-fenchone (compare this vol., i, 809). *iso*Fenchocamphoric acid, m. p. 158—159°, has $[\alpha]_D + 12^\circ$.

On repeating the synthesis from nopinone, there was obtained *Ll*-fenchene, which resembles the *Ld*-isomeride and on hydration forms *isofenchyl* alcohol, but on oxidation yields hydroxyfenchenic acid, m. p. 135—136°. It is found that the nature of the end-product depends on the manner in which water is split off from ethyl nopinolacetate (I). If the dehydrating agent employed is acetic anhydride, the end-product is a mixture of fenchene and β -pinene, the latter being obtained in greatest amount if the ester is hydrolysed before the dehydration.

Nopinolacetic acid (II), formed by hydrolysis of its ester by means of alkalis, crystallises from light petroleum in prisms, m. p. 83—85°, and is stable towards lead dioxide, but is readily attacked by boiling dilute sulphuric acid, yielding *isofenchyl* alcohol and an acid substance. When heated with potassium hydrogen sulphate, nopinolacetic acid is converted into an isomeric *acid*, m. p. 85—86°, and a volatile acid, m. p. 174—175°, which may be homodihydrocuminic acid. The action of acetic anhydride on nopinolacetic acid leads to the formation of two unsaturated acids, one of which loses carbon dioxide during the reaction and forms *l*- β -pinene (III), b. p. 163—164°, D^{22}_D 0.8660—0.8675, n_D^{20} 1.4724—1.4749, α $-22^\circ 5'$ to $-22^\circ 20'$; this on oxidation

with permanganate forms nopic acid identical with that obtained from natural β -pinene. The second acid is more stable, and decomposes only on distillation, yielding fenchene.

A sparingly soluble *glycol* (IV), crystallising in leaflets, m. p. 75—77° (compare Wagner, Abstr., 1894, i, 610), is obtained together with nopic acid by careful oxidation of the synthetical, as also of the natural, β -pinene. When heated with dilute acids, it yields an *aldehyde*, which has an odour of cuminol, forms a *semicarbazone*, and reduces silver solutions with formation of a silver mirror. When heated at 60° with glacial acetic-sulphuric acid, β -pinene yields terpinene, b. p. 175—180°, and small amounts of *isofenchyl acetate*, which suggests the presence of traces of fenchene in the synthetical pinene.

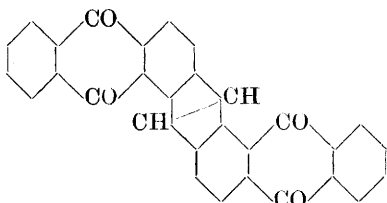
The action of hydrogen chloride on synthetical β -pinene in cooled glacial acetic acid, or anhydrous ethereal solution, leads to the formation of bornyl chloride, m. p. 117—120°, $[\alpha]_D - 22.75^\circ$, and dipentene dihydrochloride, m. p. 49—50°.

Camphene, formed from the synthetical *l*-bornyl chloride by the action of sodium acetate and glacial acetic acid at 190—200°, is converted by way of its acetate into *isoborneol*, which on oxidation with chromic acid yields camphor. This series of reactions constitutes the first synthesis of camphor from a compound (nopinone) containing a smaller number of carbon atoms.

It is considered that the first product of the dehydration of nopinol-acetic acid (II) is probably β -pinene (III), which undergoes transformation into *Ll*-fenchene, this finally changing into *Ld*-fenchene (V). Such a series of changes must entail a considerable intramolecular transformation, the mechanism of which remains to be investigated.

G. Y.

[Preparation of Complex Anthracene Derivatives.] BADISCH ANILIN- & SODA-FABRIK (D.R.-P. 199756).— β -Methylantraquinone, when heated at 150—170° with alcoholic potash, gives rise to a



condensation product, at first present as a dihydroanthracene derivative, but which on oxidation with alkali hypochlorite or atmospheric oxidation yields the annexed compound. This substance separates from hot nitrobenzene in golden-yellow crystals, not melting below 360°. The oxidation may also be

effected by adding sodium nitrate to the alcoholic potash; the reaction then takes place at 140—150°.

The halogenated derivatives of β -methylantraquinone give similar condensation products.

G. T. M.

Preparation of Citral Hydrate. PIERRE COULIN (D.R.-P. 198483).—The dihydrodisulphonic derivative of citral was obtained when citral or lemon-grass oil was treated with aqueous sodium sulphite, dilute sulphuric acid being slowly added to neutralise the alkali hydroxide.

The liquid was then cooled to 0° , and treated with 50% sulphuric acid or 30% hydrochloric acid to form an additive compound, from which citral hydrate can be regenerated by the action of alkali hydroxides.

G. T. M.

[Isolation of an Isomeride of Citral Hydrate.] PIERRE COULIN (D.R.-P. 198714. Compare preceding abstract).—The product obtained by the action of acids on the labile dihydrodisulphonic derivative of citral consists of citral hydrate, which is not volatile in steam, and an isomeric compound, which is readily volatile under these conditions. This *isomeride* of citral hydrate has the following properties: b. p. $93.2-95.2^{\circ}/13$ mm., D_{20}^{15} 0.964, n_{20}^{20} 1.44991, semicarbazone, m. p. 172° , and thiosemicarbazone, m. p. 129° .

When condensed with acetone or methyl ethyl ketone in the presence of alkali hydroxides, this isomeride of citral hydrate gives rise to condensation products, which, by heating with water or a hydrogen sulphite, or treatment with acid, yield perfumes having respectively the formulæ $C_{13}H_{22}O_2$ and $C_{14}H_{24}O_2$.

G. T. M.

[The Condensation of Ketones and Citral Hydrate.] PIERRE COULIN (D.R.-P. 200654).—The condensation of citral hydrate with acetone or methyl ethyl ketone in the presence of sodium peroxide or potassium hydroxide leads to the production of ψ -ionone hydrate and methyl- ψ -ionone hydrate respectively.

G. T. M.

Preparation of Neutral Esters from Sandal Wood Oil. KNOLL & Co. (D.R.-P. 201369).—*Santolyl succinate* was prepared either by mixing sandal wood oil and succinyl chloride in the presence of pyridine, or by heating the oil with phenyl succinate at 200° in the presence of sodium hydroxide.

Santolyl phosphate is prepared from sandal wood oil, triphenyl phosphate, and sodium hydroxide at 200° . The santolyl esters of other polybasic acids, such as phthalic, citric, and methylenecitric acids, are obtained by similar means.

G. T. M.

Identity of Ilcyl Alcohol and α -Amyrin. ÉMILE JUNGFLEISCH and HENRI LEROUX (*Compt. rend.*, 1908, 147, 862—864*).—The specimen of ilcyl alcohol obtained by Personne from the bird-lime yielded by the common holly, to which the formula $C_{25}H_{41}O$ was ascribed (Abstr., 1884, 1365), formed colourless needles, m. p. 175° . After several recrystallisations from alcohol, however, it has m. p. $181-181.5^{\circ}$, $[\alpha]_D + 91.8^{\circ}$ (α -amyrin has $181-181.5^{\circ}$ and $\alpha + 91.6^{\circ}$ respectively), and the results of its analysis agree closely with the formula, $C_{30}H_{50}O$, of α -amyrin. Further, the acetate prepared either from ilcyl alcohol or from α -amyrin has m. p. 220° and $[\alpha]_D + 77.9^{\circ}$ or $+ 77.0^{\circ}$, whilst the benzoate has m. p. 192° and $[\alpha]_D + 93.1^{\circ}$ or $+ 93.58^{\circ}$, according to the source of preparation.

The identity of the two benzoates is, moreover, rendered conclusive by the fact that both are dimorphous. The acetone solution deposits the benzoate, sometimes separately, sometimes simultaneously, in the form of very long, silky needles, m. p. 170° (on Maquenne block), and

* and *J. Pharm. Chim.*, 1908, 28, 481—486.

as prisms with brilliant facets, m. p. 192° (on Maquenne block). If shown with one form, the solution deposits the whole crop in that form, but both can exist together in solution for several days. The needles, if cooled after melting at 170° , re-melt at 192° (on Maquenne block), which is also the m. p. of the needles if previously heated at 110° for fifteen hours. The needle crystals, if slowly heated, have m. p. 192° , and if melted at 170° , resolidify on continued heating and again melt at 192° . Wyrnboff finds that the prismatic benzoates of the two origins are optically identical. E. H.

Bakankosin. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1908, 147, 750—752; *J. Pharm. Chim.*, 1908, [vi], 28, 433—439).—*Strychnos Bakanko*, from which the authors have isolated (Abstr., 1907, i, 33C) the glucoside bakankosin, has been shown by Jumelle to be identical with Baillon's *Strychnos Vacacoua*. The fruit originally employed by the authors was not ripe; they have now examined the seeds from the ripe plant, and find that they also contain the new glucoside, although in less amount (0.92% instead of the 3.6% from the unripe seeds). One part of anhydrous bakankosin dissolves in 3164 parts of ethyl acetate (anhydrous), 55 parts of 95% alcohol, 12 parts of water, or 4 parts of methyl alcohol. Analysis and a cryoscopic determination of the molecular weight show that the glucoside has the formula $C_{16}H_{23}O_8N \cdot H_2O$. Bakankosin is not racemised by baryta, thus being unlike other nitrogenous glucosides. The equation $C_{16}H_{23}O_8N + H_2O = C_6H_{12}O_6 + C_{10}H_{13}O_3N$ is provisionally proposed to represent the hydrolysis effected by emulsin.

Neither the shell of the seed nor the pulp of the fruit contains any glucoside hydrolysed by emulsin. E. H.

Preparation of a Derivative of Gallocyanin. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 198508).—*m*-Chloro-*p*-nitrosodiethylaniline, m. p. $76-77^{\circ}$, a green base, dissolves in alcohol to a yellow solution; its hydrochloride, when condensed with gallaminic acid, gives rise to a gallocyanin derivative analogous to cœlestine-blue, but of a greener shade. G. T. M.

Salts of Guanidine, Dicyanodiamide, and Melamine with Acid Dyes. LEOPOLD RADLBERGER (*Monatsh.*, 1908, 29, 937—950. Compare Suida, Abstr., 1907, ii, 112).—Guanidine, dicyanodiamide, and melamine behave as monoacidic bases towards the following acid dyes: crystal-ponceau, $C_{20}H_{14}O_7N_2S_2$; ponceau 2G, $C_{16}H_{12}O_7N_2S_2$; chromotrope 2R, $C_{16}H_{12}O_8N_2S_2$; orange IV, $C_{18}H_{15}O_3N_3S$, and orange II, $C_{16}H_{12}O_4N_2S$. The salts formed are analogous to ammonium salts, and are obtained, as a rule, in a crystalline form. The following salts were prepared: guanidine with crystal-ponceau, $C_{22}H_{24}O_7N_3S_2 \cdot H_2O$, small, reddish-brown needles; with ponceau 2G, $C_{18}H_{20}O_7N_3S_2$, red powder; with chromotrope 2R, $C_{18}H_{22}O_8N_3S_2$, small, short, brown needles; with orange II, $C_{17}H_{17}O_4N_3S$, yellowish-orange leaflets; with orange IV, $C_{19}H_{20}O_3N_3S$, yellow, monoclinic leaflets.

Dicyanodiamide with crystal-ponceau, $C_{24}H_{22}O_7N_{10}S_2 \cdot 2H_2O$, small, brownish-red needles; with ponceau 2G, $C_{20}H_{20}O_7N_{10}S_2$, red powder; with chromotrope 2R, $C_{20}H_{20}O_8N_{10}S_2$, brown powder; with orange

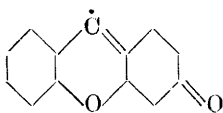
II, $C_{18}H_{16}O_4N_6S$, orange, irregular leaflets; with orange IV, $C_{20}H_{19}O_3N_7S$, orange-yellow prisms.

Melamine with crystal-ponceau, $C_{26}H_{26}O_7N_{14}S_2$, red, crystalline powder; with orange II, $C_{19}H_{18}O_4N_8S$, small, pale yellow crystals.

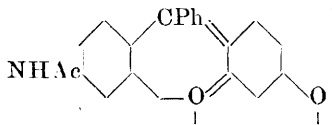
W. H. G.

Carboxonium Dyes. I. The Chromogen of Fluorescein and the Simplest Rosamine. FRIEDRICH KEHRMANN and O. DENGLE (Ber., 1908, 41, 3440—3447).—Following Möhlau and Koch (Abstr., 1895,

i, 46), the authors give the name "fluorone" to the annexed group, but prefer the ortho-quinonoid structure depicted in the annexed formulae.



When *m*-acetylaminophenol and benzotrichloride are heated at 150—160° in the presence of nitrobenzene, several substances are obtained, from which, after somewhat complicated treatment, two acetylated bases are isolated and separated from each other by alcohol. The less soluble one is *acetylaminophenyl-fluorone* (annexed constitution), m. p. above

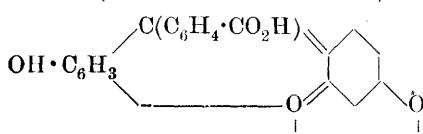


360°, which crystallises in tufts of red needles, is insoluble in alkalis, and gives strongly fluorescent solutions in alcohol, glacial acetic acid, benzene, or warm dilute mineral acids. In concentrated

sulphuric acid it gives a yellow solution with a strong green fluorescence, which remains unchanged by the addition of ice. By hydrolysis by moderately concentrated hydrochloric acid and boiling alcohol, it yields the chloride of the base, which crystallises in red leaflets with a blue reflex. The base, $NH_2 \cdot C_6H_3 \cdot \text{CPh} \cdot O \cdot C_6H_3 \cdot O$, liberated by excess

of ammonium hydroxide, has m. p. 305°, crystallises in dark red needles, forms orange-red salts, and by the elimination of the amino-group yields *phenylfluorone*, m. p. 204°, which forms orange-yellow crystals, is insoluble in alkalis or dilute mineral acids, and gives fluorescent solutions. The substance is the chromogen of fluorescein, and shows a striking analogy to *aposafranone*, *oxazone*, and *thiazone*.

Hydroxyphenylfluorone, obtained by replacing the amino-group of the preceding base by hydroxyl, is identical with Doebner's resorcinolbenzein (Annalen, 1878, 217, 234), and shows a remarkable similarity



in its colour phenomena to fluorescein, which, as its carboxylic acid, must have the annexed constitution (compare R. Meyer and Hoffmeyer, Abstr., 1892, 970.)

The other product isolated from the substances obtained from *m*-acetylaminophenol and benzotrichloride is *diacetylphenorosamine*, the chloride of which, $NHAc \cdot C_6H_3 \cdot \text{CPh} \cdot O \cdot Cl \cdot C_6H_3 \cdot NHAc$, forms a yellow, fluorescent solution in hot water without hydrolysis. By treatment with ammonium hydroxide, the chloride is changed to a magenta-red, unstable colour base, which is spontaneously transformed to a colourless,

stable form, from which dilute acids regenerate yellow salts. By hydrolysis, the simplest rosamine is obtained as a yellowish-red, extremely fluorescent dye. C. S.

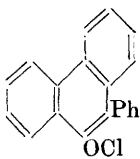
Quinonoid Ester Salts of Fluoran. ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1908, 41, 3434—3440. Compare Abstr., 1906, i, 670; 1907, i, 933).—In support of their ortho-quinonoid formula for the oxonium salts of quinolphthalein derivatives, the authors have prepared similar oxonium salts of the esters of fluoran and of 2:7-dimethylfluoran. The substances are unstable and extremely soluble, and their isolation is only possible in the form of the tin or zinc double chlorides. When hydrogen chloride is passed into hot methyl alcohol containing fluoran and stannic chloride, orange, prismatic crystals of the *stannichloride*, $\left[\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{smallmatrix} \text{OCl} \right]_2 \cdot \text{SnCl}_4$, are obtained on keeping. The corresponding *stannichloride* of the ethyl ester crystallises in large, yellow prisms, containing 1 mol. EtOH. The *stannichloride* of the oxonium chloride of the methyl ester of 2:7-dimethylfluoran contains equal molecular quantities of the oxonium and of the metallic chloride; this appears to depend on the solubility, for zincchlorides containing one or two mols. of the oxonium chloride to one mol. of zinc chloride have been prepared, namely,

$\text{C}_{21}\text{H}_{16}\text{OCl}(\text{CO}_2\text{Me})_2 \cdot \text{ZnCl}_2$
and $[\text{C}_{21}\text{H}_{16}\text{OCl}(\text{CO}_2\text{Me})]_2 \cdot \text{ZnCl}_2$.

2:7-Dichlorofluoran, $\text{C}_{20}\text{H}_{10}\text{O}_3\text{Cl}_2$, m. p. 256—258°, is obtained by condensing phthalic anhydride and *p*-chlorophenol with concentrated sulphuric acid at 150—160°. The halogen atoms are not readily displaced, and the substance, as also the corresponding dinitrofluoran, does not readily esterify under the preceding conditions. C. S.

Dibenzopyryonium. HERMANN DECKER and HEINRICH FELSER (*Ber.*, 1908, 41, 3755—3757. Compare Abstr., 1907, i, 1064).—It has been found possible to prepare derivatives of dibenzopyryonium, the oxygen isologue of phenanthridine.

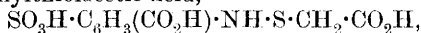
9-Phenyldibenzopyryonium may be obtained by the method of Bünzly and Decker (Abstr., 1904, i, 912), namely, by the action of magnesium phenyl bromide on diphenylmethylolide (compare Graebe and Schestakoff, Abstr., 1895, i, 372). The *carbinol base* is not such a strong base as 9-phenyl-xanthonium carbinol; the *chloride* (annexed formula) dissolves in hydrochloric acid, forming a yellow solution without fluorescence; the *ferrichloride*, $\text{C}_{19}\text{H}_{13}\text{OCl} \cdot \text{FeCl}_3$, crystallises in lemon-yellow leaflets, m. p. 163°. W. H. G.



Preparation of 3-Oxythionaphthen. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 200200).—Methyl *o*-methylthiolbenzoate, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, needles, m. p. 67°, volatile in steam, produced by alkylating *o*-methylthiolbenzoic acid, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 168—169°, or the corresponding sodium, potassium, or calcium methylthiolbenzoate, when heated with sodium and potassium hydroxides (equal mols.) at 200° gives rise to 3-oxythionaphthen;

this condensation takes place even more readily when some sodium or potassium ethoxide is present in the fusion. G. T. M.

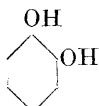
Preparation of a Dihydroxythionaphthencarboxylic Acid. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 200202).—5-Sulphoanthranlylthiolacetic acid,



prepared from 5-sulphoaniline-2-carboxylic acid, yields a mono-potassium salt; this compound when heated with alkali hydroxides, first at 130—140° and then at 160—185°, gives rise to a yellow fusion product, which, when dissolved in water and acidified, furnishes a *dihydroxythionaphthen-2-carboxylic acid*. On boiling with water, this acid yields a dihydroxythionaphthen, needles, m. p. 198°.

G. T. M.

[Preparation of Bases of the Adrenaline Series.] CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 201245).—The



NOH:C:CR:NOH

acid reduction with sodium, potassium, or aluminium amalgams of 3:4-dihydroxyphenylglyoxime and the 3:4-dihydroxyphenylalkylglyoximes of the annexed general formula leads to the production of bases having a very intense hæmostatic action, but which are less toxic than adrenaline. Neither the bases nor their salts have yet been isolated in a pure state.

G. T. M.

Preparation of a Double Compound of Caffeine and Lithium Benzoate. PETER BERGELL (D.R.-P. 199108).—A crystalline double compound, $2\text{C}_8\text{H}_5\cdot\text{CO}_2\text{Li}\cdot\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$, is obtained in needles by evaporating below 50° under reduced pressure an aqueous solution of caffeine and lithium benzoate.

G. T. M.

Solubility of True and False Tannates of Quinine. F. MURARO (*Gazzetta*, 1908, 38, ii, 507—511).—A reply to Biginelli's criticisms (this vol., i, 562) on the author's previous paper (this vol., i 451).

T. H. P.

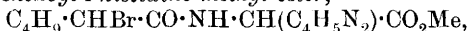
Preparation of α -Bromoisovalerylquinone. KNOLL & Co. (D.R.-P. 200063).—Quinine or its salts, when heated for three hours at 120° with α -bromoisovaleryl chloride or bromide, gives rise to α -bromoisovalerylquinine, an amorphous, yellow substance, dissolving in alcohols and in acids, but less soluble in benzene, toluene, light petroleum, or ether. From acid solution, it is precipitated by potassium mercuri-iodide.

G. T. M.

Synthesis of Polypeptides. XXVII. I. Derivatives of Histidine. EMIL FISCHER and LEE H. CONE (*Annalen*, 1908, 363, 107—117. Compare this vol., i, 773).—So far there has been described only one dipeptide, histidylhistidine, derived from histidine, which itself is widely spread amongst the natural proteins. It was of special interest, therefore, to undertake the synthesis of mixed peptides derived from this amino-acid, especially as these may be expected to occur amongst the degradation products of the proteins,

The combination of *l*-leucine with histidine is described in the present paper. As oxyhæmoglobin contains considerable quantities of *l*-leucine and histidine, which are present probably as a mixed dipeptide, and as *l*-leucyl-*l*-histidine is stable towards concentrated hydrochloric acid, it was hoped to find this dipeptide amongst the products of the action of concentrated hydrochloric acid on oxyhæmoglobin. In this the authors have been unsuccessful, as also, so far, in attempts to prepare the isomeride, *l*-histidyl-*l*-leucine. It is found that histidine hydrochloride is stable towards cold phosphorus pentachloride and acetyl chloride. Experiments with formylhistidine, which is described, are in progress.

d- α -Bromoisohexoyl-*l*-histidine methyl ester,



prepared from *d*- α -bromoisohexoyl chloride and histidine methyl ester (Fischer and Suzuchi, Abstr., 1906, i, 73) in chloroform solution, crystallises from ethyl acetate in strongly refracting, colourless, hexagonal plates, m. p. 175° (corr.), dissolves in dilute mineral acids, and is reprecipitated by sodium carbonate.

d- α -Bromoisohexoyl-*l*-histidine, $\text{C}_{12}\text{H}_{18}\text{O}_3\text{N}_3\text{Br}$, prepared by hydrolysis of the ester with *N*-sodium hydroxide at the laboratory temperature and evaporation of the product after neutralisation with sulphuric acid, separates from water in crystals, m. p. 118° (corr.), has an acid reaction in aqueous solution, and gradually becomes yellow when dissolved in alkalis.

l-Leucyl-*l*-histidine, $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_5\text{N}_2)\cdot\text{CO}_2\text{H}$, is best prepared by the action of 25% aqueous ammonia on the preceding bromo-compound at 25° . It separates from water in prisms or plates containing H_2O , loses H_2O at $100^\circ/15-20$ mm., when anhydrous has m. p. 178° (corr.) (decomp.), has a strong alkaline reaction in aqueous solution, gives a colourless precipitate with mercuric chloride solution and a red coloration with *p*-diazobenzenesulphonic acid, and becomes dark coloured when boiled with dilute bromine water; these reactions show that the iminazole nucleus of the histidine is present unchanged in the dipeptide. The dipeptide is soluble in dilute acids and alkalis; the acid solutions give a heavy precipitate with phosphotungstic acid. The copper salt, $\text{C}_{12}\text{H}_{18}\text{O}_3\text{N}_4\text{Cu}\cdot 4\text{H}_2\text{O}$, formed by boiling the aqueous solution of the dipeptide with precipitated copper oxide, or by adding copper sulphate to the solution of the dipeptide in sodium hydroxide, is obtained in deep violet-blue crystals, which lose $4\text{H}_2\text{O}$, becoming lilac at $100^\circ/15-20$ mm. over phosphoric oxide, and dissolve in alcohol, forming a violet-blue solution. Whilst it is stable towards cold concentrated mineral acid, the dipeptide is hydrolysed completely in twenty-four hours by 20% hydrochloric acid at 100° , yielding *l*-leucine and *l*-histidine.

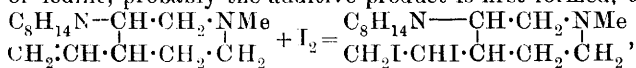
Formyl-*l*-histidine, $\text{C}_7\text{H}_9\text{O}_3\text{N}_3$, formed by heating histidine with anhydrous formic acid on the water-bath and evaporating the solution under 15–20 mm. pressure, crystallises from aqueous-methyl alcohol in slender needles, m. p. 203° (corr.), is readily soluble in water, slightly so in methyl alcohol, but almost insoluble in other organic solvents, has an acid reaction in aqueous solution, and gives a deep red coloration with *p*-diazobenzenesulphonic acid, which points to

the formyl group as having entered into combination with the amino-group of the histidine. G. Y.

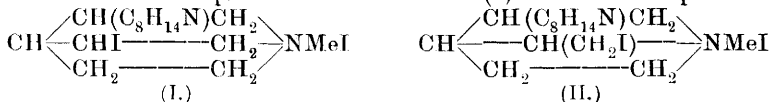
Action of Ozone on Thebaine. J. D. RIEDEL (D.R.-P. 201324).—Thebaine hydrochloride in 10% aqueous solution is treated with ozonised oxygen at the ordinary temperature until the product is soluble in alkali hydroxides. The ethereal extract of the solution, when dried with potassium carbonate and concentrated, furnishes a compound, $C_{19}H_{21}O_5N$, which crystallises in needles or leaflets, m. p. 125—126°. This oxidation product still contains two methyl groups, and loses one of these by alkaline hydrolysis; it has probably the formula $C_{15}H_{15}ON(CO_2Me)(CO) \cdot OMe$. The substance is readily soluble in water, ethyl acetate, and alcohol.

G. T. M.

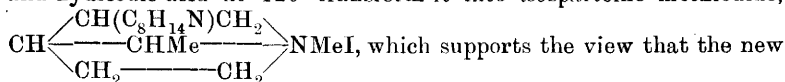
Sparteine. New Method of Ring-formation of α -Methylsparteine by the Action of Iodine. AMAND VALEUR (*Compt. rend.*, 1908, 147, 864—867).—Although the α -methylsparteine obtained by Moureu and Valeur (this vol., i, 44) by heating methylsparteinium hydroxide is certainly an unsaturated base, since it reduces a cold sulphuric acid solution of potassium permanganate, it is not reduced by sodium and ethyl or amyl alcohol, or by tin and hydrochloric acid. It combines with iodine, however, forming *di-iodo- α -methylsparteine*, $C_{15}H_{25}N_2MeI_2$, m. p. 177—178°, which does not behave as a simple additive product, has a very feebly alkaline reaction, and when treated in aqueous solution with freshly prepared silver oxide gives a strongly alkaline liquid, from which the di-iodide is re-formed by addition of potassium iodide. The latter observation indicates that the new compound is a quaternary ammonium iodide, and therefore must be the methiodide of an iodo-base. In the action of iodine, probably the additive product is first formed, thus:



from which iodosparteine methiodide (I) or iodoisosparteine



methiodide (II) can be formed according to which iodine atom wanders to the nitrogen. Whilst zinc and water or zinc and acetic acid reduce the di-iodide, giving α -methylsparteine only, phosphorus and hydriodic acid at 120° transform it into isosparteine methiodide,



which supports the view that the new di-iodide should be represented by formula (II). It is possible, however, that the isosparteine methiodide is formed by isomeric change from the α -methylsparteine under the influence of hydrogen iodide. These results confirm the analogy which exists between the two bases dimethylpiperidine and α -methylsparteine (compare Willstätter, *Abstr.*, 1900, i, 249; Valeur, this vol., i, 736).

E. H.

Iodine Derivatives of Strychnine and Brucine. JÓZEF BURACZEWSKI and TAD. KOŹNIEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 644—649).—By the addition of a somewhat concentrated solution of iodine in carbon disulphide to a hot alcoholic solution of strychnine or brucine, di-iodo-derivatives are precipitated, from which the alkaloids are regenerated by alcoholic alkalis; it is not yet determined whether the compounds are produced by addition or by substitution.

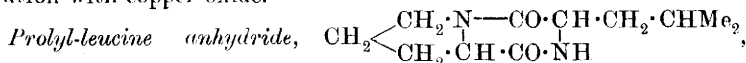
The *strychnine* derivative, $C_{21}H_{22}O_2N_2I_2$ or $C_{21}H_{20}O_2N_2I_2$, m. p. 196—197°, forms red crystals; after prolonged boiling with alcohol, the solution deposits ruby-red crystals of a *substance*, $C_{21}H_{23}O_2N_2I_3$, m. p. 253—254°, which seems to be identical with Jørgensen's periodide (*J. pr. Chem.*, 1870, [i], 2, 434). The *brucine* derivative, $C_{23}H_{26}O_4N_2I_2$ or $C_{23}H_{24}O_4N_2I_2$, m. p. 222·5°, is converted, after prolonged boiling with alcohol, into a ruby-red, crystalline substance, m. p. 251—252°. C. S.

A New Base from Putrefying Pancreas. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1908, 57, 28—29).—A new base, *viridinine*, $C_8H_{12}O_8N_2$, has been isolated from ox pancreas which had been allowed to undergo decomposition by exposure to the atmosphere during two months. It may be extracted by Kutscher's method, and is found in the same fraction as δ -aminovaleric acid, but may be separated from this by means of the slight solubility of its aurichloride or platinichloride. The *hydrochloride* forms glistening, green needles, only moderately soluble in cold water, and when heated produces yellow vapours with an aromatic odour. The *aurichloride*, $C_8H_{12}O_8N_2 \cdot HAuCl_4$, forms glistening, blackish-green or blackish-yellow plates, or, after recrystallisation, brownish-black needles, m. p. 176° (decomp.). The *platinichloride*, $(C_8H_{12}O_8N_2)_2 \cdot H_2PtCl_6$, has an intense yellow colour, and has m. p. 212—216° (decomp.). J. J. S.

Synthesis of Polypeptides. XXVII. 2. Derivatives of Proline. [Pyrrolidine-2-carboxylic Acid]. EMIL FISCHER and GEORG REIF (*Annalen*, 1908, 363, 118—135).—Leven and Beatty isolated from the product of the tryptic digestion of gelatin a prolyl-glycine anhydride which, on hydrolysis, yields glycine and optically active proline (Abstr., 1906, i, 718). As other similar substances may be formed by the decomposition of proteins, it was thought of interest to study the synthesis of polypeptides derived from active proline.

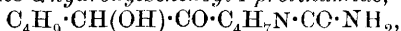
l-Proline, prepared from gelatin, is best purified by conversion into the *copper* salt, $C_{10}H_{16}O_4N_2Cu$, which crystallises from alcohol in dark blue, rhombic prisms, and when treated with hydrogen sulphide in hot aqueous solution yields proline, $[\alpha]_D^{20} - 76\cdot7^\circ$. When treated with acetyl chloride, cooled by ice, and then with phosphorus pentachloride, *l*-proline forms *l*-prolyl chloride hydrochloride, $C_4H_8N \cdot COCl, HCl$. This, when treated with glycine ethyl ester in chloroform solution at -10° , and then, after removal of the chloroform and excess of glycine ester, with dilute sodium ethoxide, yields prolyl-glycine anhydride and a brown oil. The anhydride, on extraction with boiling ethyl acetate or acetone, is obtained in microscopic leaflets, m. p. 213° (182—183° : Levene and Beatty, *loc. cit.*), $[\alpha]_D^{20} - 216\cdot2^\circ$ to $-217\cdot4^\circ$, has a bitter

taste, and does not give a blue coloration when boiled in aqueous solution with copper oxide.



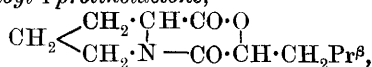
prepared in the same manner from *l*-prolyl chloride hydrochloride and *l*-leucine ethyl ester, crystallises from water in microscopic leaflets, m. p. 160° (corr.), $[\alpha]_D^{20} - 142.6^\circ$ to -143.4° . When boiled with 20% hydrochloric acid, the anhydride yields proline, $[\alpha]_D^{20} - 56.9^\circ$, and leucine, $[\alpha]_D^{20} + 10.1^\circ$; hence racemisation must have taken place to the extent of one-third of the substance during the hydrolysis.

d-*a*-Bromoisohexoyl-*l*-proline, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO} \cdot \text{C}_4\text{H}_7\text{N} \cdot \text{CO}_2\text{H}$, formed by the action of *d*-bromoisohexoyl chloride and sodium hydroxide on *l*-proline, separates from acetone in crystals, m. p. 158° (corr.) (decomp.). When treated with concentrated aqueous ammonia at 25°, it is converted into *α*-hydroxyisohexoyl-*l*-prolinamide,



which is formed also by the action of liquid ammonia on bromoisohexoylproline. It crystallises from water in prisms, m. p. 123—124° (corr.), evolves ammonia at about 140°, $[\alpha]_D^{20} - 78.3^\circ$ to -78.6° , and yields ammonia when boiled with sodium hydroxide.

α-Hydroxyisohexoyl-*l*-prolinolactone,



formed when the amide is heated at 140—145°, or when *d*-*a*-bromoisohexoyl-*l*-proline is treated with sodium hydroxide at the ordinary temperature, and, after twenty-four hours, is neutralised with hydrochloric acid and evaporated, crystallises from water in thin needles, m. p. 164° (corr.), $[\alpha]_D^{20} - 166.8^\circ$, has a slightly bitter taste, and behaves towards alkalis and acids in the ordinary manner of the lactones.

The substance described previously (Abstr., 1904, i, 917) as *i*-leucylproline is now found to be *i*-hydroxyisohexoyl prolinamide; on hydrolysis with acids, it yields ammonia, *dl*-*α*-hydroxyisohexoic acid, and *dl*-proline. The anhydride, previously termed leucylproline anhydride (*loc. cit.*), is *i*-hydroxyisohexoylproline anhydride; it has m. p. 124° (corr.). G. Y.

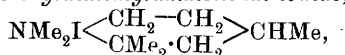
New Isomerides of Coniine and other Hydrogenated Bases.

IGILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1908, 43, 1095—1099. Compare following abstract).—No isomeride of coniine or other alkyl derivative of piperidine is known in which two alkyl groups are united to one and the same carbon atom. Such a derivative, namely, 2:2:4-trimethylpiperidine, should be obtainable from 5-cyano-2:2:4-trimethyldihydro-6-pyridone (compare Abstr., 1894, i, 484) by reduction with sodium and alcohol, whilst cyano-1-methylpyridones should yield the corresponding 1-methylpiperidines, 5-cyano-2:3:4-trimethyl-6-pyridone, and 2:3:4-trimethylpiperidine. In the last case, profound reduction by means of zinc dust gives 2:3:4-trimethylpyridine (compare Abstr., 1900, i, 558). Reduction of 3:5-dicyano-2:6-diketo-4-methyl-4-ethylhexahydropyridine should also give an isomeride of coniine, 4-methyl-4-ethylpiperidine, T. H. P.

New Isomeride of Coniine from 5-Cyano-2:2:4-trimethyl-dihydro-6-pyridone. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1908, 43, 1100—1121. Compare preceding abstract).—The author has investigated the products of reduction of 5-cyano-2:2:4-trimethyl-dihydro-6-pyridone (compare Guareschi, *Abstr.*, 1893, i, 484) by means of (1) sodium and ethyl alcohol, and (2) sodium and amyl alcohol. The first method of reduction yields 2:2:4-trimethylpiperidine and 5-cyano-2:2:4-trimethylpiperidine (?) in small quantities, whilst the use of amyl alcohol leads to the formation of (1) 2:2:4-trimethylpiperidine, (2) a hexamethyldipiperidine, as the result of the condensing action of the excess of sodium on the preceding compound, and (3) 2:2:4-trimethylnipecotinic acid, derived from the complete hydrogenation of the pyridone and the hydrolysis of the cyanogen residue. The normal reduction of the cyanogen group to $\cdot\text{CH}_2\cdot\text{NH}_2$ by means of sodium and alcohol is not observed in this case.

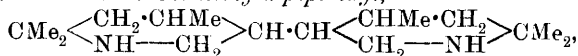
5-Cyano-2:2:4-trimethylpiperidine (?), $\text{NH} \begin{smallmatrix} \text{CH}_2\cdot\text{CH}(\text{CN}) \\ \text{CMe}_2-\text{CH}_2 \end{smallmatrix} \text{CHMe}$, crystallises from water in mammillary masses, m. p. 155° .

2:2:4-Trimethylpiperidine, $\text{NH} \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CMe}_2\cdot\text{CH}_2 \end{smallmatrix} \text{CHMe}$, is a mobile liquid, b. p. 148° , D^{15}_4 0.832, has an intense alkaline reaction, and forms white fumes with hydrogen chloride; with copper sulphate it gives a blue precipitate, soluble in excess of reagent, and with Nessler's reagent, a white precipitate. The aqueous solution of its hydrochloride gives precipitates with the ordinary alkaloidal reagents. The *platinichloride*, $(\text{C}_8\text{H}_{17}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, forms orange-red, mammillary masses, m. p. $215-216^\circ$ (decomp.). The *aurichloride*, $\text{C}_8\text{H}_{17}\text{N}\cdot\text{HAuCl}_4$, crystallises in yellow prisms, m. p. 135° . With methyl iodide, it gives 2:2:4-trimethylpiperidyltrimethylammonium iodide,

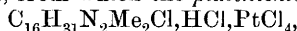


which separates from a mixture of alcohol and ether as a white, crystalline powder, m. p. 266° (decomp.).

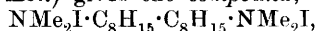
2:2:4:2':2':4'-Hexamethyldipiperidyl,



b. p. $266-267^\circ/745$ mm. and $237^\circ/40$ mm., D^{15}_4 0.869, has an odour resembling that of nicotine, and exhibits intense alkaline properties. Its *platinichloride*, $\text{C}_{16}\text{H}_{32}\text{N}_2\cdot\text{H}_2\text{PtCl}_6\cdot 3\text{H}_2\text{O}$, forms orange-yellow laminae, m. p. 262° (decomp.); its *picrate*, pale yellow needles, m. p. 230° ; its *aurichloride*, $\text{C}_{16}\text{H}_{32}\text{N}_2\cdot 2\text{HAuCl}_4$, separates as a yellow powder, which changes gradually into laminae, m. p. $183-184^\circ$; its *mercurichloride*, $\text{C}_{16}\text{H}_{32}\text{N}_2\cdot 2\text{HgCl}_2$, forms short, colourless prisms, m. p. 270° (decomp.). When heated in a sealed tube with methyl iodide (2 mols.), the base (1 mol.) forms the compound, $\text{C}_8\text{H}_{16}\text{N}\cdot\text{C}_8\text{H}_{15}\text{NMe}_2\text{I}$, which is obtained as a dense oil, and, when evaporated with hydrochloric acid, gives a syrupy residue, from which the *platinichloride*,

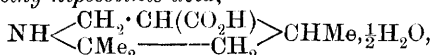


m. p. 214° , is obtained. With 4 mols. of methyl iodide in methyl alcohol, the base (1 mol.) gives the compound,



which crystallises from methyl alcohol in monoclinic laminæ, m. p. 236—237°; the action of moist silver oxide gives the corresponding hydroxide, which is an energetic base, and in presence of hydrochloric acid gives the *platinichloride*, $C_{16}H_{30}N_2Me_4Cl_2 \cdot PtCl_4$, m. p. 227—228°.

2 : 2 : 4-*Trimethylnipecotinic acid*,



crystallises from alcohol in groups of hard, white prisms, m. p. 123° (efferves.). T. H. P.

Preparation of Basic Compounds from Methyl Ethyl Ketone. WILHELM TRAUBE (D.R.-P. 200203).—Acetone absorbs much more ammonia than its homologues, giving rise to diacetoneamine, and in smaller proportion, triacetoneamine; but by saturating an alcoholic solution of methyl ethyl ketone, a basic condensation product, $C_{12}H_{23}ON$, may be obtained, having probably the constitution $NH \begin{array}{c} \text{CMeEt} \cdot \text{CHMe} \\ \text{CMeEt} \text{-----} \text{CH}_2 \end{array} \text{CO}$. In accordance with this view of its structure, the compound is called either 2 : 3 : 6-*trimethyl-2 : 6-diethyl-4-piperidone* or *trimethyldiethylketoneamine*. It is a yellow oil, b. p. 247°/740 mm. and 157—159°/30 mm.; hydrochloride, m. p. 128°; *sulphate*, decomposes at 188°; *nitrate*, m. p. 169—172°; *hydrogen oxalate*, m. p. 183°. Another basic product, b. p. 104°/30 mm., is also formed in this condensation, and is separated from the preceding compound by means of its more soluble oxalate. G. T. M.

Preparation of Anthracene Derivatives containing Nitrogen. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 199713).—It was shown previously (compare this vol., i, 699) that the acetyl derivatives of the secondary α -aminoanthraquinones, when condensed with the aid of alkalis, gave rise to products of the pyridone series. Similarly, sulphonated pyridones are obtained from the sulphonic acids of acetyl- α -methylaminoanthraquinone. G. T. M.

Preparation of Phenoxazines. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 200736).—The substituted nitrohydroxydiphenylamines having the constitution :



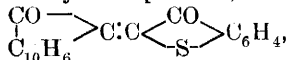
readily give rise to phenoxazines; this reaction, however, does not take place in the absence of a substituent in position 6, denoted by X.

5-*Nitrophenoxazine*, reddish-violet needles, m. p. 165°, was obtained from 2 : 6-dinitro-2'-hydroxydiphenylamine by warming with 5% aqueous sodium hydroxide. The patent contains a description of six phenoxazine-carboxylic and -sulphonic acids derived from carboxy- and sulpho nitro-2-hydroxy-diphenylamines. G. T. M.

Some Unsymmetrical Analogues of Indigotin. ARMIN GROB (*Ber.*, 1908, 41, 3331—3334).—The two dyes referred to below have been recently described by Bezdrík and Friedländer (this vol., i, 674), but the author claims priority, as a patent for their preparation had been applied for by the Basler Chemische Fabrik in January—June, 1907.

8-Oxy-7-indoxylacenaphthene, $\begin{array}{c} \text{CO} - \\ | \\ \text{C}_{10}\text{H}_6 \end{array} > \text{C} : \text{C} < \begin{array}{c} \text{CO} \\ | \\ \text{NH} \end{array} > \text{C}_6\text{H}_4$, gives an additive product with bromine, from which hydrogen bromide is expelled on heating, leaving a violet bromine-substituted dye. The solution of the leuco-compound of 8-oxy-7-indoxylacenaphthene is violet.

8-Oxy-7-oxythionaphthenylacenaphthene,

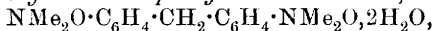


may be prepared by condensing *o*-carboxyphenylthioglycolic acid with acenaphthenequinone in acetic anhydride solution. It gives a bromine additive compound, and the solution of its leuco-compound is reddish-violet. J. C. C.

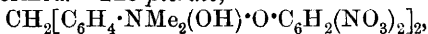
Amino-oxides of Leuco-bases of the Di- and Tri-phenylmethane Series. EUGEN BAMBERGER and LEO RUDOLF (*Ber.*, 1908, 41, 3290—3315).—The authors have investigated the action of hydrogen peroxide and of Caro's acid on tetramethyldiaminodiphenylmethane, tetramethyldiaminotriphenylmethane, and hexamethyltriaminotriphenylmethane, and find that oxides are formed analogous to those obtained from dimethylaniline, etc., thus: $\text{R} \cdot \text{NMe}_2$.



4 : 4'-Tetramethyldiaminodiphenylmethane dioxide,



is most conveniently prepared by the use of Caro's acid. It forms hard, colourless, glistening needles, m. p. 147°. When heated, it evolves vapours of formaldehyde. The aqueous solution has a faint alkaline reaction, and does not reduce Fehling's solution or oxidise potassium iodide. When exposed for three months over concentrated sulphuric acid at 12—15 mm. pressure, the anhydrous compound, m. p. 156°, is formed. The *picrate*,

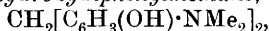


long, pale yellow needles, darkening at 130°, sintering at 145°, m. p. 150·5—151° (decomp.); *hydrochloride*,



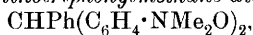
colourless, glistening needles, turning brown at 150°, m. p. 165·5—166° (decomp.); *platinichloride*, *aurichloride*, and *hydrogen ferrocyanide* are described. On reduction, the hydrochloride yields tetramethyldiaminodiphenylmethane, and when iron is used, traces of tetramethyldiaminobenzhydrol and tetramethyldiaminobenzophenone appear to be formed. With nitrous acid, the hydrochloride gives 3 : 3'-dinitrotetramethyldiaminodiphenylmethane, and when the dioxide is treated with sulphur dioxide, *tetramethyldiaminodiphenylmethane-3 : 3'-disulphonic acid* is produced.

By treating the dioxide with acetic anhydride and sulphuric acid, the substance undergoes intramolecular change, partly into *tetramethyldiamino-3:3'-dihydroxydiphenylmethane*,



colourless, hard, glassy prisms, m. p. 114.5—115°, and partly, with simultaneous formation of tetramethyldiaminodiphenylmethane, into *tetramethyldiamino-3-hydroxydiphenylmethane*, white, silky needles, m. p. 111—111.5°.

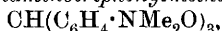
4:4'-*Tetramethyldiaminotriphenylmethane dioxide*,



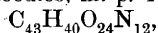
crystallises with 2H₂O (analysis by Rudolf) or 4H₂O (analysis by Reber), forming white, glistening needles, m. p. 131.5—132.5°. Its properties resemble those of the diphenylmethane derivative. The anhydrous substance has m. p. 188—189° (decomp.). The *picrate*, C₃₅H₃₂O₁₆N₈, *platinichloride*, and *hydrogen ferrocyanide* are described. On reduction, the dioxide yields leuco-malachite-green, and, when iron is used, also probably some tetramethyldiaminotriphenylcarbinol.

By the action of nitrous acid, an orange-yellow, uncrystallisable powder is formed, which is probably 3:3'-*dinitrotetramethyldiaminotriphenylmethane*, CHPh[C₆H₃(NO₂)·NMe₂]₂; on reduction, this yields 3:3'-*diaminotetramethyldiaminotriphenylmethane*, pale brown, amorphous flakes; the *platinichloride*, C₂₃H₂₆N₄·H₂PtCl₆, was prepared. By the action of acetic anhydride and sulphuric acid, the dioxide is converted into 4:4'-*tetramethyldiamino-3:3'-dihydroxytriphenylmethane*, colourless needles, m. p. 183—184°.

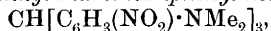
4:4':4''-*Hexamethyltriaminotriphenylmethane trioxide*,



forms hair-like, colourless needles, m. p. 176°; the *picrate*,



and *platinichloride* are described. On reduction, it yields leuco-crystal-violet, and by the action of nitrous acid it gives 3:3':3''-*trinitro-4:4':4''-hexamethyltriaminotriphenylmethane*,



orange-yellow flakes, which, on reduction, furnishes 3:3':3''-*triamino-4:4':4''-hexamethyltriaminotriphenylmethane*, white needles, m. p. 221.5—223.5°; the *platinichloride* is described.

By the action of acetic anhydride and sulphuric acid, the trioxide is converted into leuco-crystal-violet and 4:4':4''-*hexamethyltriamino-3:3':3''-trihydroxytriphenylmethane*, a pale bluish-green powder.

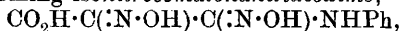
J. C. C.

Negative Substituted Amino-oximes. II. Phenylnitro-ethenylamino-oxime. WILHELM STEINKOPF and CZESLAU BENEDEK (*Ber.*, 1908, 41, 3566—3568. Compare Steinkopf and Bohrmann, *Abstr.*, 1907, i, 480; this vol., i, 327).—It has been shown previously that the ease with which the halogenated and nitro-substituted ethenylamino-oximes are formed, and their comparative stability towards water, results from the negative influence of the substituting groups. It was of interest, therefore, to study the influence of a phenyl-substituting group, which is negative like the

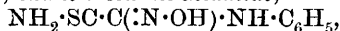
halogens and nitro-group, but occupies a greater volume. It is now found that, whilst phenylnitroethenylamino-oxime is readily formed, it is unstable, and decomposes in a closed vessel in the course of a few days, or more slowly in an open vessel. Hydroxylamine can be detected in the cold aqueous solution of the amino-oxime.

Phenylnitroethenylamino-oxime, $\text{NO}_2\cdot\text{CHPh}\cdot\text{C}(\text{NOH})\cdot\text{NH}_2$, prepared by the action of hydroxylamine hydrochloride on a concentrated aqueous solution of sodium *aci*-phenylnitroacetoneitrile at the laboratory temperature, forms white crystals, m. p. 125° , reduces mercuric chloride in cold alkaline solution, gives a violet coloration with ferric chloride, and forms a *hydrochloride*, which separates in white crystals, m. p. 153° . The amino-oxime acts as a dibasic acid, forming two series of salts. The *copper*, $\text{C}_8\text{H}_7\text{O}_3\text{N}_3\text{Cu}$, and *barium*, $(\text{C}_8\text{H}_8\text{O}_3\text{N}_3)_2\text{Ba}$, salts were analysed. G. Y.

Indigotin Group. HEINRICH WIELAND and ERWIN GMELIN (*Ber.*, 1908, 41, 3512—3517. Compare Wieland and Semper, this vol., i, 108).—The ethyl glyoximeperoxidedicarboxylate discovered by Pröpper (*Annalen*, 1884, 222, 46) is converted by barium hydroxide into barium furoxandicarboxylate. This salt reacts with aniline hydrochloride, forming *isonitrosomalonanilideoxime*,



and this when warmed with acetic anhydride is converted into *cyano-N-acetylformanilideoxime*, $\text{CN}\cdot\text{C}(\text{:N}\cdot\text{OH})\cdot\text{NAcPh}$. On warming with ammonium sulphide, *oxanilideoxime-thiamide*,



is formed, which, on warming with concentrated sulphuric acid, gives α -isatoxime, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ < \text{NH} \end{smallmatrix} > \text{C}\cdot\text{N}\cdot\text{OH}$.

Ethyl furoxandicarboxylate is hydrolysed with baryta and heated at $30\text{--}40^\circ$ with concentrated aqueous aniline hydrochloride. The *aniline* salt of *isonitrosomalonanilideoxime* separates in yellow crystals, m. p. 133° ; the corresponding acid obtained by hydrolysis with hydrogen chloride forms colourless plates, m. p. $165\text{--}166^\circ$ (decomp.); it gives a blackish-green coloration with ferric chloride. The *barium* salt is light yellow; the *sodium hydrogen* salt, colourless. *Cyano-N-acetylformanilideoxime* crystallises in large, colourless prisms, m. p. 135° ; it does not give a coloration with ferric chloride. *Oxanilideoxime-thiamide* forms bright yellow crystals, m. p. $169\text{--}171^\circ$, and shows the characteristic dark green ferric chloride reaction. It is added in portions to sulphuric acid, maintained at 60° , and the temperature is gradually raised until sulphur dioxide fumes are evolved, when the solution is poured on to ice, neutralised, and the α -isatoxime extracted with ethyl acetate. E. F. A.

Hydrazones of Sugars. A. RECLAIRE (*Ber.*, 1908, 41, 3665—3671).—The *o*-, *m*-, and *p*-nitrophenylhydrazones of various sugars have been prepared in aqueous-alcoholic or in acetic acid solution. Many of them have already been described by Alberda van Ekenstein and

Blanksma (Abstr., 1904, i, 98). The following new compounds are mentioned: Dextrose forms a *m*-nitrophenylhydrazone, m. p. 115—116°, *m*-nitrophenyllosazone, m. p. 228°, *o*-nitrophenylhydrazone, m. p. 148°, and *o*-nitrophenyllosazone, m. p. 215—217°. Mannose forms a *m*-nitrophenylhydrazone, m. p. 162—163°, an impure *m*-nitrophenyllosazone, m. p. 214° (decomp.), and an *o*-nitrophenylhydrazone, m. p. 173°. Lævulose forms an *o*-nitrophenylhydrazone, m. p. 155—156°. Galactose forms a *m*-nitrophenylhydrazone, m. p. 181—182°, and an *o*-nitrophenylhydrazone, m. p. 172. Arabinose forms a *m*- and an *o*-nitrophenylhydrazone, m. p. 179—180° and 180° respectively. Xylose forms a *m*-nitrophenylhydrazone, m. p. 130° (decomp. at 120°). Rhamnose forms a *m*- and an *o*-nitrophenylhydrazone, m. p. 104—105° and 151° respectively. C. S.

Action of Secondary *as*-Hydrazines on Carbamide. Hugo MILRATH (*Monatsh.*, 1908, 29, 909—935).—Most of the matter in this communication has already been abstracted (this vol., i, 581). Phenylbenzylsemicarbazide, when heated with acetic anhydride, yields *diacetyl-as-phenylbenzylhydrazine*, $C_{17}H_{18}O_2N_2$, m. p. 128° (compare Milrath, *loc. cit.*), which may also be prepared directly from *as*-phenylbenzylhydrazine.

Diphenyldimethylsemicarbazide may be prepared by heating carbamide (1 mol.) with *as*-phenylmethylhydrazine (2 mols.) at 170—180°.

The substance, m. p. 167—168°, described previously (*loc. cit.*), is now shown to be 1-benzylbenzopyrazolone, $C_6H_4 \begin{smallmatrix} \text{N}(\text{CH}_2\text{Ph}) \\ \text{CO} \end{smallmatrix} \text{NH}$.

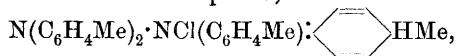
It may also be prepared by acting on benzopyrazolone (anhydro-*o*-hydrazinobenzoic acid: Fischer and Renouf, Abstr., 1882, 1068) with benzyl chloride and sodium methoxide. The white, crystalline *hydrochloride*, $C_{14}H_{12}ON_2 \cdot HCl$, yellow, crystalline *platinichloride*, m. p. 134—138° (decomp.), and *picrate*, $C_{14}H_{12}ON_2 \cdot C_6H_3O_7N_3$, large, dark yellow plates, m. p. 154—155° (decomp.), were prepared. 1-Benzylbenzopyrazolone in alkaline solution is converted by methyl sulphate into 1-benzyl-2-methylbenzopyrazolone, $C_6H_4 \begin{smallmatrix} \text{N}(\text{CH}_2\text{Ph}) \\ \text{CO} \end{smallmatrix} \text{NMe}$, which crystallises with $1H_2O$ in long, slender, silky, white needles, softens at 65°, and has m. p. 75—80°.

1-Methylbenzopyrazolone, $C_6H_4 \begin{smallmatrix} \text{NMe} \\ \text{CO} \end{smallmatrix} \text{NH}$, obtained by heating carbamide (1 mol.) with *as*-phenylmethylhydrazine at 170—180°, and finally at 270—280°, has m. p. 153—154°. W. H. G.

Decomposition of Tetra-arylhydrazines. IV. HEINRICH WIELAND (*Ber.*, 1908, 41, 3478—3498. Compare Abstr., 1907, i, 1076).—Aromatic hydrazines are decomposed by various acid reagents in accordance with the equation: $Ar_2N \cdot NAr_2 + HR \rightarrow Ar_2NH + RNaAr_2$. Diarylamines and a molecule comprising the acid residue R result. In the case of hydrogen chloride, the hypothetical product will be a diarylamine containing chlorine attached to nitrogen, $NaAr_2Cl$. Such secondary aromatic chloroamines are not known, and attempts to

synthesise them have only yielded hydrazines, $\text{Ar}_2\text{N}\cdot\text{NAr}_2$, or compounds substituted in the nucleus. On decomposition of tetraphenylhydrazine, two molecules of chloroamine unite, with elimination of hydrogen chloride, in the para-position, $\text{C}_6\text{H}_5\cdot\text{NCl}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}_2$. This primary product undergoes rearrangement to *p*-chloroanilinetriphenylamine, $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}_2$ (Gambarjan, following abstract).

In the case of tetra-*p*-tolylhydrazine, two molecules of the chloroamine unite in the ortho-position, two mols. of hydrogen chloride being eliminated, and a completely substituted phenazine ring compound is obtained. In addition, chlorinated phenazine compounds containing two halogen atoms in the nucleus are formed, due to the oxidising action of the chloroamine. The first product of the decomposition is the violet quinonoid additive compound,



already described (Abstr., 1907, i, 1076).

Other acids act similarly to hydrogen chloride, and the primary products of the type $\text{NAr}_2\cdot\text{OR}$ are to be regarded as derivatives of the hypothetical diphenylhydroxylamine, $\text{NPh}_2\cdot\text{OH}$.

Tetra-anisylhydrazine is not obtained on oxidation of *p*-dianisylamine, but a ditertiary azine is formed by elimination of water from two molecules of the unstable hydroxylamine.

The ditertiary phenazine derivatives, conveniently termed "perazines," are stable towards oxidising agents. They form coloured salts with mineral acids, carboxylic acids, or phenols in anhydrous solvents, which are, as a rule, mono-acid, and are regarded as quaternary quinolimonium compounds. On oxidation, a series of salts of other colours are obtained, which possibly represent the *o*-quinonoidbisphenazonium series.

By the action of hydrogen chloride in ether on tetratolylhydrazine in chloroform solution, the violet solution of the quinolimonium salt is first obtained, which changes subsequently to red, and deposits glistening, dark green, flat needles of *dichloroditolyltolazonium hydrochloride*. Alkalis decompose this into *dichloroditolylldihydrotolazine*, which is obtained from xylene in lustrous, garnet-red, four-sided prisms. It is very stable, and begins to decompose above 360° . With bromine, it forms a dark violet additive product containing one mol. of bromine. By reduction with sodium and amyl alcohol, *p*-ditolylldihydrotolazine, $\text{C}_6\text{H}_3\text{Me}\langle\text{N}(\text{C}_6\text{H}_4\text{Me})\rangle\text{C}_6\text{H}_3\text{Me}$, is quantitatively formed, crystallising in long, orange-yellow, glistening needles, m. p. 269° ; it can be distilled without decomposition. Both ditolylldihydrotolazine and its dichloro-derivative are formed by the action of hydrogen chloride on tetratolylhydrazine, but the latter is the main product.

Ditolylldihydrotolazine itself does not exhibit the properties of a base, and can be heated with aqueous acids without forming salts. With alcoholic or ethereal acid solutions, it forms dark green azonium salts, of which the *hydrochloride* is particularly characteristic; it separates in dark green, glistening, broad needles. The normal salt contains one molecule of acid, but there is a tendency to form an acid

salt. The *nitrate* forms minute, dark green needles, decomp. 236° . Decomposition of the salts with sodium hydroxide leads to the formation of basic by-products; alcoholic potassium hydroxide or zinc dust afford better means of effecting the decomposition.

Acetic acid acts very readily on tetratolylhydrazine; the solution becomes at first dark violet, owing to the formation of the quinonoid hydrazonium acetate, and then dark green, owing to conversion into tolazonium acetate. On adding water, *p*-ditolylamine separates, and ditolylidihydrotolazine may be obtained from the mother liquors.

Phosphoryl chloride or phosphorus trichloride and benzoyl chloride do not react with tetratolylhydrazine in the absence of water. When moisture is present, large, dark green crystals are obtained; their formation is due to the hydrogen chloride slowly liberated by the chlorides, which gives rise to dichlorotolazonium chloride and phosphate.

p-Dianisylamine, $(\text{OMe} \cdot \text{C}_6\text{H}_4)_2\text{NH}$, prepared by Goldberg's method (this vol., i, 17), does not yield tetra-anisylhydrazine on oxidation, but an *azine*, $\text{C}_{28}\text{H}_{26}\text{O}_4\text{N}_2$, crystallising in stellar aggregates of bright yellow needles, m. p. 290° . The *anisazonium* salts are similar to the tolylazonium compounds; the *hydrochloride* forms green, glistening needles; the *nitrate* is obtained as a wine-red precipitate, m. p. 223° (decomp.). The *ferrichloride* separates in bronze, glistening, violet-red plates; the *chromate* forms dark red needles; the *platinichloride* is insoluble in water, and likewise the *ferro*- and *ferri-cyanides*, of which the former yields a rose-red, the latter a brownish-red, precipitate.

Wool is quickly dyed by anisazonium salts in fast, scarlet-red shades. Anisazonium chloride is dissolved by pyridine without change, but gives an intense sea-blue coloration with aniline. Oxidising agents convert the anisazonium salts into green compounds, which are unstable, and pass slowly in solution into carmine substances. The new perazonium salts have characteristic absorption bands in their spectra.

E. F. A.

Decomposition of Tetraphenylhydrazine with Hydrogen Chloride. STEFAN GAMBARJAN (*Ber.*, 1908, 41, 3507--3512).—In a previous paper (Wieland and Gambarjan, *Abstr.*, 1906, i, 453) it was stated that tetraphenylhydrazine, when treated with hydrogen chloride in anhydrous ethereal solution, formed diphenylamine hydrochloride and *p*-chlorodiphenylamine. It is now found that the latter compound is not produced, but that a secondary base, *p*-chloroanilinotriphenylamine, is formed. The constitution of this has been established by elimination of the chlorine by means of sodium and the identification of the product with *anilinotriphenylamine* (triphenyl-*p*-phenylenediamine), prepared synthetically by treating diphenylamine with *p*-iodonitrobenzene, reducing the nitro-group, acetylating, and again treating with iodobenzene.

The decomposition of the tetraphenylhydrazine is quantitative. The dark green quinolimonium salt is first formed, and decomposes

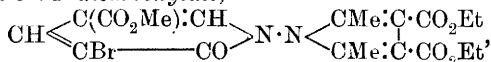
to colourless diphenylamine and diphenylchloroamine. Two molecules of the latter then interact, and chlorine is eliminated.

p *Chloroanilino*triphenylamine, $\text{NPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$, has b. p. 205—215°/0.01 mm., m. p. 77—81°, and forms a crystalline *hydrochloride* and an *acetyl* derivative, m. p. 199—200°. p-*Anilino*triphenylamine, prepared from this by means of sodium, has m. p. 134°, and yields an *acetyl* derivative, m. p. 184°.

p-*Nitro*triphenylamine crystallises in rectangular plates, m. p. 144°, insoluble in acetic acid. p-*Amino*triphenylamine has m. p. 145—148°, and forms an *acetyl* derivative, crystallising in silvery plates, m. p. 195°. E. F. A.

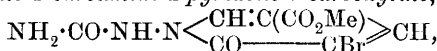
Action of *N*-Amino-compounds on Bromocoumalinic Acid Esters. CARL BÜLOW and HANS FILCHNER (*Ber.*, 1908, 41, 3281—3285).—Compounds containing two similar ring systems united by the $>\text{N} \cdot \text{N} <$ group have been described by Bülow and Sautermeister (*Abstr.*, 1904, i, 690) and by von Pechmann and Mills (*Abstr.*, 1904, i, 1042). Bülow (*Abstr.*, 1906, i, 905; 1907, i, 99) has also prepared a compound containing two different five-membered rings united by the same grouping. The authors have not succeeded in preparing a compound containing a five-membered and a six-membered ring joined together by the group $>\text{N} \cdot \text{N} <$.

5-*Methyl* 3' : 4'-diethyl 1'-(3-bromo-5-carboxy-2-pyridonyl)-2' : 5'-dimethylpyrrole-3' : 4'-dicarboxylate,



prepared by condensing methyl bromocoumalinate with ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate in presence of glacial acetic acid, forms colourless needles, m. p. 155°.

Methyl 3-bromo-1-carbamido-2-pyridone-5-carboxylate,



prepared by condensing semicarbazide with methyl bromocoumalinate, forms colourless needles, m. p. 223°. On hydrolysis, it yields 3-bromo-1-carbamido-2-pyridone-5-carboxylic acid, m. p. 252°. J. C. C.

Preparation of 5:5-Dialkylbarbituric Acids. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 201244).—Dimethyl- and diethyl-malonylguanidines, when hydrolysed with boiling 10% sulphuric acid, or at 120° with concentrated hydrochloric or hydrobromic acid, give rise to the corresponding 5:5-dialkylbarbituric acids. G. T. M.

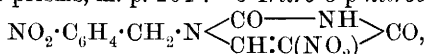
4 : 6-Dihydroxy-2-phenylpyrimidine. E. L. PINNER (*Ber.*, 1908, 41, 3517—3519).—4 : 6-*Dihydroxy-2-phenylpyrimidine*, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$, prepared by the interaction of equivalent quantities of benzamidine hydrochloride and ethyl malonate in the presence of sodium ethoxide at the ordinary temperature, forms crystals, m. p. 325—330°. It is converted by bromine in glacial acetic acid into 5-bromo-4 : 6-dihydroxy-2-phenylpyrimidine, $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2\text{Br}$, crystallising in pale yellow needles, m. p. 320° (decomp.), and by acetic anhydride into a *monoacetate*,

$C_{12}H_{10}O_3N_2$, glistening, flat prisms, m. p. 195° , and a *diacetate*, $C_{14}H_{12}O_4N_2$, brilliant, flat prisms, m. p. $93-94^\circ$. 4-Hydroxy-6-ethoxy-2-phenylpyrimidine, $C_{12}H_{12}O_3N_2$, is formed by heating the dihydroxy-compound with ethyl bromide and an alcoholic solution of potassium hydroxide under pressure at 100° ; it crystallises in flat prisms, m. p. 174° .

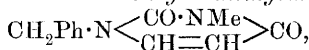
W. H. G.

Pyrimidines. XXXVIII. Syntheses of some Benzyl Derivatives of Uracil and Thymine. TREAT B. JOHNSON and JOHN H. DERBY, jun. (*Amer. Chem. J.*, 1908, 40, 444-458).—The authors have synthesised 1- and 3-benzyluracil and 1- and 3-benzylthymine.

2-Ethylthiol-6-oxy-1-benzylpyrimidine, $N \begin{smallmatrix} \text{C(SET) \cdot N(CH}_2\text{Ph)} \\ \text{CH} \text{---} \text{CH} \end{smallmatrix} \text{CO}$, prepared by the action of benzyl chloride on 2-ethylthiol-6-oxy-pyrimidine, forms prisms, m. p. 77° . 2-Ethylthiol-6-oxy-3-benzylpyrimidine, $CH_2Ph \cdot N \begin{smallmatrix} \text{C(SET) \cdot N} \\ \text{CH} \text{---} \text{CH} \end{smallmatrix} \text{CO}$, formed by the same reaction and isolated through its insolubility in ether, crystallises in long, slender prisms and hexagonal prisms or flat tablets, m. p. 139° . 5-Bromo-2-ethylthiol-6-oxy-3-benzylpyrimidine, prepared by the interaction of benzyl chloride and 5-bromo-2-ethylthiol-6-oxy-pyrimidine (Wheeler and Johnson, *Abstr.*, 1904, i, 624), crystallises in needles, m. p. 129° . 1-Benzyluracil, $NH \begin{smallmatrix} \text{CO \cdot N(CH}_2\text{Ph)} \\ \text{CH} \text{---} \text{CH} \end{smallmatrix} \text{CO}$, prepared by evaporating 2-ethylthiol-6-oxy-1-benzylpyrimidine with hydrochloric acid, forms prismatic crystals, m. p. 175° . It gives a red colour with diazobenzenesulphonic acid. 3-Benzyluracil, prepared similarly from 2-ethylthiol-6-oxy-3-benzylpyrimidine, crystallises in stout prisms, m. p. 173° . It gives only a yellow colour with diazobenzenesulphonic acid (distinction from 1-benzyluracil). 5-Bromo-3-benzyluracil, prepared by brominating 3-benzyluracil or by digesting 5-bromo-2-ethylthiol-6-oxy-3-benzylpyrimidine with concentrated hydrochloric acid, forms hexagonal prisms, m. p. 204° . 5-Nitro-3-p-nitrobenzyluracil,



prepared by nitrating 3-benzyluracil, crystallises in slender prisms, decomposing at $235-240^\circ$. 3-Benzyl-1-methyluracil,



prepared by treating 3-benzyluracil with methyl iodide or from 1-methyluracil and benzyl chloride, forms needles, m. p. 75° . On bromination, it gives 5-bromo-3-benzyl-1-methyluracil, which is also formed by the interaction of methyl iodide and 5-bromo-3-benzyluracil; it crystallises in diamond-shaped prisms, m. p. 123° . 2-Ethyl-

thiol-6-oxy-1-benzyl-5-methylpyrimidine, $N \begin{smallmatrix} \text{C(SET) \cdot N(CH}_2\text{Ph)} \\ \text{CH} \text{---} \text{CMe} \end{smallmatrix} \text{CO}$,

prepared by the interaction of benzyl chloride and 2-ethylthiol-6-oxy-5-methylpyrimidine, forms stout prisms, m. p. 70° ; in the same reaction there is also formed (insoluble in ether) 2-ethylthiol-6-oxy-3-benzyl-5-methylpyrimidine, crystallising in hexagonal plates, m. p.

121—122°. 1-Benzylthymine, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{N}(\text{CH}_2\text{Ph}) \\ \text{CH} = \text{CMe} \end{array} \text{CO}$, prepared by digesting 2-ethylthiol-6-oxy-1-benzyl-5-methylpyrimidine with concentrated hydrochloric acid, forms clusters of radiating prisms, m. p. 204—205°; with diazobenzenesulphonic acid it gives a claret-red solution. 3-Benzylthymine, $\text{CH}_2\text{Ph} \cdot \text{N} \begin{array}{c} \text{CO} - \text{NH} \\ \text{CH} : \text{CMe} \end{array} \text{CO}$, similarly prepared from 2-ethylthiol-6-oxy-3-benzyl-5-methylpyrimidine, forms diamond-shaped prisms, m. p. 160°. It gives only a yellow colour with diazobenzenesulphonic acid. 3-Benzyl-1-methylthymine, obtained by the action of methyl iodide on 3-benzylthymine, forms prismatic crystals, m. p. 101°; it does not react with diazobenzenesulphonic acid. On nitration it yields 5-nitro-4-hydroxy-3-p-nitrobenzyl-dihydrothymine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N} \begin{array}{c} \text{CO} - \text{NH} \\ \text{CH}(\text{OH}) : \text{CMe}(\text{NO}_2) \end{array} \text{CO}$, which forms prisms decomposing at 176°.

J. C. C.

Preparation of 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone. EMIL SCHEITIN (D.R.-P. 199844).—4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone is readily obtained in good yield by heating 4-sulphonylamino-1-phenyl-2:3-dimethyl-5-pyrazolone with methyl sulphate in alcoholic solution at 100—115° (compare this vol., i, 688).

G. T. M.

Preparation of Chlorobromoindigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 198816. Compare this vol., i, 695).—Chlorobromoindigotin, obtained by heating at 226° in nitrobenzene, chloroindigotin (1 mol.) and bromine (1 mol.), is a blue, crystalline powder, sparingly soluble in water, alcohol, or benzene, but dissolving more readily in warm aniline or nitrobenzene.

On reduction with alkaline reducing agents, it furnishes a light yellow leuco-derivative.

G. T. M.

Halogen Indigotins. CARL G. SCHWALBE and HERMANN JOCHHEIM (*Ber.*, 1908, 41, 3796—3798).—A table is given of the colours of *o*-, *m*-, and *p*-dichloroindigotin and indigotin in sulphuric acid, alcohol, chloroform, acetic acid, pyridine, aniline, and nitrobenzene solutions, together with observations on the preparation of the three chloro-*o*-nitrobenzaldehydes; Müller's fourth isomeride is a mixture of *m*-chloro-*o*-nitrobenzaldehyde and unchanged aldehyde. W. R.

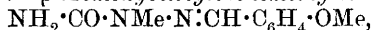
Halogen Indigotinsulphonic Acids. CARL G. SCHWALBE and HERMANN JOCHHEIM (*Ber.*, 1908, 41, 3798—3802).—A halogen phenylglycine mixed with sand, when washed with excess of cold sulphuric acid (60% SO_3), yields a halogen indigotinsulphonic acid; the purification is carried out by extraction with amyl alcohol and fractional precipitation with petroleum or benzene, the usual methods not giving satisfactory results. *m*-Chlorophenylglycine gives a dichlorotetrasulphonic acid; the *p*-chloro-derivative, a dichlorohexasulphonic acid, and the 2:4-dichloro-compound, a tetrachlorodisulphonic acid; *o*-chlorophenylglycine does not form a dye; the *o*-bromo-

compound gives a dye which does not contain halogen. A comparison of the aqueous solutions of these sulphonic acids and indigo-carmines as regards colour and dyeing properties is given. W. R.

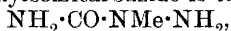
Constitution of the Acid Derivatives of Methylhydrazine.

AUGUST MICHAELIS and ERICH HADANCK (*Ber.*, 1908, 41, 3285—3290).—In attempting to prepare 5-phenyl-1-methyl-3-pyrazolone by the action of phosphorus trichloride on a mixture of ethyl benzoylacetate and an acid derivative of methylhydrazine, the authors invariably obtained 3-phenyl-1-methyl-5-pyrazolone, which is also produced by the condensation of methylhydrazine and ethyl benzoylacetate. As 3-pyrazolones are so often obtained by Michaelis and Mayer's reaction, the above fact could only be explained by the migration of the methyl group from the one nitrogen atom to the other, or else by the more probable assumption that the acid derivatives of methylhydrazine employed have an unsymmetrical constitution. The authors find that methylsemicarbazide, methylthiosemicarbazide, and mono- and dibenzoylmethylhydrazines have an unsymmetrical constitution, as they condense readily with aldehydes with the formation of hydrazones, whilst oxalyldimethylhydrazine appears to be symmetrically constituted.

Benzylidenemethylsemicarbazide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{N} : \text{CHPh}$, prepared by the action of benzaldehyde on methylsemicarbazide, forms white needles, m. p. 162°. *p-Methoxybenzylidenemethylsemicarbazide*,



similarly prepared from anisaldehyde, forms silky needles, m. p. 191°. The constitution of methylsemicarbazide is therefore



and, in accordance with this, it reacts with carbon disulphide to form *bis-methylcarbamidothiocarbamide*, $\text{CS}(\text{NH} \cdot \text{NMe} \cdot \text{CO} \cdot \text{NH}_2)_2$, white needles, m. p. 253.5°. When methylhydrazine is treated with carbon disulphide, there is formed the *salt*, $\text{NHMe} \cdot \text{NH} \cdot \text{CS} \cdot \text{S} \cdot \text{NH}_2 \cdot \text{NHMe}$, which loses hydrogen sulphide and yields *bis-methylaminothiocarbamide*, $\text{CS}(\text{NH} \cdot \text{NHMe})_2$, white needles, m. p. 241°.

Phenylbenzylidenemethylthiosemicarbazide, $\text{NHPh} \cdot \text{CS} \cdot \text{NMe} \cdot \text{N} : \text{CHPh}$, prepared by the interaction of benzaldehyde and phenylmethylthiosemicarbazide, forms long, glistening needles, m. p. 131.5°.

Benzoylbenzylidenemethylhydrazine, $\text{NMeBz} \cdot \text{N} : \text{CHPh}$, prepared by the interaction of benzaldehyde and crude *monobenzoylmethylhydrazine* (an oil from benzoic anhydride and methylhydrazine), forms small, white needles, m. p. 82°.

Benzoylanisylidenemethylhydrazine, $\text{NMeBz} \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, prepared from anisaldehyde, forms slender, white needles, m. p. 115°. When benzoylmethylhydrazine in alcoholic or ethereal solution is shaken with yellow mercuric oxide, an oil is obtained which has the properties of a tetrazone; this could not, however, be prepared in the pure state.

Dibenzoylmethylhydrazine can be prepared by treating methylhydrazine with benzoic anhydride; it has m. p. 145° (von Brüning, *Abstr.*, 1890, 23, gives 143°).

Diacetylmethylhydrazine, $\text{NMeAc} \cdot \text{NHAc}$, is a colourless oil, b. p. 280° .

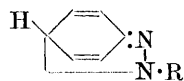
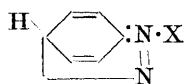
Oxalyl dimethylhydrazine does not yield a hydrazone with either benzaldehyde or anisaldehyde. J. C. C.

Constitution of the Endoxypyrrhodiazoles [4:5-Oxy-1:2:5-osotriazoles]. GIACOMO PONZIO (*Gazzetta*, 1908, 38, ii, 522–524. Compare Abstr., 1898, i, 386; 1899, i, 717, 827; 1900, i, 588; 1901, i, 169; 1902, i, 190).—The author's conclusion, that the compounds obtained by the oxidation of the hydrazoximes (*loc. cit.*) contain the nucleus $\text{O} \begin{array}{c} \diagup \text{N} \cdot \text{N} \diagdown \\ | \quad | \\ \text{C} \quad \text{C} \\ | \quad | \\ \text{N} \quad \text{N} \end{array}$, is confirmed by the recent work of Wieland and Semper (this vol., i, 108), who find that phosphorus pentachloride does not react with compounds containing the group $\text{:N} \cdot \text{O}$, whilst it readily transforms compounds containing the complex $\text{O} \begin{array}{c} \diagup \text{C} \\ | \quad | \\ \text{N} \quad \text{N} \end{array}$ into the corresponding compounds containing the grouping $\text{:C} \cdot \text{N} \cdot$.

The interaction of phosphorus pentachloride and 4:5-oxy-1-phenyl-3:4-dimethyl-1:2:5-osotriazole yields 1-phenyl-3:4-dimethyl-1:2:5-osotriazole, which partly undergoes chlorination to 1-*p*-chlorophenyl-3:4-dimethyl-1:2:5-osotriazole. T. H. P.

Cain's Theory of Diazo-compounds and Ammonium Salts.

ARTHUR HANTZSCH (*Ber.*, 1908, 41, 3532–3536).—A criticism of Cain's theory of diazo-compounds (compare Trans., 1907, 91, 1049) and of ammonium salts. The main objections raised by the author are briefly as follows: (1) diazobenzene salts have the properties of true benzene derivatives, and not those of derivatives of dihydrobenzene, as represented by the annexed formula; (2) the behaviour of diazo-salts when reduced or oxidised, or when treated with halogen, is not in agreement with the presence of an unsaturated ring, as shown by this formula; (3) a compound having such a constitution, when reduced, should yield *p*-phenylenediamine; (4) since both normal and isodiazocompounds are very similar in their chemical behaviour,



they cannot be represented by formulæ so different as those annexed. The fact that the isomeric diazocyanides give similar absorption spectra (compare Dobbie and Tinkler, Trans., 1905, 87, 273) shows that these compounds must have very similar constitutions; (5) if tetraethylammonium chloride has the formula $\text{NEt}_3 \cdot \text{Cl} \cdot \text{Et}$, and undergoes ionisation in aqueous solution, thus: $\text{NEt}_3 \cdot \text{Cl} \cdot \text{Et} \rightarrow \text{NEt}_3 + \text{Et} \cdot \text{Cl} \rightarrow \text{NEt}_4^+ + \text{Cl}^-$, it should be possible to detect the triethylamine and ethyl chloride produced as intermediate products, since these compounds interact but very slowly at low temperatures. As the formation of these compounds cannot be detected, the above supposition is untenable. W. H. G.

Decomposition of Diazo-solutions. ARTHUR HANTZSCH and KENWORTHY J. THOMPSON (*Ber.*, 1908, 41, 3519–2532).—An

investigation on the rates of decomposition of aqueous solutions of various diazo-salts, carried out with the object of clearing up several points which were still unsettled (compare Schwalbe, Abstr., 1905, i, 618; Cain, *ibid.*, i, 724).

Freshly prepared diazobenzene chloride contains traces of a substance, the nature of which could not be determined, which acts as a preservative. It disappears when the diazo-compound is kept for some time in a desiccator, or when a current of dry air is passed over the substance; consequently, solutions of the freshly prepared salt are more stable ($k = 0.0008 - 0.0009$) than those of the substance which has been kept for some days, or treated with a current of dry air, when the maximum value of k found was 0.00118 (compare Hantzsch and Osswald, Abstr., 1900, i, 703; Euler, Abstr., 1903, i, 298). It is therefore evident that the keeping qualities of aqueous solutions of diazo salts may be greatly influenced by very slight traces of unknown impurities. Diazobenzene bromide in dilute solutions decomposes at about the same rate as the chloride. The velocity of decomposition increases slowly with the concentration, the increase in the case of the bromide being slightly greater than that of the chloride, probably because the undissociated bromide is less stable than the undissociated chloride. Further, the velocity of decomposition increases with the decomposition of the salt; this is probably due to the formation of a halogenated benzene, produced by the action of the hydrogen halide which is liberated. Diazobenzene iodide, even in very dilute solutions, decomposes far more rapidly than the chloride or bromide, probably because the chief reaction which takes place in this case, namely, the formation of iodobenzene, proceeds at a greater rate than the production of phenol. A velocity constant could not be obtained, owing to the complexity of the many reactions which take place during the decomposition of solutions of diazonium iodides.

The rate of decomposition of *p*-nitrodiazobenzene chloride increases with the concentration; since it is greatly accelerated by light, the solutions were kept as far as possible in the dark, the value obtained being $k = 0.00020$ at 50° ($v = 9$). Neither hydrochloric acid nor acetic acid influences the rate of decomposition of solutions of pure *p*-nitrodiazobenzene chloride to any marked degree (compare Schwalbe, *loc. cit.*).

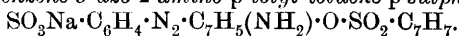
Diazo-acetates in aqueous solution do not decompose in a normal manner; the weaker the diazo-base the more abnormal is the course of the reaction. As was stated by Schwalbe, the presence of sodium chloride increases the stability of solutions of *p*-nitrodiazobenzene acetate.

Solutions of diazo-salts are slowly decomposed by nitrous acid (compare Cain, *loc. cit.*); the nitrous acid does not act as a catalyst, as stated by Schwalbe, but slowly disappears, since it is directly concerned in the decomposition.

W. H. G.

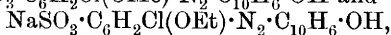
[Preparation of Disazo-derivatives of 2-Amino-*p*-cresol.]
ANILINFARBEN & EXTRACT FABRIKEN VORM. J. R. GEIGY (D.R.-P. 201377).—2-Amino-*p*-tolyl toluene-*p*-sulphonate, $C_7H_7 \cdot SO_2 \cdot O \cdot C_7H_6 \cdot NH_2$,

lustrous prisms, m. p. 78° , is obtained by reducing 2-nitro-*p*-tolyl toluene-*p*-sulphonate; it couples with diazonium salts and diazoaryl-sulphonic acids, yielding diazotisable *p*-aminoazo-derivatives, such as sodium sulphobenzene-5-azo-2-amino-*p*-tolyl toluene-*p*-sulphonate,



The diazo-compounds of these *p*-aminoazo-derivatives couple with naphthol in alkaline solution, and the resulting disazo-derivatives give valuable colouring matters on removing the toluene-*p*-sulphonic group by hydrolysis. G. T. M.

Azo-derivatives of 2-Chloro-*p*-anisidine- and 2-Chloro-*p*-phenetidine-sulphonic Acids. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKEN (D.R.P. 189469).—Insoluble coloured salts of the azo-compounds, $\text{NaSO}_3\cdot\text{C}_6\text{H}_2\text{Cl}(\text{OMe})\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ and



are produced by double decomposition with barium or other metallic chlorides. When mixed with aluminium hydroxide, these substances give rise to scarlet lakes of great brilliancy and fastness. G. T. M.

Azo-derivatives of Phenol and of the Phenolcarboxylic Acids. EUGÈNE GRANDMOUGIN and HANS FREIMANN (*J. pr. Chem.*, 1908, [ii], 78, 384—408).—A continuation and extension of former work (compare Abstr., 1907, i, 664, 986, 987; this vol., i, 926).

Azo-derivatives of Phenols.—The benzenesulphonyl ester of *p*-hydroxyazobenzene crystallises in yellow needles, m. p. 109° . The acetyl derivative of bis-benzeneazophenol has m. p. 116° , and the benzenesulphonyl ester forms yellowish-brown needles, m. p. 99° . The benzenesulphonyl ester of tris-benzeneazophenol forms red crystals, m. p. 202° .

o-Tolueneazophenol has m. p. 107 — 108° (Noelting and Werner, Abstr., 1891, 212, give 102 — 103° ; Paganini, Abstr., 1891, 556, gives 101°); the acetyl derivative crystallises in reddish-yellow leaflets, m. p. 68° , and the benzenesulphonyl ester forms small, orange leaflets, m. p. 64° . Bis-*o*-tolueneazophenol has m. p. 116° (Noelting and Werner, *loc. cit.*, give 146° ; Paganini, *loc. cit.*, gives 116°). The acetyl derivative forms reddish-yellow needles, m. p. 75 — 76° . When bis-*o*-tolueneazophenol is prepared from diazotised *o*-toluidine and ethyl *p*-hydroxybenzoate, it has m. p. 150° , and the acetyl derivative has m. p. 98° . The nature of this difference is not yet known.

Bis-*m*-tolueneazophenol forms yellowish-brown needles, m. p. 94° ; the acetyl derivative crystallises in yellow needles, m. p. 75° . Tris-*m*-tolueneazophenol, prepared by the action of *m*-diazotoluene on salicylic acid, forms brown needles, m. p. 160° . The acetyl derivative of *p*-tolueneazophenol has m. p. 95° ; the benzenesulphonyl ester forms brownish-yellow leaflets, m. p. 114° . Bis-*p*-tolueneazophenol has m. p. 176° , and the acetyl derivative has m. p. 138° (Goldschmidt and Pollak, Abstr., 1892, 974, give 170° and 128° respectively). Tris-*p*-tolueneazophenol forms brownish-red needles, m. p. 238° ; the acetyl derivative crystallises in golden needles, m. p. 187° . 2-*p*-Nitrobenzene-azo-4-benzeneazophenol, prepared by treating *p*-hydroxyazobenzene with

diazotised *p*-nitroaniline, has m. p. 196°; the *acetyl* derivative has m. p. 189°. 4-*p*-Nitrobenzeneazo-2-benzeneazophenol, prepared from *o*-hydroxyazobenzene and diazotised *p*-nitroaniline, has m. p. 189°; the *acetyl* derivative has m. p. 154°. 4-Acetylamino-2-*p*-nitrobenzeneazophenol, prepared by the interaction of *p*-nitrodiazobenzene and *p*-acetylaminophenol, forms brown needles, m. p. 227°; it is hydrolysed by 60% sulphuric acid to 4-amino-2-*p*-nitrobenzeneazophenol, golden crystals, m. p. 211°. β -Naphthaleneazophenol forms bronze needles, m. p. 240°; the *acetyl* derivative crystallises in brown needles, m. p. 180°.

Azo-derivatives of Salicylic Acid.—Methyl *p*-nitrobenzeneazosalicylate forms silky, orange needles, m. p. 166°; the *acetyl* derivative forms orange-yellow needles, m. p. 131°. The *acetyl* derivative of phenyl benzeneazosalicylate (Limpricht, Abstr., 1891, 1036) forms golden needles, m. p. 132°. Limpricht's phenyl bis-benzeneazosalicylate is hydroxyazobenzene. Phenyl *p*-nitrobenzeneazosalicylate crystallises in yellow needles, m. p. 165°; the *acetyl* derivative forms yellow needles, m. p. 155°. *o*-Nitrobenzeneazosalicylaldehyde forms brown crystals, m. p. 141°; the phenylhydrazone forms brown needles, m. p. 192°. Methyl bis-benzeneazosalicylate forms brown crystals, m. p. 141°; the *acetyl* derivative forms yellowish-red needles, m. p. 145°. Methyl bis-*o*-tolueneazosalicylate forms brownish-yellow needles, m. p. 154°. Bis-*m*-tolueneazosalicylic acid forms brownish-olive needles, m. p. 210°; the *acetyl* derivative forms yellow needles, m. p. 170°. Bis-*p*-tolueneazosalicylic acid crystallises in brown, felted needles, m. p. 214°; the *acetyl* derivative forms reddish-brown tablets, m. p. 198°. These bisazo-derivatives of salicylic acid are all prepared in alkali hydroxide solution.

Azo-derivatives of p-Hydroxybenzoic Acid.—The *acetyl* derivative of benzeneazo-*p*-hydroxybenzoic acid has m. p. 205°, not 198—199° as previously given. *o*-Tolueneazo-*p*-hydroxybenzoic acid crystallises in orange-yellow needles, m. p. 223°. In the preparation of this substance from diazotoluene chloride and *p*-hydroxybenzoic acid in alkali hydroxide solution, there are also formed bis-*o*-tolueneazophenol and *o*-tolueneazoindazole; the *acetyl* derivative of the latter forms golden-yellow needles, m. p. 163°, and the *benzoyl* derivative, yellow needles, m. p. 179.5°. *p*-Tolueneazo-*p*-hydroxybenzoic acid forms yellow needles, m. p. 236°; the *acetyl* derivative forms yellow needles, m. p. 205°.

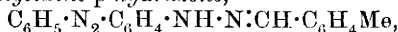
Ethyl benzeneazo-*p*-hydroxybenzoate (Auwers and Röhrig, Abstr., 1897, i, 341) is readily prepared by the action of diazobenzene chloride on ethyl *p*-hydroxybenzoate; the *acetyl* derivative forms yellowish-orange needles, m. p. 137°. Ethyl *o*-tolueneazo-*p*-hydroxybenzoate has m. p. 105°.

Azo-derivatives of m-Hydroxybenzoic Acid.—Benzeneazo-*m*-hydroxybenzoic acid has m. p. 221° (Limpricht, *loc. cit.*, gives 213°); the methyl ester forms brown needles, m. p. 78—79°. Bis-benzeneazo-*m*-hydroxybenzoic acid occurs in two isomeric forms, namely, the 2:6- and the 4:6-bis-benzeneazo-derivatives. Of these, the α -acid (not specified) forms brown needles, m. p. 222—223°, and the β -acid has m. p. 226—227°; it is sparingly soluble in methyl alcohol, whilst the

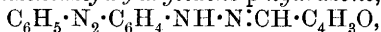
α -acid is readily soluble in this solvent. The *methyl* ester of the β -acid forms bronze-yellow, felted needles, m. p. 183°. J. C. C.

Azobenzene-*p*-hydrazinesulphonic Acid resulting from the Action of Sulphur Dioxide on Diazobenzene Sulphate and its Condensation with Aldehydes and Ketones. JULIUS TRÖGER and O. MÜLLER (*J. pr. Chem.*, 1908, [ii], 78, 369—383).—In continuation of previous work (Tröger, Berlin, and Franke, *Abstr.*, 1906, i, 994), the authors have prepared a further number of hydrazones by condensing azobenzene-*p*-hydrazinesulphonic acid with aldehydes and ketones in the presence of glacial acetic acid or alcoholic hydrochloric acid.

Benzeneazo-p-tolylidene-p-hydrazone,

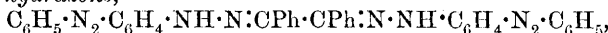


prepared from *p*-tolualdehyde, crystallises in orange-yellow needles, m. p. 178°; the *hydrochloride* forms small, blue needles. *Benzeneazocumylidene-p-hydrazone*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_7$, prepared from cuminaldehyde, forms yellowish-red needles, m. p. 144—145°; the *hydrochloride* is dark blue. *Benzeneazo-m-chlorobenzylidene-p-hydrazone*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$, prepared from *m*-chlorobenzaldehyde, forms small, glistening, golden-yellow leaflets, m. p. 160·5°; the *sulphate* forms dark blue needles. *Benzeneazo-m-bromobenzylidene-p-hydrazone* crystallises in small, glistening, golden-yellow leaflets, m. p. 173°; the *sulphate* is blue. *Benzeneazo-p-aminobenzylidene-p-hydrazone*, prepared from *p*-aminobenzaldehyde, forms small, reddish-brown leaflets, darkening at 136°, and decomposing above this, the residue being completely melted at 180·5°. *Benzeneazo-p-dimethylaminobenzylidene-p-hydrazone* crystallises in cinnabar-red needles, m. p. 185·5°; the *hydrochloride* forms small, glistening, blue needles. *Benzeneazo-p-hydroxybenzylidene-p-hydrazone* forms dark red needles, m. p. 196°; the *hydrochloride* consists of dark blue needles. *Benzeneazofurfurylidene-p-hydrazone*,



prepared from furfuraldehyde, forms reddish-brown tablets, m. p. 133°; the *hydrochloride* is brownish-black.

Benzeneazobenzophenone-p-hydrazone, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CPh}_2$, prepared from benzophenone, forms brownish-red leaflets, m. p. 144°; the *hydrochloride* forms blue needles or plates. *Benzeneazobenzil-p-hydrazone*,



prepared from benzil, forms orange-red needles, m. p. 184—185°; the *hydrochloride* is blue. *Benzeneazobenzylidene-p-hydrazone hydrochloride* is a black powder. J. C. C.

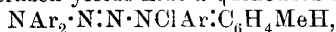
Trisbenzeneazophenol. LÉO VIGNON (*Bull. Soc. chim.*, 1908, [iv], 3, 1030—1031).—In previous work (*Abstr.*, 1904, i, 699) on bisbenzeneazophenol, the author obtained indications of the formation of a substance richer in nitrogen, and this has led him to repeat Grandmougin and Freimann's work on trisbenzeneazophenol (*Abstr.*, 1907, i, 664). He confirms their results, but points out that the yield of the trisazo-substance is only 1% of the theoretical.

T. A. H.

Aromatic Tetrazens. V. HEINRICH WIELAND (*Ber.*, 1908, 41, 3498—3506).—The tetrazens are decomposed by hydrogen chloride in a similar manner to the tetra-arylhydrazines:



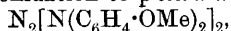
Thus tetratolyltetrazen yields first a quinonoid salt,



indicated by a violet coloration in solution, which is decomposed with evolution of nitrogen, and finally *p*-ditolylamine, tolazonium and dichlorotolazonium chloride result. Tetra-anisyltetrazen behaves similarly; acetic acid brings about this decomposition in the cold with remarkable ease.

p-Tetratolyltetrazen, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{N} \cdot \text{N}(\text{C}_7\text{H}_7)_2$, prepared by oxidation of *p*-ditolylhydrazine, preferably with permanganate, crystallises in glistening, yellow needles, decomp. 134° . It is decomposed by hydrogen chloride or acetic acid to tolazine derivatives. With bromine, a bluish-violet coloration indicates a primary additive product, which changes to a brownish-green; but little ditolylamine along with much dibromotolazine is formed.

To prepare *p*-dianisylhydrazine, *p*-dianisylamine is converted into the *nitrosoamine*, crystallising in flat, bright yellow needles, m. p. 79° , and dissolving in concentrated sulphuric acid with a greenish-blue coloration. On reduction with zinc dust and acetic acid, the *dianisylhydrazine*, $\text{NH}_2 \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$, is obtained in mother-of-pearl-like, broad pointed, colourless needles, m. p. 111° . The *hydrochloride* is sparingly soluble. The oxidation to *p*-tetra-anisyltetrazen,



could only be effected by means of *p*-benzoquinone. The tetrazen forms citron-yellow, four-sided plates, m. p. 117° (violent decomp.). Decomposition with acids gives the characteristic anisazonium compounds.

Tetratolyltetrazen dissolved in xylene, when heated for a few minutes, shows a violent evolution of nitrogen and formation of tetratolyldiazine. E. F. A.

Catabolism of Proteins. FRANZ HOFMEISTER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 273—281).—This paper is mainly a review of recent work on the cleavage of proteins, and the importance of such work and the necessity of dealing with pure substances are among the points insisted upon. W. D. H.

Effect of Acid and Alkali on the Osmotic Pressure of the Serum Proteins. L. ADAMSON and HERBERT E. ROAF (*Bio-Chem. J.*, 1908, 3, 422—438).—Alkali increases (although not proportionally to the amount added) the osmotic pressure of the serum proteins. Acid causes this pressure to fall to zero, but larger amounts of acid increase it again. The point of zero pressure corresponds with the "alkaline reactivity" of serum ash. When the amount of alkali added is corrected by this "alkaline reactivity," the relationship of the osmotic pressure to the amount of alkali is a logarithmic one. The experiments with alkali are limited by the breaking up of the protein into particles small enough to pass a parchment paper membrane, and with acid by the partial precipitation of the protein. W. D. H.

Dissociation of Solutions of the Basic Caseinates [Caseinogenates] of Sodium and Ammonium. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1908, 12, 473—483).—In a previous paper (Abstr., 1907, i, 1096), it has been shown that the solutions of sodium and ammonium caseinate are neutral to litmus obey Ostwald's dilution law for binary electrolytes. Sackur (Abstr., 1903, ii, 4) had previously carried out electrical conductivity measurements with solutions of the corresponding "basic" salts, which were obtained by adding sufficient alkali to make the solutions neutral to phenolphthalein, the amounts of alkali required to produce the basic and neutral solutions being in the ratio 8 : 5. The author now shows from Sackur's results that the solutions of the basic caseinates also follow the dilution law for binary electrolytes, so that casein appears to behave as a monobasic acid in both solutions. Sackur has suggested that casein behaves to alkalis as a tetrabasic acid, but it is shown that the evidence for this view is untrustworthy.

The above results are best accounted for on the view that complex ions containing casein are present. The neutral caseinates are amphoteric salts of the combined base, containing the ions NaX' and XXOH' (X = casein), whilst the basic caseinates are true salts of the combined base, the solutions containing the ions Na' and XXOH' . In all the solutions there is an equilibrium of the type $\text{NaX}' + \text{HXOH} \rightleftharpoons \text{Na}' + \text{HXXOH}$, which is not displaced by dilution.

From Sackur's results, the value 15.2×10^{-5} cm./sec. is obtained for the velocity of the casein ion in solutions of basic sodium caseinate, and 9.1×10^{-5} cm./sec. for the velocity of the same ion in solutions of ammonium caseinate.

The dissociation constants for the "basic" sodium and ammonium salts of casein are 0.0499 and 0.0404 respectively. G. S.

Action of Iron and of Heavy Metals [as Oxygen Carriers]. VINCENZO CERVELLO (*Arch. exp. Path. Pharm., Suppl.*, 1908, 107—109).—The oxidation of guaiacum resin is accelerated by the salts of heavy metals, and most of all by those of iron and copper. In the case of ferric salts, a partial reduction to the ferrous state occurs. The part played by iron as a constituent of hæmoglobin is discussed. G. B.

Urochrome. I. HERMANN HOHLWEG (*Biochem. Zeitsch.*, 1908, 13, 199—204).—The pigment was prepared from human urine, which was made alkaline with calcium hydroxide, precipitated with calcium chloride, the filtrate neutralised with acid, and evaporated in a vacuum to a syrup; after separation of the greater part of the salts, the syrup was diluted and shaken for several hours with animal charcoal, which absorbed the pigment, and from which it was afterwards removed by glacial acetic acid. From the solution thus obtained, it was precipitated by ether. The brown powder prepared in this way contained 8.22% of ash, and was soluble in water and methyl alcohol, but insoluble in strong ethyl alcohol and other organic solvents. Its spectrum showed no absorption bands, and it did not give the urobilin reaction with ammoniacal zinc chloride. It gave the

Garrod reaction with acetaldehyde and subsequent treatment with ammoniacal zinc chloride; also the Molisch reaction with α -naphthol.

S. B. S.

Urochrome. II. K. E. SALOMONSEN (*Biochem. Zeitsch.*, 1908, 13, 205—207).—The product was prepared by a slight modification of Hohlweg's method (preceding abstract). It was purified by conversion into its calcium salt. On treatment of an aqueous solution of the pigment with bromine in the cold, a yellow *bromo*-derivative was obtained, which was soluble in alkalis. On warming an aqueous solution of urochrome with bromine, a more vigorous bromination accompanied by oxidation takes place.

S. B. S.

Urochrome. III. STEFANO MANCINI (*Biochem. Zeitsch.*, 1908, 13, 208—214).—The bromo-derivative of Hohlweg and Salomonsen (preceding abstracts) was prepared by a modified method, unconcentrated urine being employed for the purpose. It was purified by dissolving in alkali, precipitating by acid, dissolving the substance thus obtained in water, and treating again with bromine. The doubly-refracting, yellow product thus prepared, when heated with zinc dust or calcium hydroxide, gives strong pyrrole reactions. Its composition corresponds approximately with the formula $C_{36}H_{41}O_{12}N_7Br_6$, which would be a bromo-derivative of $C_{36}H_{47}O_{12}N_7$. This is not far removed from the formula $C_{36}H_{43}O_{10}N_7$, which Thudichum ascribed to uromelanin. For it the name *uropyrryl* is proposed. By oxidation of crude bromouropyrryl with bromine water, oxalic acid, an oily acid, which gives the pyrrole reaction, and also, most probably, bromoanil were obtained. Neither oxalic acid nor bromoanil were obtained when a product, purified by repeated solution in alkali, re-precipitation with acids, and re-bromination, was employed. The relation of uropyrryl to urochrome is not yet ascertained.

S. B. S.

Hippomelanin. I. PETER RONA and O. RIESSER (*Zeitsch. physiol. Chem.*, 1908, 57, 143—153).—Hippomelanin, purified by Fürth and Jerusalem's method (Abstr., 1907, ii, 797), has been oxidised by a 3% solution of hydrogen peroxide containing a small amount (0.002%) of hydrochloric acid in solution. The total nitrogen of the aqueous solution was 7.5%, and the ammoniacal nitrogen 4.2%, that is, 56% of the total nitrogen present in the hippomelanin. Attempts were made to isolate the other nitrogenous products in the form of copper compounds. A copper derivative was obtained which was insoluble in alcohol and water. This contained a small amount of copper oxalate, but no other constituent was obtained in a pure form.

A copper derivative soluble in alcohol and water was also obtained. From this a *base*, which was precipitated by phosphotungstic acid, was isolated. The *hydrochloride* is readily soluble in water or alcohol. The *picate* is deposited as an oil sparingly soluble in alcohol; the *picrolonate* is a deep red compound sparingly soluble in water, and the *platinichloride*, N = 16.14%, forms ochre-yellow prisms, m. p. 280°, insoluble in alcohol.

J. J. S.

Inosic Acid. CARL NEUBERG and B. BRAHN (*Ber.*, 1908, 41, 3376—3381. Compare Abstr., 1907, i, 1097).—It is pointed out that the sugar obtained by hydrolysing inosic acid cannot be *r*-arabinose, as stated by Bauer (Abstr., 1907, i, 1098). The authors confirm their view that it is *l*-xylose. They have obtained it in a syrupy form, have shown that it gives the pentose reactions, and that it is dextrorotatory. They further show that it does not yield a diphenylhydrazone as readily as does *r*-arabinose.

Levene and Jacob's conclusion (this vol., i, 931), that in place of a pentose inosic acid yields a tetrose-carboxylic acid, is shown to be untenable. J. J. S.

Glucothionic Acid. JOHN A. MANDEL and CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 13, 142—147. Compare Abstr., 1905, ii, 736).—Preliminary investigations show that the product obtained from the kidneys contains sulphuric acid in a conjugated form. Dextrose is not a product of hydrolysis, and neither is the substance of polysulphide nature. For these reasons, the name glucothionic acid is inapplicable. Names indicating the origin of the product are suggested, for example, *renosulphuric acid*. S. B. S.

Jecorin and other Lecithin-like Substances in the Liver of the Horse. A. BASKOFF (*Zeitsch. physiol. Chem.*, 1908, 57, 395—460).—Jecorin was prepared so that it gave a constant N:P ratio and a constant yield of sugar (about 14%). It is a diamino-monophosphatide in Erlandsen's sense.

The alcoholic extract of the liver is evaporated to a syrupy consistency, and treated with ether; a jecorin-like substance forms as a heavy layer at the bottom of the vessel; there is also a brown precipitate, insoluble in ether and alcohol, which was not further investigated. The addition of alcohol to the ether extract produces a precipitate of crude jecorin, lecithin remaining in solution. The precipitate is again treated with ether, and a jecorin-like substance remains insoluble; the extract, however, contains Drechsel's jecorin, which is precipitable by alcohol, and can be purified by the repetition of this process three or four times. W. D. H.

Glutamic Acid in Various Keratins. EMIL AEDERHOLDEN and DÉNES FUCHS (*Zeitsch. physiol. Chem.*, 1908, 57, 339—341).—The following table gives the mean analytical results obtained, in parts %:

	Hoof of ox.		Horn of ox.		Hoof of horse.
	1 yr. old.	4 yrs. old.	1 yr. old.	4 yrs. old.	
Dry residue	90.5	91.5	96.0	96.5	75.4
Ash	0.14	0.16	0.22	0.36	0.45
Melaine substances	0.22	0.12	1.65	0.96	0.9
Glutamic acid hydrochloride in ash-free dry residue.....	18.0	16.8	13.8	12.9	18.2

Attention is called to the variable numbers obtained, and to the fall of glutamic acid and rise of ash with increasing age. W. D. H.

The Composition of the Protamine from Salmon Spermatozoa. LOUIS NELSON (*Arch. exp. Path. Pharm.*, 1908, 59, 331—335).—The protamine was prepared by Schmiedeberg's method, and converted into the platinichloride. It was found that an impurity could be removed from the latter by hot water. The protamine was found then to have a composition corresponding with the formula $C_{16}H_{27}O_3N_9$.
S. B. S.

Chemistry of Protamines. I. Protamine from the Spermatozoa of the Caspian Sturgeon, *Accipenser Guldenstädtii*. W. D. MALENÜCK (*Zeitsch. physiol. Chem.*, 1908, 57, 99—112. Compare Kuračeff, Abstr., 1901, ii, 462).—For isolating protamines and determining the yield, the method of precipitating with sodium picrate is preferred to Kossel's method of repeated solution of the sulphate in water and precipitation with alcohol. The sulphuric acid extract is stirred continuously with the aqueous picrate solution until a flocculent, orange-yellow precipitate is formed. The filtrate should be clear and free from opalescence, and should yield a further precipitate with sodium picrate. The precipitated picrate is washed, dried, dissolved in acetone, and decomposed with sulphuric acid. A portion of the picrate is insoluble in acetone, and this is shown to consist of adenine picrate, whereas the protamine picrate is readily soluble. In decomposing the acetone solution of the picrate, it is essential that an excess of sulphuric acid is not added.

The last traces of picric acid can be removed by solution in water, evaporating the solution, carefully precipitating with alcohol and acetone, and rubbing the sticky mass in a mortar with acetone until hard. The dry sulphate prepared by such a method usually contains only 0.3% of ash when dried at 108—110°, and gave the following analytical results: C, 37.64; H, 6.61; N, 20.92, and H_2SO_4 , 22.59%. Similar data were obtained with a sulphate which had been converted into the chloride by Goto's method. The formula $C_{27}H_{55}O_7N_{13} \cdot 2H_2SO_4$ agrees best with these data.
J. J. S.

Thymamine, a Protamine from the Thymus Gland. LOUIS NELSON (*Arch. exp. Path. Pharm.*, 1908, 59, 336—340).—The protamine was prepared by extracting the coagulated proteins of the gland with copper chloride solution by Schmiedeberg's method, by means of which a solution of the hydrochloride is obtained. Sodium hydroxide is added until the reaction is neutral, and the filtrate from the precipitate thus produced evaporated, when copper protein combinations separate. The filtrate from these is diluted and evaporated, and more protein separates and is filtered off. These processes are repeated until a solution which no longer gives a reaction with Millon's reagent is obtained. The protamine is prepared from this by precipitating as phosphotungstate, and is finally obtained in the form of a platinichloride, the purification of which is described in detail. Its composition corresponds with the formula $C_{22}H_{40}O_5N_6$.
S. B. S.

The Action of Tyrosinase from *Russula delica* on Polypeptides which contain Tyrosine and on Suprarenine. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Zeitsch. physiol. Chem.*, 1908, 57,

329—331. Compare this vol., i, 237).—In addition to the polypeptides previously used, tyrosinase rapidly splits *d*-alanyl-*l*-tyrosine and *l*-leucyl-*l*-tyrosine. It also decomposes suprarenine (adrenaline), with the rapid formation of a red colour, and later of dark-coloured flocculi; *l*-, *d*-, and *dl*-suprarenines are all decomposed with equal rapidity.

W. D. H.

Milk Proteins and Enzymes. GEORGE A. OLSON (*J. Biol. Chem.*, 1908, 5, 261—282).—After removal of the caseinogen and albumin, milk, cream, and butter are stated to yield a new protein, which is precipitable by hydrochloric acid. It contains 18.9% of nitrogen. When it is added to milk, it produces partial digestion of the caseinogen; this power is most active at 65°, and is destroyed at 80°. After removal of the new protein, the filtrate also has the same property; the ferment action of the protein is therefore believed to be due to incorporation.

W. D. H.

The Scission by Diastase of Lactose, Maltose, and their Derivatives. H. BIERRY and J. GIAJA (*Compt. rend.*, 1908, 147, 268—270).—The lactone of lactobionic acid was treated with macerations of foetal intestines (sheep and oxen) and with digestive juices of snails. The former was inactive, whereas the latter caused the production of galactose; it also acts on lactosazone with the production of galactose. Similar results were obtained with the lactone of maltobionic acid. These facts afford further evidence of the specific nature of the ferments.

S. B. S.

Action of Organo-magnesium Compounds on Arsenious Oxide. FRANZ SACHS and HANS KANTOROWICZ (*Ber.*, 1908, 41, 2767—2769).—The addition of powdered arsenious oxide to an ethereal solution of magnesium phenyl bromide leads to the formation of diphenylarsine oxide after thirty minutes' heating, and of triphenylarsine after three hours. With magnesium *p*-tolyl bromide, only tri-*p*-tolylarsine is obtained, whilst with magnesium benzyl bromide, after three hours' heating, a substance, $\text{As}(\text{CH}_2\text{Ph})_2 \cdot \text{OH}, \text{H}_2\text{O}$, m. p. 215—216°, is formed after the usual operations.

C. S.

Triphenylstibine Sulphide. LUDWIG KAUFMANN (*Ber.*, 1908, 41, 2762—2766).—Contrary to the statement of Michaelis and Reese (*Abstr.*, 1886, 884), triphenylstibine sulphide can be prepared under the following conditions: Pfeiffer's triphenylstibine (*Abstr.*, 1905, i, 164) is converted into a haloid additive compound, preferably the dibromide, which is dissolved in alcoholic ammonia, and hydrogen sulphide passed through the solution until a faint yellow coloration appears in the liquid; the crystals which have separated are recrystallised from alcohol, whereby colourless triphenylstibine sulphide, SbPh_3S , is obtained, m. p. 119—120°. Prolonged heating of its solutions or treatment with acids, even acetic, causes decomposition into sulphur and triphenylstibine.

If, during the preparation, the current of hydrogen sulphide is continued, the crystals redissolve to a yellowish-red solution, which

probably contains a very labile antimony compound, for, by keeping, the liquid deposits sulphur, and the colourless filtrate, which is free from sulphur, yields pure triphenylstibine by evaporation. C. S.

Action of Grignard Reagents on Ethyl Orthosilicate.

EUGEN KHOTINSKY and BASILE SEREGENKOFF (*Ber.*, 1908, 41, 2946—2953).—When ethyl orthosilicate, dissolved in dry ether, is added gradually to a cold ethereal solution of a Grignard reagent, the mixture heated for ten to fifteen minutes on the water-bath, and decomposed by 50% acetic acid, compounds are obtained of the type $R\cdot Si(OEt)_3$. Only one ethoxyl group can be replaced (compare Tschitschibabin, *Abstr.*, 1905, i, 283). If the heating is prolonged, or if excess of the Grignard reagent is used, complex silicon compounds are formed. In order to prevent the presence of any trace of moisture, the reaction is carried out in a current of dry hydrogen.

Ethyl orthosilicobenzoate, $SiPh(OEt)_3$, b. p. 232—234°, has been prepared by Ladenburg (*Annalen*, 1874, 173, 151); it is hydrolysed by cold hydriodic acid, D 1.7, yielding Ladenburg's silicobenzoic acid, $C_6H_5\cdot SiO_2H$, m. p. 92°, which is also obtained when the reaction product of an excess of magnesium phenyl bromide and ethyl orthosilicate (1 mol.) is decomposed by sulphuric acid. By prolonged heating of the mixture before decomposition by sulphuric acid, trisilicobenzoysilicic acid, $OH\cdot Si(O\cdot SiPhO)_3$, is obtained, which is also found in the high-boiling residue in the preparation of the ortho-ester; it appears to be identical with 'Polis' compound (*Abstr.*, 1886, 618). *Ethyl ortho-2 : 4-dimethylsilicobenzoate*, $C_6H_3Me_2\cdot Si(OEt)_3$, b. p. 268—271°, obtained in a similar manner from magnesium *m*-xylyl iodide, yields, by hydrolysis, the acid, $C_6H_3Me_2\cdot SiO_2H$, m. p. 118—121°. The residue in the distillation of the ester contains *trisilico-xylyloylsilicic acid*, $Si(O\cdot SiO\cdot C_6H_3Me_2)_3\cdot OH$, an infusible, non-volatile, greyish-white powder.

Ethyl α -orthosiliconaphthoate, $C_{10}H_7\cdot Si(OEt)_3$, has b. p. 293—295°, and yields, by hydrolysis with cold hydriodic acid, *α -siliconaphthoic acid*, $C_{10}H_7\cdot SiO_2H$, m. p. 239°, softening at 225°, and, by hydrolysis with cold concentrated sulphuric acid, a *sulpho- α -siliconaphthoic acid*, $SO_3H\cdot C_{10}H_6\cdot SiO_2H$, m. p. 88—90°. *Ethyl β -orthosiliconaphthoate*, $C_{10}H_7\cdot Si(OEt)_3$, has b. p. 270—273°, and the acid, $C_{10}H_7\cdot SiO_2H$, m. p. 248—250°. C. S.

A Zirconium Mercury Double Salt. WALTER PETERS (*Ber.*, 1908, 41, 3173—3175).—Although zirconium tetrachloride and mercury phenyl may be heated in a closed tube or under a pressure of 1 mm. without undergoing change, interaction takes place if the tube is evacuated by a water pump, owing to the presence of water vapour. The white, hygroscopic needles of the salt, $ZrOCl_2\cdot 2HgClPh$, are soluble in ether, and, when submitted to vacuum distillation at 170—210°, give a sublimate of mercury phenyl chloride and a residue of the composition $Zr_3O_4Cl_4\cdot 6HgClPh$. Mercury ethyl and mercury *o*-tolyl are without action. W. R.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Development of General and Physical Chemistry in the last Forty Years. WALTHER NERNST (*Ber.*, 1907, 40, 4617—4626).—A lecture delivered before the German Chemical Society. W. H. G.

Refractometric Researches. JOHAN F. EYKMAN (*Chem. Zentr.*, 1907, ii, 1205—1211; from *Chem. Weekblad*, 1906, 3, 653—662, 685—693, 701—715; 1907, 4, 41—52).—In previous papers (Abstr., 1893, ii, 1; 1894, ii, 173; 1895, ii, 33, 65; 1896, ii, 133; 1897, ii, 1), it has been shown (1) that the molecular dispersion and refraction of atoms and groups of atoms in different compounds can only be regarded as constant if such atoms or groups exert identical functions in the compounds; (2) that the constants for the atoms and groups, and even for the CH_2 increment of homologous series, have not yet been determined with sufficient accuracy, and (3) that it is not possible to find a simple general formula which will render the molecular refractions and dispersions independent of the temperature, and that the Lorenz formula gives the least useful results.

In the present paper, the author deals with (a) the refraction of homologous compounds for different rays of the visible spectrum; (b) with the applicability of Cauchy's formula; (c) with the relation of the dispersion quotients; (d) with the influence of ring formation and (e) of the double carbon linking on dispersion and refraction.

The values of n for the hydrocarbons C_8H_{18} and $\text{C}_{32}\text{H}_{66}$ for the α , β ,

and γ hydrogen rays have been determined, and from them the molecular refractions have been calculated by the formulæ and corrections of Gladstone and Dale, Lorenz, and Eykman. By subtracting the values found for C_8H_{18} from those found for $C_{32}H_{66}$, and dividing the difference by 24, the following molecular refractions for CH_2 were obtained for red light, r : 7.7664 (G. and D.), 4.6101 (L.), 10.253 (E.). The dispersions, also measured from r , were for α , +0.0053; β , +0.1443; γ +0.2238 (G. and D.); α , 0.0031; β , 0.0750; γ , 0.1156 (L.); and α , 0.007; β , 0.179; γ , 0.278 (E.). Starting from octane, by means of these values the corresponding values have been calculated for the two hydrogen atoms at the ends of the chain: r , 2.143; α , 2.144; β , 2.158; γ , 2.172 (G. and D.); r , 2.121; α , 2.120; β , 2.148; γ , 2.170 (L.); and r , 3.727; α , 3.726; β , 3.759; γ , 3.792 (E.); or, starting from methane, 2.12 (G. and D.), 2.0 (L.), and 3.85 (E.).

The constants calculated by means of Cauchy's formula are in good agreement with those found in the region $\gamma - r$. According, however, to the degree in which constitutional functions appear in a compound which abnormally increase the dispersion, Cauchy's formula is more or less inapplicable. The ratio $H_{\beta-\alpha} : H_{\gamma-\alpha}$ according to this formula is 1:1.563. The ratio found for CH_2 is 1:1.572, whereas in the case of ethyl *p*-methoxycinnamate it is 1:1.786, and in that of ethyl cinnamylacrylate is 1:1.828. As the dispersion quotients vary from the normal, so are the molecular refractions abnormally increased and differ from the values calculated from the so-called atomic constants. Since the cause of this variation lies in differences of constitution, it follows that the comparison of different compounds by means of mean atomic refraction values has but little significance.

Contrary to Brühl's opinion, the increment for double linkings is not constant. A comparison of the optical values for *cyclopentane*, *cyclohexane*, *dicyclononane*, and *tricyclodecane* with those of the corresponding paraffin hydrocarbons (C_5-C_{10}) (calculated from octane) shows that, in consequence of ring formation with elimination of H_2 , the increase of refraction for each of several ring formations is nearly the same for each H_2 . The mean values found were 3.03 (G. and D.), 2.20 (L.), and 4.41 (E.), which, with the exception of that calculated by the Lorenz formula, vary considerably from the values for H_2 already given, and from the values for free H_2 , 3.09 (G. and D.), 2.06 (L.), 4.40 (E.), markedly in the case of (L.), and scarcely at all in that of (E.). Ring formation in the cyclic hydrocarbons does not increase the dispersion.

The optical values of a large number of compounds have been determined in order to study the points referred to, and the results are recorded. Variations from the normal values are explained by consideration of the constitution of the different compounds.

E. G.

Magnetic Double Refraction of Organic Liquids. A. COTTON, HENRI MOUTON, and P. WEISS (*Compt. rend.*, 1907, 145, 870—872).—The magnetic double refraction of organic liquids which are active in this respect (Abstr., 1907, ii, 727) varies directly with the square of the

strength of the magnetic field. Nitrobenzene exhibits the phenomenon to a more marked extent than any of the other liquids, and, by employing a great thickness of liquid, the angle measuring the double refraction of this compound exceeds 6° ; the corresponding values for benzene and carbon disulphide under the same conditions are 0.24 and -0.19 respectively of that of nitrobenzene. M. A. W.

Apparatus for the Production of Spark Spectra of Solutions. COMTE ANTOINE DE GRAMONT (*Compt. rend.*, 1907, 145, 1170—1173).—The author has designed an apparatus by means of which the spark spectrum of solutions can be obtained free from lines due to the gold, platinum, or graphite electrodes, or to impurities present in the glass. The method consists in passing the spark between two drops of the liquid fed by two capillary silica tubes inclined at an angle of 45° , which also carry the platinum electrodes. For details of the method, as also for a sketch of the apparatus, the original must be consulted. M. A. W.

Gradual Modification of the First Linear Spectrum of Emission of Mercury. ENRICO CASTELLI (*Phil. Mag.*, 1907, [vi], 14, 784—785).—In taking spectrophotographs of the electric arc in the vapour of mercury in a Uviol lamp, it has been observed that the spectrum lines, whilst remaining constant in position, gradually show a variation in their photochemical action, the lines corresponding with the less refrangible, monochromatic rays producing an increasing, those corresponding with the more refrangible rays a decreasing, effect on orthochromatic plates. Thus the photographic impression of the three lines, of the wave-lengths 3663.3, 3654.9, and 3650.3 Ångström units, nearly completely vanished, whilst that of the lines 5790.49, 5769.45, and 5460.97, which at first were scarcely visible, became the most intense. This change must be ascribed to an alteration in the character of the positive univalent ions, which renders oscillations of higher frequency impossible, but favours vibrations of less wave-length. G. Y.

Use of very low Temperatures for Spectrum Analysis, and for the Study of the Magneto-optical Phenomena of Solutions. JEAN BECQUEREL (*Compt. rend.*, 1907, 145, 1150—1153).—The author has extended the study of the effect of low temperatures on the absorption bands of solids (*ibid.*, 144, 420, 1032, 1336) to the case of solidified solutions with similar results. The large band observed in alcoholic solutions of the nitrates of didymium, neodymium, erbium, or samarium at 20° becomes separated into numerous components, frequently of great clearness and intensity, at -188° . In the case of neodymium nitrate, certain bands show a very slight diminution in wave-length as the concentration of the solution increases, and the groups of bands afforded by equivalent methyl- and ethyl-alcoholic solutions of this salt are very different.

The absorption spectra of solutions at the temperature of liquid air are modified similarly to those of crystals in a magnetic field (compare *Abstr.*, 1906, ii, 317; 1907, ii, 147). M. A. W.

Artificial Dichroism of Blue Rock Salt. H. SIEDENTOPF (*Ber. deut. phys. Ges.*, 1907, 5, 621—623).—When blue rock salt is subjected to pressure at right angles to a hexahedron surface, it exhibits dichroism. This phenomenon is confined to blue and violet colorations of sodium chloride, but always makes its appearance in these cases whether the coloration is of natural or artificial origin. The artificial coloration may be effected by the action of cathode rays.
J. C. P.

Dependence of Colour on Temperature, and the Importance of this Phenomenon for the Theory of Colours and of Radiation. W. J. KURBATOFF (*Chem. Zeit.*, 1907, 31, 1169).—The effect of change of temperature on the colour of about three hundred and fifty substances, both in the solid state and in solution, has been investigated. It is found that the decrease in colour intensity, produced by lowering the temperature, is most marked with substances having a greenish-yellow colour, much less with yellow, orange, red, and purple substances, whilst the change with violet substances is hardly perceptible. The effect produced by the change of temperature is attributed to an alteration in the rate with which various atoms or radicles in the molecule unite and disunite.
W. H. G.

Decoloration of Pigments in the Visible Spectrum. P. P. LAZAREFF (*J. Russ. Phys. Chem. Soc. [Phys. Part]*, 1907, 39, 236—246).—The aim of the research was to trace the connexion existing between the process of decoloration and the optical properties of pigments in the visible spectrum, and to deduce the quantitative relation between the amount of substance decomposed and the wave-length and energy of the incident light. Experiments were made with cyanin, lepidinecyanin, pinacyanol, pinaverdol, quinaldinecyanin, and pinachrome in the form of thin layers of collodion impregnated with the dye, which were decolorised in the region of the absorption bands, but in no other part of the spectrum. An apparatus is described for investigating photometrically various parts of the coloured plate when under the influence of the rays which produce coloration. In this way, the energy absorbed by the plate, as also the amount of substance decomposed, can be estimated, and the following relations are deduced : $\Delta c/c = (\log J_2 - \log J_1) / (\log J_0 - \log J_1)$ and $Q = E[1 - (J_1 + J_2)/2J_0]\Delta t$ (where c = the concentration of the pigment ; Δc , the change in concentration in the time, Δt ; J_0, J_1, J_2 , the relative intensities of the two fields of the spectrophotometer ; J_0 , without a coloured plate ; J_1 , when a coloured plate is first inserted ; J_2 , after an interval, Δt ; Q , the energy absorbed during Δt ; E , the energy falling on the plate). Only a small fraction of E is used for producing the photochemical reaction, most of it only serving to heat the absorbing layer. Curves are drawn showing that, in the region of the absorption bands, the amount of substance decomposed is proportional to the energy absorbed, and is independent of the wave-length and intensity of the incident light.
Z. K.

Protochemical Reactions. II. Gaseous Reactions which are Photochemically Sensitised. A Theory of the Catalytic Influence of Light. FRITZ WEIGERT (*Ann. Physik.*, 1907, [iv], 24, 243—266. Compare Abstr., 1907, ii, 835).—When gaseous systems containing chlorine are exposed to light, molecular complexes are probably produced, which act catalytically as reaction nuclei. At these nuclei, it may be supposed, equilibrium between the reacting gases is established with such rapidity that the further progress of the reaction is conditioned by the rate of diffusion to these nuclei of the remaining portions of the gases. According to this theory, therefore, photochemical reactions may be brought under the category of heterogeneous reactions.

Experimental evidence is brought forward showing that when chlorine is exposed to ultraviolet, violet, or blue light, the production of fog may actually be observed (compare Bevan, Abstr., 1904, ii, 21; Burgess and Chapman, Trans., 1906, 89, 1423).

If the author's view is correct, then reactions which are not themselves affected by light should be catalytically affected by the presence of the reaction nuclei already mentioned. In this connexion, it is shown that the formation of water, the formation of sulphur trioxide, the dissociation of carbonyl chloride, the decomposition of ozone, the Deacon chlorine process, and the formation of ammonia from its elements are reactions which, although not themselves sensitive to light, may be sensitised, that is, catalytically accelerated, by adding chlorine and exposing to light.

The same hypothesis of the formation of reaction nuclei may be extended to solutions, and special reference is made to Kistiakowsky's observations (Abstr., 1901, ii, 58).

The fact that all photochemical reactions yet studied are unimolecular, and the fact that the temperature-coefficient of these reactions is of the same order as the temperature-coefficient of a diffusion process, are regarded as lending support to the conception of photochemical reactions as heterogeneous catalytic reactions. The fact that the activity of chlorine and other substances sensitive to light does not cease immediately when exposure is stopped, is also in favour of the foregoing view that definite nuclei are produced. J. C. P.

The Absolute Distribution of Intensity in the Continuous Background of the Spectra of the Alkali Metals; the Radiation of the Hefner Lamp and of Osmium. F. LEDER (*Ann. Physik.*, 1907, [iv], 24, 305—325).—Photometric measurements of the continuous background of the spectra of the alkali metals by means of a spectrophotometer. The radiations of the Hefner lamp and the 36-volt osmium lamp used as the lights for comparison were also investigated. J. C. P.

Fluorescence and Chemical Constitution. HUGO KAUFFMANN (*Ber.*, 1907, 40, 4547—4555. Largely polemical in reply to Hantzsch, Abstr., 1907, ii, 834).—The author states that potassium quinol-disulphonate fluoresces even in the purest water, and describes a simple apparatus for observing fluorescence. The fluorescence observed with

alkaline solutions of the potassium salt is not due to oxidation, as the same phenomenon is observed in an atmosphere of hydrogen and in sodium carbonate solution. The intensity of the fluorescence decreases with rise of temperature, but is again restored as the solution cools; the operations may be repeated indefinitely with the same results. The fluorescence is not due to impurities, as the salt when prepared by different methods and repeatedly purified still fluoresces. The potassium salts of the sulphonic acids derived from *p*-aminophenol and *p*-phenylenediamine also fluoresce. J. J. S.

Production and Origin of Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1907, [vi], 14, 733—749).—An account is given of previous investigations on the genesis of radium, and a number of new experiments are described. It is now found that over the period of observation (three hundred and five days), radium is formed in actinium preparations at a constant rate. This rate diminishes as the actinium is purified by repeated solution in hydrochloric acid and precipitation with ammonium sulphide, and finally with ammonia, whereby both radium and actinium-*X* are removed, until a preparation is obtained which produces radium extremely slowly, if at all. The active deposit of actinium-*A* and -*B* was concentrated on a platinum plate by keeping this negatively charged in presence of the emanation from an active, solid actinium preparation. After fourteen days, the platinum plate was placed in hydrochloric acid and tested for radium, which was not found in measurable amount, and was certainly less than 1/180 of the amount to be expected if actinium-*B* changed directly into radium. This result, which is in agreement with the constant rate of growth of radium in an actinium solution freed from actinium-*X*, shows conclusively that actinium-*B* does not change directly into radium, but does not exclude the possibility of the existence of a slowly changing product between actinium-*B* and radium.

The results indicate that in ordinary actinium preparations there exists a new substance which is transformed slowly into radium and can be separated chemically both from radium and actinium, since the actinium precipitated by ammonium sulphide contains this parent of radium in excess over the normal, but the filtrate from which the remainder of the actinium may be precipitated by adding ammonia does not contain it even in traces. The observations have not extended over sufficient time to determine if this parent of radium has or has not any direct genetic connexion with actinium.

G. Y.

Certain Properties of the Radium Atom. EDUARD RIECKE (*Chem. Zentr.*, 1907, ii, 1221—1222; from *Nachr. K. Ges. Wiss. Göttingen*, 1907, 162—170).—The disintegration constants of radium can be calculated by three different methods: (1) from the volume of the emanation evolved per second from 1 gram of radium; (2) from the amount of heat developed, and (3) from the quantity of electricity given off in the form of β -rays. Calculating by the first method, Ramsay's determinations lead to the value one thousand and forty years for the average life of a radium atom, whilst by the second method,

Precht's measurements indicate a period of one thousand five hundred and ninety years. The third method, however, according to Wien's determinations, leads to a quite different and probably untrustworthy value.

The amount of energy contained in the radium atom is discussed, and, from the assumption that the atom consists of positive ions and negative electrons, the deduction is made that the energy liberated on disintegration was formerly present in the atom as potential energy.

E. G.

Amount of Radium Emanation in the Atmosphere near the Earth's Surface. A. S. EVE (*Phil. Mag.*, 1907, [vi], 14, 724—733).—The radium emanation in the atmosphere near the earth's surface is measured by passing a known volume of air through cocoanut charcoal, which is afterwards heated, the absorbed emanation being driven over into an electroscope. The absorption of the emanation is complete only if the current of air is extremely slow, but in faster currents the charcoal absorbs the same fraction of the emanation at any given velocity. Hence, the air is passed through the absorption tubes at a convenient rate, and the results obtained compared with those from air which has first been passed through a solution containing a known amount of radium. Four determinations were made in Montreal at different seasons of the year, and the results are given in terms of the amount of radium required to maintain the supply of emanation per cubic metre constant. The smallest value obtained was 24×10^{-12} ; the largest 127×10^{-21} . The probable average value is 80×10^{-12} . The amount of emanation is of the correct order to account for the active deposits of radium-C, which may be collected from the atmosphere on negatively charged wires.

G. Y.

Condensation of Water Vapour in the Presence of Radium Emanation. Madame MARIE CURIE (*Compt. rend.*, 1907, 145, 1145—1147).—The apparent gravitation of the induced radioactivity suspended in a moist gas containing radium emanation (Abstr., 1907, ii, 728) is due to the condensation of the water vapour on the particles of the induced radioactivity, with the formation of a mist, invisible in ordinary light, but visible in the light of the electric arc. The experiments were conducted in small flasks of 35 to 50 c.c. capacity, containing the maximum emanation from a solution of 0.05 gram of radium chloride. In the case when the air in the flask was saturated with water vapour, the initially opaque mist gradually changed into larger drops, and was perceptible after twenty days; for a pressure of water vapour of half the preceding value, the mist persisted for ten days, and a visible mist was also produced when the pressure of the water vapour was reduced to that of 1 cm. of mercury. When, however, the air in the flask was dried by means of phosphoric oxide, no mist was formed by the dry emanation, but the introduction of light petroleum into such a flask led to the formation of a mist of greater intensity than that produced in air saturated with water vapour. When a difference of potential is established between two platinum electrodes in a flask containing radium emanation and air saturated with water vapour, the mist rapidly disappears, but forms again when the

electric field is suppressed. These results show that it is the particles of induced radioactivity (radium-*A*) and not the emanation molecules that form the nuclei for the condensation of the water vapour, since the former particles move rapidly towards the cathode in an electric field, whilst the latter do not suffer any appreciable movement.

M. A. W.

Action of Radium Bromide on Precious Stones of the Family of Aluminides. FRÉD. BORDAS (*Compt. rend.*, 1907, 145, 800—801. Compare Abstr., 1907, ii, 956).—By bringing a tube of radium bromide of very high activity (1,800,000) into direct contact with a corundum, and varying its position every few hours, the coloration can be effected evenly in some days. Darkness is not necessary for the action, which proceeds in daylight. Colourless corundums can be rendered yellow, and the colour of natural topazes and faintly coloured rubies intensified in colour. Artificial rubies are similarly effected. The emanation is inactive. When a colourless corundum in contact with 0.001 gram of radium bromide of high activity, contained in a glass tube, is immersed in liquid nitrogen, it becomes yellow at the end of several days. It is therefore improbable, since potassium is not oxidised by liquid oxygen, that the coloration is due to oxidation of the trace of foreign metallic oxide in the corundum.

E. H.

Coloration of Certain Precious Stones under Radioactive Influences. DANIEL BERTHELOT (*Compt. rend.*, 1907, 145, 818—820. Compare Marcellin Berthelot, Abstr., 1906, ii, 863).—Specimens of certain minerals, placed by Marcellin Berthelot in November, 1906, in the neighbourhood of radiferous barium chloride, were examined in October, 1907, and found to have undergone the following changes. A colourless quartz from la Gardette and a white, cleavable fluorspar were unchanged. A violet, amethystine quartz (containing manganese) from Uruguay, which had been previously decolorised by heating, was re-coloured, and a violet fluorspar from Weardale (Durham) had behaved similarly. The above white, cleavable fluorspar, after soaking in a saturated solution of manganese acetate, becomes faintly rose-coloured in the interior when exposed to radium; the colourless quartz does not exhibit this phenomenon. A green emerald from the Tyrol, decolorised by heating and left in the evolved vapour, when exposed to radium is unchanged, as is also a natural, white emerald. Saturated solutions of manganese acetate and chloride are not changed by radium. The latter experiment disproves the hypothesis which attributes the coloration of glass under the influence of radium to the existence in it of the metal as ions, their discharge by the β -rays, and precipitation of the metal in a finely-divided state. If crystals of potassium sulphate which are coloured by radium radiations are heated to redness, the coloration is no longer produced, probably owing to the destruction of organic impurities as in the case of emeralds. Moreover, some small crystals of potassium sulphate, which had become green after exposure in an india-rubber tube to the action of radium, were decolorised by washing with chloroform, and the latter on evaporation left a green residue.

E. H.

Action of Röntgen Rays on Corundum. FRÉD. BORDAS (*Compt. rend.*, 1907, 145, 874—875).—The coloration of crystallised alumina by exposure to radium bromide (Abstr., 1907, ii, 956; preceding page) is not due to the action of the α -rays, since these were absorbed by the glass envelope containing the bromide. In the present paper, it is shown that the γ -rays are operative in this respect, for colourless corundum becomes distinctly yellow after forty minutes, and topaz coloured after several hours' exposure to the action the Röntgen rays, and these rays are analogous to the γ -rays of radium.

M. A. W.

Radioactivity of Vesuvian Cotunnite. PAOLO ROSSI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 630—638. Compare Zambonini, Abstr., 1907, ii, 663).—Vesuvian cotunnite does not contain radium in appreciable proportion, the substances which render it active being those which cause the so-called induced activity of radium, namely, radium-*D*, radium-*E*, and radium-*F*. That this is the case is shown by the laws governing both the re-activation and the diminution of the β -activity due to radium-*E*, and is confirmed by the separation of polonium by the ordinary methods. A difference is observed between the law of increase of activity of a preparation rendered inactive and that according to which the activity tends to disappear when the radium-*D* substance is separated; this is explained by assuming that radium-*E* is composed of two succeeding compounds in the series of transformations, the second only of these being endowed with β -activity. That other radioactive substances do not seem to accompany cotunnite is shown by the absence of uranium and of emanation, and the corresponding induced activity.

T. H. P.

Radioactivity of the Kissingen Mineral Springs. FELIX JENTZSCH (*Physikal. Zeitsch.*, 1907, 8, 887—890).—The radioactivity of the waters from the Pandur, Max, Rakoczy, Saline, and Schönbörn springs and of the deposits from the last three has been measured at the respective sources.

Air which has been bubbled through the first three spring waters contains a large quantity of a rapidly decaying emanation (thorium emanation?). The induced activity has a decay curve which closely resembles that of the induced thorium activity. These facts point to the presence of thorium salts in the springs. The decay curves of the induced activity from the Saline and Schönbörn sedimentary deposits closely resemble the decay curve of radium.

H. M. D.

The Lithium contained in Radioactive Minerals. Mlle. ELLEN GLEDITSCH (*Compt. rend.*, 1907, 145, 1148).—The transformation of copper into lithium by radium emanation, observed by Cameron and Sir William Ramsay (Trans., 1907, 91, 1593), has led the author, at Madame Curie's suggestion, to investigate radioactive minerals for the presence of copper and lithium, and to determine, if possible, the ratio between the quantities of the two elements when present. In this preliminary note, the result of an examination of Joachimsthal pitchblende is given; the mineral contains a small quantity of lithium

(compare McCoy, *Nature*, Nov. 28th, 1907), the residue containing the alkali metals showing a feeble, although distinct, red lithium line when examined spectroscopically.

M. A. W.

Lancien's Radioactive Molybdenum Compound. AUREL VON BARTAL (*Chem. Zeit.*, 1907, 31, 1156—1157. Compare Lancien, Abstr., 1907, ii, 697).—The author's results are in agreement with those of Szilárd (Abstr., 1907, ii, 731) and Wedekind (*ibid.*, 922).

W. H. G.

Electric Arc between Metal Electrodes. W. G. CADY and H. D. ARNOLD (*Physikal. Zeitsch.*, 1907, 8, 890—906).—The phenomena accompanying the transition from the glow to the arc discharge between electrodes of different metals have been examined. The character of the discharge between iron electrodes in air changes completely when the strength of the current reaches a certain value. With electrodes of 3—6 mm. diameter, the "critical point" corresponds with a current of about 1 ampere. The condition of the discharge with lower currents than this is called the "first stage," that with higher currents the "second stage," of the discharge. Measurements of the loss of weight of the electrodes as well as spectroscopic and thermoelectric observations indicate that, in the "first stage," the anode is not volatilised. The existence of two stages, separated by a critical point, has also been observed in the discharge between copper electrodes in air, and between a carbon cathode and anodes of lead, silver, and carbon in nitrogen under diminished pressures. With anodes of aluminium, zinc, mercury, cadmium, and tin, no indications of the "first stage" were obtainable, and with a bismuth anode the "first stage," although it appears to exist, was too unstable for measurements to be taken. A stable "first stage" was also not obtainable with platinum or iron electrodes when oxygen had been completely removed from the system.

The transition through the "critical point" is accompanied by a fall of potential between the electrodes, and this is ascribed partly to a decrease in opposing thermoelectric force at the anode and partly to the increased conductivity of the vapours in the arc discharge.

With an arc discharge of somewhat less than two amperes between iron electrodes, rotation of the positive end of the arc takes place, this being accompanied by the emission of a whistling sound, which, on increasing the current, gradually passes into a hissing sound, when the rotation ceases. Lecher's observations relating to the continuity of the discharge have been confirmed for high current discharges. Whilst, however, the "first stage" discharge between iron electrodes is continuous, that between silver and copper anodes and a carbon cathode exhibits very definite alternations.

H. M. D.

Experimental Investigation of the High Tension Arc. BRION (*Zeitsch. Elektrochem.*, 1907, 13, 761—786).—The arc studied was produced between two short cylindrical electrodes having a common, vertical axis. The arc was thus horizontal. A magnetic

field at right angles to the direction of the electric current in the arc was produced by means of a solenoid surrounding the electrodes, the arc was thus caused to rotate in a horizontal plane, producing a thin disc of white-hot gas between the electrodes. The whole arrangement was enclosed in a chamber, the walls of which were made of bad conductors of heat, and air was passed upwards through the arc. The electrical properties of the arc were first studied in considerable detail, both with direct and alternating currents. The *E.M.F.* (between the electrodes) required to produce a steady arc is greater the smaller the current. In general, anything which raises the temperature of the electrodes or of the gas between them diminishes the *E.M.F.* required. The *E.M.F.* required with alternating current is greater than with continuous current. Arcs with small current are much less stable than those with larger currents. A large number of experiments were made on the yield of nitric oxide obtained with the rotating arc. Continuous and direct current arcs gave practically the same results; when the velocity of the air was reduced so as to raise the quantity of nitric oxide above about 1.5%, the yield began to diminish. Increasing the diameter of the outer electrode from 16 to 24 cm. increased the yield by about one-fifth. Small currents and strong magnetic fields appear to improve the yield slightly; different methods of surrounding the electrodes had no noticeable effect. The best yields obtained were 57 to 58 grams of nitric acid per kilowatt hour. T. E.

Action of an Incandescent Electric Conductor on the Surrounding Gas. H. COURIOT and JEAN MEUNIER (*Compt. rend.*, 1907, 145, 1161—1163).—The authors have shown previously (Abstr., 1898, i, 545; *Compt. rend.*, 1898, 127, 559) that an inflammable mixture of methane and air is not ignited by an incandescent filament or wire unless the wire fuses and a spark is produced. In explanation of this phenomenon, it is suggested that the incandescent filament attracts the oxygen molecules and repels those of the hydrocarbon in the mixture; the zone of gas therefore surrounding the filament is too poor in the hydrocarbon to be inflammable, and slow or rapid combustion occurs with the formation of water and carbon dioxide (Abstr., 1898, i, 545). When, however, the filament employed is sufficiently voluminous to raise by radiation the temperature of the inflammable mixture beyond the inert zone to about 650°, an explosion occurs, and Hauser has shown recently that, whilst an incandescent ferro-nickel wire 0.3 mm. diameter does not ignite a mixture of air and 9% of methane, a soft iron wire 0.9 mm. diameter caused an explosion in six out of seventeen times. M. A. W.

Cathode Potential Fall and Spectra in some Compound Gases. GEORG GEHLHOFF (*Ann. Physik*, 1907, [iv], 24, 553—578).—When a current of a compound gas is passed continuously through a Geissler tube, it is possible to eliminate the influence of the decomposition and to obtain a constant discharge. It is possible also in this way to obtain spectra of such compound gases as are too rapidly decomposed in a closed Geissler tube. The gases investigated by the

author were ammonia, carbon monoxide, carbon dioxide, methane, nitrogen peroxide, nitric and nitrous oxides.

Capstick's rule, according to which the cathode potential fall of a compound gas is the sum of the separate values calculated for the component atoms, has not been verified. J. C. P.

Aluminium in the Potential Series. CHARLES M. VAN DEVENTER and H. VAN LUMMEL (*Chem. Weekblad*, 1907, 4, 771—781. Compare Neumann, Abstr., 1894, ii, 373).—The chemical behaviour of amalgamated aluminium supports Neumann's view that this metal should be placed to the left of zinc in the potential series. The inactivity of ordinary aluminium in a zinc | acid | aluminium cell is caused by a coating of aluminium oxide, which with amalgamated aluminium is much less stable. The fact that this coating is a leaking insulator explains the abnormal electrical behaviour of ordinary aluminium, a view in accord with the experimental results obtained with such leaking insulators as ethyl and propyl alcohols containing water or acid. A. J. W.

A Gas Generated from Aluminium Electrodes. R. VON HIRSCH and FREDERICK SODDY (*Phil. Mag.*, 1907, [vi], 14, 779—784).—It has been shown (Hirsch, *Physikal. Zeitsch.*, 1907, 8, 461) that when cathode rays are generated by means of an influence machine in pure gases, the relation between the gas pressure, p , and the discharge potential, V , can be represented by the expression: $p^2V = \text{constant}$. This does not hold good for gaseous mixtures, as is now confirmed with mixtures of hydrogen with nitrogen and helium. During the passage of the discharge, a gas is evolved continuously from the electrodes if these are of aluminium. This is a pure gas, as the value 10,292 for p^2V remains satisfactorily constant. As hydrogen has $p^2V = 38,120$, the molecular weight of the new gas must be 4 or some multiple. It is shown to be not identical with helium, water vapour, carbon dioxide, methane, acetylene, cyanogen, or hydrogen cyanide; with the exception of helium, these gases either decompose or polymerise under the influence of the discharge. The new gas is obtained from German-, but not from English-made bulbs, apparently because of the presence of sodium in the aluminium electrodes of the former. An English bulb, having the aluminium electrodes alloyed with sodium on the surface, evolved a gas similar to that obtained from the German bulbs, but containing small amounts of carbon dioxide. It is suggested that the unknown gas may be a modification of hydrogen, as ozone is of oxygen, capable of withstanding the discharge of an influence machine, but decomposed by that of a coil. G. Y.

Nickel Oxide Electrode in the Jungner-Edison Accumulator. JULIAN ZEDNER (*Zeitsch. Elektrochem.*, 1907, 13, 752—755. Compare Abstr., 1906, ii, 65, 595).—Polemical. A criticism of a paper by Foerster (*Zeitsch. Elektrochem.*, 1907, 13, 414). The author maintains that (1) the recently-charged nickel oxide electrode does not contain the oxide, NiO_2 ; (2) the oxide in the recently-charged electrode has

the composition $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and not $\text{Ni}_2\text{O}_3 \cdot 1 \cdot 2\text{H}_2\text{O}$, whilst in the discharged electrode it has the composition $\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, and not $\text{Ni}(\text{OH})_2$.
W. H. G.

Signification of so-called Alternating Current Passivity.

ALBERT LÖB (*Zeitsch. Elektrochem.*, 1907, 13, 789—790. Compare Le Blanc and Schick, Abstr., 1904, ii, 229).—When an alternating current is passed through a solution of potassium cyanide between copper electrodes, the amount of copper which dissolves not only depends on the frequency of the current alternation, the concentration of the solution, and the current density, but also on the surface condition of the electrodes. The diminution in the amount of copper which passes into solution after suitable treatment of the electrodes has been ascribed to a passive condition of the metal, but, as the author shows, the observed facts can be readily explained on the assumption of super-tension phenomena. The ease with which hydrogen is liberated depends on the character of the electrode surface, and, as the super-tension increases, the amount of hydrogen liberated by the current will decrease, and, as a consequence, the amount of copper liberated will increase. Corresponding with the higher value of the super-tension of a zinc electrode, the phenomenon is more pronounced than in the case of copper, whilst with nickel it is less evident by reason of the smaller super-tension value.

The differences between the quantities of crystalline and polished metals which pass into solution are not constant, but decrease with decreasing frequency of alternation. As the time intervals between one current impulse and the subsequent opposing impulse increases, the metal ions are in increasing numbers converted into complex ions. As a consequence of this, super-tension has a gradually diminishing influence on the result of the electrolysis, and hydrogen will be liberated almost exclusively, in spite of the increased voltage necessitated by the existence of super-tension.
H. M. D.

Dulong and Petit's Law. ALBERT WIGAND (*Ann. Physik*, 1907, [iv], 24, 601—606. Compare Abstr., 1907, ii, 70).—A criticism of Laemmel's views (Abstr., 1905, ii, 300; 1907, ii, 530). J. C. P.

Critical Temperatures of Solutions. III. Solutions in Methyl Chloride, Ethyl Ether, and Methyl Alcohol. MIECZYSLAW CENTNERSZWER (*Zeitsch. physikal. Chem.*, 1907, 61, 356—365. Compare Abstr., 1906, ii, 272).—The author has determined the critical temperature of variously concentrated solutions of (1) triphenylmethane, anthracene, phenanthrene, diphenylamine, resorcinol, and benzil in methyl chloride; (2) triphenylmethane, naphthalene, phenanthrene, diphenylamine, resorcinol, and benzil in ethyl ether; (3) potassium iodide in methyl alcohol. Whereas, according to van't Hoff, the "relative molecular elevation of the critical temperature" K/MT_1 (K =molecular elevation of the critical temperature, M =molecular weight of the solvent, T_1 =critical temperature of the solvent) should be a constant, the author's results show that this is only approximately the case. The value of K/MT_1 is to some extent dependent on the

nature of the solvent and of the dissolved substance; it diminishes as the interval between the critical temperatures of the solvent and solute diminishes.

The more exact formula advanced by van Laar has also been considered, but the available data are hardly sufficient for a strict examination of its applicability.

J. C. P.

Condition of Substances in Absolute Sulphuric Acid. ARTHUR HANTZSCH (*Zeitsch. physikal. Chem.*, 1907, 61, 257—312).—Sulphuric acid, which from analysis appears to be 100% strength, may not be cryoscopically pure; that is, its freezing point may be raised by the addition of water or sulphur trioxide. For the purposes of this research, the author has prepared absolute sulphuric acid by starting with an acid containing a little anhydride, and adding weighed quantities of water until the maximum freezing point, $10\cdot46^{\circ}$, was reached. Acid which has this maximum freezing point has also a minimum conductivity $k=0\cdot01$ at 25° .

The latent heat of fusion of sulphuric acid has been determined by Knietsch, at the author's request, and found to be $22\cdot82$ cal. per gram. The mean molecular depression of the freezing point, deduced from the behaviour of trinitrobenzene, trinitrotoluene, dinitromesitylene, trinitrophenol, trichloroacetic acid, phthalic anhydride, anhydrous oxalic acid, methyl sulphate, and tellurium as solutes, is 70° . When this figure is put in van't Hoff's formula, the latent heat of fusion is calculated to be $22\cdot94$ cal., in good agreement with the direct experimental figure just recorded. This agreement shows that the foregoing solutes dissolve in sulphuric acid without decomposition or dissociation; this result is confirmed by the fact that these substances, unlike many others, do not increase the conductivity of the absolute sulphuric acid.

The majority of inorganic and organic substances which dissolve in absolute sulphuric acid without decomposition depress the freezing point to an abnormally great extent, and appear therefore either to be ionised themselves or to unite with the sulphuric acid to form dissociable compounds. Among the substances which exhibit this behaviour are water, sodium, potassium, ammonium, and diazonium acid sulphates, dimethylpyrone, methyl alcohol, ethyl ether, anthraquinone, ethyl acetate, acetic, monochloroacetic, benzoic, malonic, and fumaric acids.

It is noteworthy that in all these cases the molecular weight calculated from the freezing-point depression is about two-thirds of the theoretical value. With the sulphates of bivalent metals, carbamide, succinic, maleic, and phthalic acids, the molecular weight calculated from the freezing-point depression is about half the theoretical value. In other cases, still more abnormal values are observed; the molecular weights calculated for triphenylcarbinol and *p*-tri-iodotriphenylcarbinol are about one-third of the normal values; paraldehyde and metaldehyde are first depolymerised, and then give a value of the molecular weight from one-half to two-thirds of the normal value for acetaldehyde. Nitric acid (not quite absolute) gives a depression which is rather more than double the theoretical depression. In all the cases referred to,

the calculated molecular weight, even where it is abnormally small, is independent of the concentration.

The substances for which abnormally small molecular weights are found by the cryoscopic method have the power of increasing the conductivity of absolute sulphuric acid, and it is found that the specific conductivity of these solutes increases proportionally to the concentration, so that over the range of concentration studied by the author the molecular conductivity is constant.

In explaining the difference from water, in that many electrolytes dissolved in absolute sulphuric acid have constant molecular weight, and constant molecular conductivity, it must be borne in mind that sulphuric acid must itself contain considerable quantities of the ions H^+ and HSO_4' , and that the concentrations of these ions will be markedly affected by the addition of an acid sulphate. The author considers it probable, especially in view of the very high dielectric constant of sulphuric acid, that the acid sulphates are completely dissociated.

The uniform results recorded above for solutions of water, methyl alcohol, &c., lead the author to conclude that all these varied compounds, when dissolved in absolute sulphuric acid, unite with the solvent, forming acid oxonium salts, which are dissociated in the same manner as alkali or ammonium sulphates. Just as a molecule of ammonia may attach itself to a hydrogen ion, forming the ammonium ion NH_4^+ , so it is supposed that a molecule of water may similarly attach itself, forming the "hydronium" ion H_3O^+ , so that a solution of a little water in sulphuric acid is a dissociated solution of hydronium sulphate. A similar explanation is applied in the other cases, so that solutions of methyl alcohol and ethyl ether in absolute sulphuric acid are to be regarded as containing dissociated methylhydronium sulphate and diethylhydronium sulphate. From this point of view, the pyrone derivatives fall into line with the other oxygen compounds. In the case of acetic and other weak organic acids, which in sulphuric acid solution behave themselves cryoscopically and electrically like water or ammonia, it must be supposed that they are forced by the very strong sulphuric acid to assume basic functions. Solutions of acetic and benzoic acids in sulphuric acid are therefore to be regarded as containing dissociated acetyl- and benzoyl-hydronium sulphates. The exceptional behaviour of the triphenylcarbinols, in giving abnormally great depression of the freezing point and abnormally great increase of conductivity, is probably due to their forming sulphates with elimination of water, this water being at once converted into dissociated hydronium sulphate.

When organic acids of greater strength than acetic or benzoic acid are considered, the readiness to form salts with sulphuric acid diminishes, until in the case of trichloroacetic, oxalic, and picric acids, the affinity constants of which cannot be determined directly, the salt-forming power has disappeared; these acids, when dissolved in sulphuric acid, are cryoscopically normal and electrically indifferent. A further class of substances comprises the strongest inorganic acids (such as nitric acid) and the sulphonic acids, which when dissolved in absolute sulphuric acid appear to be dissociated, not as oxonium salts,

but as acids, their dissociating tendency, $\text{XOH} \rightarrow \text{XO}' + \text{H}'$, being so great that even in sulphuric acid they are ionised in the usual way.

The molecular conductivities of the various solutes in absolute sulphuric acid differ much less than they do in water, probably because the variation in the mobilities of the cations is eclipsed by the very great mobility of the ion HSO_4' , which is not only common to the solutes, but is produced also by the dissociation of the solvent (see Hantzsch and Caldwell, *Abstr.*, 1907, ii, 328). J. C. P.

Analysis of the Lowering of the Freezing Point in Physiological Fluids. ERNST TEZNER (*Zeitsch. physiol. Chem.*, 1907, 54, 95—109).—The depression of the freezing point of an aqueous solution containing both electrolyte and non-electrolyte is (very slightly) less than the sum of the depressions caused by the components when by themselves. This difference is attributed to reduction of the dissociation of the electrolyte by the non-electrolyte. G. B.

Transition Temperature of Manganous Chloride. THEODORE W. RICHARDS and FRANZ WREDE (*Zeitsch. physikal. Chem.*, 1907, 61, 313—320. Compare Richards and Churchill, *Abstr.*, 1898, ii, 555; 1899, ii, 354; Richards and Wells, *Abstr.*, 1903, ii, 411; 1906, ii, 727).—Especially pure manganous chloride has been prepared in two ways: (1) by repeated crystallisation of the commercially pure chloride; (2) by repeated crystallisation of the nitrate, precipitation of the nitrate solution by pure ammonium carbonate, and preparation of the chloride from the precipitated carbonate. Both specimens gave the same value, $58.089^\circ \pm 0.005^\circ$ (on the international hydrogen scale), for the transition temperature, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{MnCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$. As manganous chloride is very readily prepared in a pure condition, its transition temperature is very well suited for use as a fixed point in thermometric work.

The authors describe a thermostat which enables them to keep the exposed part of the stem at nearly the same temperature as the thermometer bulb. J. C. P.

Outline of a New System of Thermodynamics. GILBERT NEWTON LEWIS (*Zeitsch. physikal. Chem.*, 1907, 61, 129—165. Compare *Abstr.*, 1901, ii, 639).—It is pointed out that in the development of physical chemistry thermodynamics has been applied along two main lines. Some investigators, for example, Gibbs, Duhem, and Planck, have started from the fundamental equations involving the entropy and the thermodynamic potential. Others, such as van't Hoff, Ostwald, Nernst, and Arrhenius, have adopted the method of applying the cycle process to special problems. The latter unsystematic method of procedure has led to a large number of independent formulæ, largely of an approximate character, and it is the author's aim to develop by ordinary operations a systematic series of thermodynamical equations, which are similar to those at present in use among physical chemists, but are at the same time strictly exact.

The author works with a magnitude which he terms "activity," to

be regarded as the ideal measure of the tendency of a given kind of molecule to depart from the conditions in which it finds itself at any given moment. The "activity" ξ is further related to the "fugacity" ψ (see *loc. cit.*) by the equation $\xi = \psi/RT$. With the help of the foregoing conception, the author reaches a number of exact general equations from which, by approximation, the common formulæ for the change of equilibrium with temperature, for the *E.M.F.* of a reversible cell, for the depression of the freezing point, &c., can be readily deduced. J. C. P.

New Apparatus. Appliance for Maintaining Constant Temperatures in Drying-Ovens. A Fractionating Column. Receiver for Mitscherlich's Apparatus (Phosphorus Distillation). JOSEF HABERMANN (*Zeitsch. anal. Chem.*, 1907, 46, 574—581).—The apparatus for maintaining a constant or predetermined temperature in a drying-oven is similar in shape to an ordinary Soxhlet extractor; there is no siphon tube, however, and a two-way tap is placed on the lower stem, so that the latter may be placed in connexion with the wide upper tube, or the two tubes may be cut off from each other and the upper one connected with an exterior vessel. The lower stem of the apparatus is fixed in an opening at the top of the oven. A mixture of amyl alcohol and ethyl alcohol is placed in the outer jacket of the drying-oven and heated to boiling. The vapour passes up through the side tube of the apparatus into a condenser at the top, and the condensed liquid is collected in the wide upper tube. If the boiling point of the alcoholic mixture be too low to give the required temperature, the collected liquid is run off into the outside vessel until the correct temperature is attained. The tap is then turned, so that the liquid condensed subsequently returns to the oven.

The fractionating column described is also of similar shape. A condenser is provided inside the top of the wide part of the apparatus, and the distilled liquid is collected at the lower part, being returned to the distillation flask or run off as desired through a two-way tap. A thermometer is placed in the side tube of the apparatus so that the temperature of the vapour can be ascertained.

The receiver consists of a flask fitted with a double-bored cork. The end of the condenser passes through one hole in the cork, whilst a delivery tube is fitted in the other. In distilling substances which yield distillates having a disagreeable odour, for instance, in testing for phosphorus poisoning, the distillate is collected in the flask while the gases pass through the flask and out of the delivery tube into a kind of filter-pump. The latter receives the waste water from the condenser, and the gases are thus carried away. W. P. S.

The Method of Limiting Densities, and its Application to the Atomic Weight of Nitrogen. PHILIPPE A. GUYE (*Compt. rend.*, 1907, 145, 1164—1166. Compare *Abstr.*, 1907, ii, 437, 605).—A reply to D. Berthelot (compare *Abstr.*, 1907, ii, 154, 155, 668, 680, 740). The author maintains that the mean value 14.005 for the atomic weight of nitrogen deduced by Berthelot from the limiting

densities of nitrogen, nitrous and nitric oxides is untrustworthy, since the values for the atomic weight of the element diminish as the critical temperatures of the gases from which they are calculated increase, as is shown in the following table :

Gas.	N ₂ .	NO.	N ₂ O.	NH ₃ .
Atomic weight of N.....	14.008	14.006	13.999	13.992
Absolute critical temperature	128°	179°	309—312°	425°

The value $N = 14.010$, obtained as the mean of six independent determinations by chemical analysis of nitrous and nitric oxides (limits 14.007 and 14.015), is more exact (compare Abstr., 1906, ii, 349).
M. A. W.

Adsorption and Occlusion. Nature of the so-called Solid Phase. MORRIS W. TRAVERS (*Zeitsch. physikal. Chem.*, 1907, 61, 241—248. Compare Abstr., 1906, ii, 730).—A criticism of some points raised in Freundlich's papers (Abstr., 1907, ii, 155, 534).

The author is strongly of opinion that the term "solid solution" should be confined to isomorphous mixtures, that is, homogeneous mixtures which are themselves crystalline, and the components of which have similar, if not the same, crystalline form. Adsorption and occlusion, apart from the formation of isomorphous mixtures and from the mechanical enclosure of the substance which appears to be dissolved, are interpreted as the formation of a solution in an amorphous substance. Such substances are practically liquid, and appear to be solid only because they have a certain mechanical rigidity.
J. C. P.

Adsorption and Occlusion. HERBERT FREUNDLICH (*Zeitsch. physikal. Chem.*, 1907, 61, 249—254).—A reply to Travers (preceding abstract). Whilst the latter considers that adsorption consists in a process of solution modified by surface phenomena, the author holds the view that surface condensation is the main element in adsorption, and that the formation of solid solutions is a secondary effect.

It is pointed out that the variation in the adsorption of carbon dioxide by charcoal with temperature (studied by Travers) is very similar to the corresponding variation in the adsorption of acetic acid by charcoal in aqueous solution (studied by the author).
J. C. P.

Dissociation by Adsorbing Substances of the Compounds formed by Basic and Acidic Dyes. LOUIS PELET-JOLIVET (*Compt. rend.*, 1907, 145, 1182—1183).—Crystal ponceau and methylene-blue form a compound containing 1 mol. of the former to 2 mols. of the latter (compare Abstr., 1904, ii, 794), and similar compounds have been prepared containing crystal ponceau, 1 mol., and magenta or safranine, 2 mols., or naphthol yellow S, 1 mol., and of methylene-blue, magenta, or safranine, 2 mols. (compare Seyewetz, Abstr., 1900, i, 356). These compounds are much less soluble in water than either of the constituents, the solubility of the compound of ponceau and methylene-blue is 0.201 gram per litre at 100°, or 0.045 gram per litre at 15°, and the solubilities at 15° of the

compound of methylene-blue with eosin and naphthol yellow S are 0.158 and 0.042 gram per litre respectively. Certain adsorbent substances, such as wool, animal charcoal, or precipitated and calcined silica, cause dissociation of aqueous solutions of these compounds, and absorb the basic constituent if the original solution is neutral or alkaline and the acidic constituent if the original solution is acid. This phenomenon is readily explained by the colloidal theory of dyeing, according to which the adsorbent substances are in the colloidal state, and are negatively charged and absorb the positive or basic constituent in neutral or alkaline solution, and positively charged and absorb the negative or acid constituent in acid solution. The behaviour of the compound of eosin and methylene-blue as a stain for certain bacilli can be explained similarly (compare Marino, *Abstr.*, 1906, ii, 189); the nucleus of the cell in the colloidal state is positively charged and absorbs the eosin, and the remainder of the protoplasm, also in the colloidal state, is negatively charged and absorbs the methylene-blue. M. A. W.

Dissociation as Measured by Lowering of Freezing Point and by Electrical Conductivity. Bearing on the Hydrate Theory. The Approximate Composition of the Hydrates formed by a Number of Electrolytes. XIX. HARRY C. JONES and J. N. PEARCE (*Amer. Chem. J.*, 1907, 38, 683—743).—A summary of the evidence so far obtained for the existence of hydrates in aqueous solutions is first given, most of which is recorded in *Abstr.*, 1905, ii, 8, 73, 445, 509, 687, 794; 1906, ii, 66, 327, 737, 827; 1907, ii, 147, 211, 212, 438, so far as the contributions of Jones and his co-workers are concerned.

In the present investigations, attention was directed to determining (a) the relation between the degree of dissociation as measured by (1) freezing-point methods and (2) conductivity methods; (b) the extent to which conductivity of a solution, and the relative velocities of different ions, are influenced by hydration of ions, and (c) the trustworthiness of conductivity methods for measurement of the degree of dissociation. For this purpose, solutions of fifteen salts and three acids have been systematically studied for concentrations ranging from 0.01 to 2.0 normal. Details of the methods of investigation and the modes of expressing the results are given in the original, together with full tabular statements of the experimental data obtained. Only the general conclusions arrived at can be given.

The molecular lowerings of freezing point in all cases pass through a well-marked minimum. The molecular lowerings, calculated from conductivity measurements of dissociation, decrease regularly with increase of concentration. The value of the molecular lowering varies directly with the number of mols. of water with which the salt under investigation crystallises from water.

The total amount of combined water decreases with increase in concentration to a minimum, and then increases regularly with the concentration. The amount of water in combination with 1 mol. of a salt is large in dilute solutions, where ions predominate, and decreases

as dissociation is lowered, becoming nearly constant at greater concentration.

The hydrating of a salt is essentially a function of the cation, and is an inverse function of the atomic volume of the latter. Those cations which possess the greatest migration velocities have the least hydrating powers, and the converse of this is also true.

The effect of the hydration of those ions with small atomic volumes on their migration velocity is greater than that of the small hydration of those possessing large atomic volumes on their migration velocity.

In all the cases examined, it was found that the dissociation in dilute solution, as measured by the conductivity method, is less than that calculated from the lowering of freezing point, and this difference is the greater the more dilute the solutions examined are, so that it is probably connected with the increase in friction between the solvent and ion due to the greater surface presented by the latter as it becomes more hydrated at greater dilution. Comparable results can only be expected by the two methods in the cases of salts which crystallise from solution in the anhydrous condition, but in cases of this type comparable values were only obtained at concentrations near to that at which molecular lowering is at a minimum.

T. A. H.

Semi-Electrolytes. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1907, 5, 497—510).—By the combination of two equations shown in a previous paper (Abstr., 1907, ii, 527) to hold for certain weak electrolytes, the equation (1) $\gamma = A \log(1 - \gamma)^{-1}$, where γ is the coefficient of ionisation, is shown to hold within wide limits of dilution for acetic acid and ammonia, and A has the same numerical value for the two electrolytes in corresponding dilution, and is constant up to fairly high dilutions. Consequently, for acetic acid and ammonia, the equation (2) $\gamma/\gamma' = \log(1 - \gamma)^{-1}/\log(1 - \gamma')^{-1}$ (where γ and γ' are the respective coefficients of ionisation in corresponding dilution) ought to hold, and this is shown to be the case. Putting $\gamma = \lambda/\lambda_{\infty}$, where λ and λ_{∞} represent the molecular conductivities at a particular dilution and at infinite dilution respectively, equation (1) may be written in the form $\lambda = A \lambda_{\infty} \log[\lambda_{\infty}/(\lambda_{\infty} - \lambda)]$, and by means of this equation λ_{∞} can be calculated for semi-electrolytes from the observed values of λ and the values of A obtained for acetic acid and ammonia. λ_{∞} has been calculated in this way for a number of weak acids and bases, and the values obtained are in satisfactory agreement with those given by the usual methods.

G. S.

Diffusion of Electrolytes in Aqueous Solutions and in Gelatin. B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 655—657).—The formation of two separate zones of precipitate when, for example, barium chloride and silver sulphate solutions are allowed to diffuse into the opposite ends of a column of gelatin is explained by Buscaglioni and Purgotti (*Atti R. Ist. Bot. Pavia*, 1905, N.S., 11) as being due to the fact that the ions in solution obey Bunsen's law for the diffusion of gases. Bruni and Vanzetti (Abstr., 1907, ii, 74), on the other hand, regard the phenomenon as one of supersaturation.

The author has made similar experiments, using, as the diffusing salts, ammonium, potassium, rubidium, or caesium chloride in 4*N*-solution, on the one side, and semi-normal sodium platinichloride on the other. With ammonium and potassium chlorides, the precipitated platinichloride is deposited at the same position in the gelatin column, and the same is the case with rubidium and caesium chlorides, in spite of the varying ionic velocities of the different metals. Buscaglioni and Purgotti's hypothesis is hence untenable. T. H. P.

Comparison of Acids and Pseudo-Acids in Pyridine Solution. ARTHUR HANTZSCH and KENNETH S. CALDWELL (*Zeitsch. physikal. Chem.*, 1907, 61, 227—240).—The authors have studied the conductivity of a number of true acids, strong and weak, and of a number of pseudo-acids in pyridine solution. The order of the true acids, arranged according to the conductivity of their pyridine solutions, is roughly the same as when they are arranged according to the magnitude of their affinity constants in aqueous solution. Pseudo-acids, compared among themselves, exhibit an exactly analogous behaviour. When, however, the conductivity of a true acid in pyridine is compared with that of a pseudo-acid which is of approximately the same strength in aqueous solution, it is found that the conductivity of the pseudo-acid is very much greater. This result has been verified in the case of nitroform and trinitrophenol in comparison with oxalic acid, also in the case of pseudo-acids which are of medium strength in aqueous solution (such as nitrourethane, dinitrophenol, benzoyleyanamide, "saccharin") and in the case of weak or very weak pseudo-acids (such as mononitrophenol, *p*-benzoquinoneoxime, cyanuric acid, methyl-nitroamine) in comparison with mediumly strong to weak monocarboxylic acids. Only in the case of the pseudo-acid, nitromethane, has no such behaviour been observed.

The conclusion may be drawn that when a hydrogen compound dissolved in pyridine conducts much better than a true acid, which in water is of about the same strength, then the former must be a pseudo-acid. Thus it is certain that hexanitrodiphenylamine undergoes isomeric change as a pseudo-acid. J. C. P.

Conductivity of the Sodium Salts of the Isomeric Hydroxybenzoic Acids. The Question of the Mobilities of Isomeric Anions. HEINRICH LEY and O. ERLER (*Zeitsch. Elektrochem.*, 1907, 13, 797—799).—The conductivity of sodium salicylate is at any given dilution greater than that of sodium *m*-hydroxybenzoate or sodium *p*-hydroxybenzoate. This cannot be due to extra dissociation of the phenolic hydrogen atom in salicylic acid, for experiments have shown that of the three disodium salts that of the ortho-acid is hydrolysed to the greatest extent, so that the second hydrogen atom of this acid is only very slightly acidic in character.

The superior conductivity of sodium salicylate is probably due to the greater mobility of the ortho-anion, this again being probably due to the greater degree of hydration of the two isomeric anions. In this connexion, it is noteworthy that the sodium salts of *o*- and *p*-methoxybenzoic acids have practically equal conductivities. J. C. P.

Polymorphism of Liquids. DANIEL VORLÄNDER (*Ber.*, 1907, 40, 4527—4537. Compare Abstr., 1907, ii, 441, 442).—The crystalline liquids obtained when various unsaturated compounds are fused cannot be chemically isomeric with the crystalline solid or amorphous liquid phases, since acetylene derivatives, such as the acetyl and benzoyl derivatives of dihydroxytolane, yield crystalline liquids like the corresponding stilbene compounds, and the possibility of isomerism, even of stereoisomerism, is excluded in these compounds.

The *dibenzoyl* derivative crystallises from a mixture of benzene and alcohol in colourless prisms, m. p. 214° and 254° . Measurements of dielectric constants show that the values are practically the same for the two liquid phases of ethyl anisylideneaminocinnamate, although discontinuities at the two transition points are observed (compare Abegg and Seitz, Abstr., 1899, ii, 623).

Various crystallographic properties of crystalline liquids can be ascertained and made use of in determining the crystalline system to which the liquid belongs. The behaviour of the liquids in converging polarised light points to their being uniaxial, a view which is supported in different ways. The liquid crystals have thus a higher degree of symmetry than the solid, crystalline phases of the same substances, which are mainly monoclinic or rhombic. The following esters: ethyl azoxybenzoate, methyl, ethyl and propyl azoxycinnamates, ethyl bromoazoxycinnamate, ethyl azocinnamate, ethyl anisylideneaminocinnamate, ethyl piperonylideneaminocinnamate, ethyl phenylbenzylaminocinnamate, ethyl anisoleazocinnamate, ethyl acetoxybenzeneazocinnamate form liquid plates and rods, and in a narrow sense of the word are thus isomorphous. The cinnamates are characterised by the readiness with which they crystallise. The five last-named substances are isodimorphous, yielding two enantiotropic, crystalline liquid modifications. The benzoate of the ester of hydroxybenzylideneaminocinnamate forms three crystalline, liquid phases. Methoxy- and phenyl derivatives of aromatic substances closely resemble one another in the crystalline, liquid state, although there are a few exceptions.

The formation of liquid crystals appears to be characteristic of para-substituted derivatives, and several examples are cited which show that the property may be made use of for determining the constitution of certain benzene derivatives. J. J. S.

Reciprocal Solubility of Oil of Turpentine and Methyl Sulphate. M. DUBROCA (*J. Chim. phys.*, 1907, 5, 463—487).—The determinations were made by Alexéeff's method at approximately atmospheric pressure, the temperatures at which the milkiness (due to partial separation of the components) just appeared on cooling slowly being observed. The methyl sulphate was purified by repeated distillation, and, although slightly acid, gave very little colour, and only a slight elevation of temperature on mixing with oil of turpentine; its density and refractive index at 15° and 25° are given.

The curve representing the results, obtained by plotting the composition of the mixture against the temperatures at which separation into two phases commences, is of the parabolic form usual

for partially miscible, binary liquids. The components are completely miscible in all proportions above 108.2° .

The effect on the miscibility of the components of the presence of sulphuric acid in the methyl sulphate, of the period during which the mixture has been kept in sealed tubes before the observations, and of the age of the turpentine has been investigated; the addition of a little petroleum to the binary mixture has the same effect as the employment of a specimen of oil of turpentine fresher than that to which the petroleum was added. G. S.

Colloidal Solutions. THE SVEDBERG (*Nova Acta Soc. Sci. Upsala*, 1907, [iv], 2, No. 1, 1—160. Compare Abstr., 1906, ii, 330; 1907, ii, 17, 160, 529, 535, 536).—The paper contains a complete account of the author's work, much of which has been already published.

New experiments on the effect of the oscillatory discharge with large capacities show that the yield of colloid increases with the capacity when the current strength is constant.

The proportion of carbon in the colloidal solutions of various metals, prepared by pulverisation in ethyl ether under constant electrical conditions, has been examined. For the same metal, the carbon content of the colloid is proportional to the specific decomposition of the medium. For different metals, the proportion of carbon increases with the decomposition of the medium, but the increase is much slower in the former case. With an oscillatory discharge, the proportion of carbon is very much smaller than with a direct current discharge. Using the oscillatory discharge and a capacity of about 0.1 micro-farad, the percentage of carbon in the separated metal is about 0.2 in the case of a metal which is readily pulverised, and about 2.0 in the case of a metal pulverised with difficulty. With larger capacities, colloidal metals, which are practically free from carbon, may be expected to be obtained.

Experiments on colloid formation in liquid methane cooled by liquid air show that the phenomenon of cathodic pulverisation is the same at this low temperature as it is at the ordinary temperature. The colloidal solution of sodium has a red colour; that of potassium is bluish.

After a critical examination of the many theories which have been put forward in regard to the nature of colloidal solutions, the author arrives at the conclusion that factors other than electrical charges and capillary forces play an important part in such systems. From a study of the behaviour of an inactive colloidal substance of small solution pressure (platinum) in a medium of small ionising power (ethyl ether), it is found that such solutions have a definite critical temperature (coagulation temperature), and that addition of a small quantity of a foreign substance raises the critical temperature. The curves which express the dependence of the critical temperature on the concentration of the added substance are asymptotic to the negative temperature axis.

Some observations relating to the Brownian movement of the colloidal particles indicate that the cessation of this movement on the addition of electrolytes is not due to any specific action of the ions,

but to the increasing size of the particles. By gradual addition of aluminium sulphate to an aqueous solution of colloidal silver, the direction of motion of the particles in an electric field can be reversed. Corresponding with this change, the velocity of the particles diminishes as the isoelectric point is approached, but the amplitude of the Brownian movement remains unchanged, and the author concludes that this movement cannot be due to electrical forces.

H. M. D.

Influence of the Reaction of the Medium on the Size of Colloidal Granules. ANDRÉ MAYER, GUILLAUME SCHAEFFER, and E. TERROINE (*Compt. rend.*, 1907, 145, 918—920).—The authors have examined a large number of colloidal solutions, including colloidal metals (gold, silver, platinum), inorganic colloids (arsenic trisulphide, mercuric sulphide), and organic colloids (soaps, dyes and indicators, alkaloids, starch, albumin). They find that the size of the colloidal granules is increased by the addition of a trace of acid to negative colloidal solutions, or of a trace of alkali to positive colloidal solutions, whilst the addition of acid to the positive, or alkali to the negative, colloidal solutions causes a diminution in the size of the granules. Further, precipitation of a colloidal solution is induced by dialysing a negative solution containing an excess of alkali, or a positive solution containing an excess of acid.

M. A. W.

Investigation of Colloids by the Filtration Method. HEINRICH BECHHOLD (*Zeitsch. physikal. Chem.*, 1907, 60, 257—318; *Biochem. Zeitsch.*, 1907, 6, 379—408).—The author describes in detail a method which has been worked at by him which permits of the separation of colloids in solution from the solvent, as well as the separation of mixtures of colloids of different-sized particles from one another by fractional filtration.

The filter material is made to impregnate filter paper in a special apparatus, and when in use the impregnated paper is supported by fine nickel gauze. The pressures used are from two to five atmospheres, and in one form of the machine a stirrer is used, by means of which the material to be filtered is kept violently agitated. The filter materials employed were gelatin of various concentrations, formalised gelatin, and acetic collodion solidified by washing in water.

The "fineness" of the filter is dependent upon the concentration of the gelatin. It was established that gelatin-filters have pores of unequal size, and that the particles in a colloidal solution are mostly of unequal size. Data are given with regard to a number of colloids, both organic and inorganic, in their relationship to gelatin-filters (Prussian blue, platinum, arsenious sulphide, gold, ferric hydroxide, silicic acid, collargol, lysargin, bismon, hæmoglobin, serum-albumin, globulin, gelatin, hæmatin, sodium lysalbinat, dextrin, litmus, chlorophyll).

A mixture of albumoses was separated into its constituents by fractional filtration. Many substances, especially those physiologically active, such as rennin, arachnolysin, staphylolysin, are strongly

adsorbed by the material of the filter, others slightly so, for instance, albumins, albumoses, hæmoglobin, anti-rennin, and diphtheria-toxin. Dissolved colloids can absorb other dissolved colloids. "Protective" colloids have a favourable influence on the filtration of inorganic colloids by diminishing friction. It is shown that the possibility of filtering certain mixtures is dependent on the sequence in which the constituents are brought together. The author calls this the "sequence phenomenon." A mixture of Prussian-blue, serum-albumin, and oxalic acid, in the order given, passes partially through a gelatin-filter, whilst amixture in sequence, Prussian-blue, oxalic acid, and serum-albumin, does not. In many cases, dialysis may be replaced by gelatin filtration, but not universally so. The great advantage of a filtration method over dialysis consists in that the solutions do not become dilute, and that the apparatus may readily be sterilised and kept sterile. The sequence of the examined colloids as regards the size of the particles, when grouped according to the filtration method, agrees with what has been deduced from theoretical considerations and the use of the ultra-microscope.

Gelatin-filters can be used for obtaining sterile filtrates. The author shows by the filtration method that in the case of a non-poisonous disinfectant (tetrachlorodiphenol), although powerfully active against broth cultures, its activity in internal antisepsis is dependent on the fact that the blood-serum combines with the disinfectant, the bacterial growths being not shown any preference in the matter. G. S. W.

Diastatic Function of Colloids. JACQUES DUCLAUX (*Compt. rend.*, 1907, 145, 802—804).—From the fact that the diastatic action (oxidation of quinol, decomposition of hydrogen peroxide) of certain salts in aqueous solution is the more energetic the weaker the acid forming the salt, that is, the more the latter is hydrolysed, it has been deduced that the active part of the dissolved salt is that which is hydrolysed. The author has studied the decomposition of hydrogen peroxide by Graham's colloidal solution of ferric hydroxide, $(\text{Fe}_2\text{Cl}_6, n\text{Fe}_2\text{O}_3)$, which is completely hydrolysed when n exceeds 40, and then consists of micro-cells of $\text{Fe}_2\text{Cl}_6, n\text{Fe}_2\text{O}_3$ in equilibrium with an intercellular, very dilute solution of hydrogen chloride containing no appreciable quantity of iron. The properties of the solution vary with the value of n , but its catalytic activity bears no fixed relation to the total quantity of iron present, even when completely hydrolysed. As n increases, the reaction-constant k increases in almost the same proportion, and is not rendered constant by multiplying by numbers expressing the acidity of the solution. But when the values of k are calculated, not from the total quantity of iron, but from that present as chloride, that is, the part which is physically and chemically "active," and corrected for the greater or lesser acidity of the liquid, concordant results are obtained for a large number of different colloidal ferric solutions. Thus it is the "active" part of the colloid which determines its catalytic power. The completely hydrolysed solution contains no iron in the intercellular liquid, but the cells contain non-hydrolysed ferric chloride, which constitutes the "active"

part, thus *the hydrolysed part of the ferric salt does not take part in the catalysis*. The latter deduction is confirmed by the fact that the catalytic activity of iron in freshly-prepared acid solutions (that is, non-hydrolysed) of ferric chloride is approximately the same as that in the colloidal solutions. The author concludes that the catalytic power is a property of the ion. The "active" part of these colloidal solutions is very sensitive to impurities, and their catalytic power is greatly weakened by addition of small quantities of such salts as potassium sulphate or ferrocyanide. E. H.

Calculation of Hydrocarbon Equilibria. H. VON WARTENBERG (*Zeitsch. physikal. Chem.*, 1907, 61, 366—372).—In reference to a recent paper by Sand (Abstr., 1907, ii, 814), it is pointed out that on the basis of Nernst's theory (Abstr., 1906, ii, 727) it is possible to predict the general course of organic reactions and the order of magnitude of the equilibrium constants. The paper contains a number of examples of the application of the said theory.

J. O. P.

Kinetics and Catalysis of the Hydrogen Peroxide-Thio-sulphate Reaction. EMIL ABEL (*Monatsh.*, 1907, 28, 1239—1312).—The velocity constant of the reaction between hydrogen peroxide and a thiosulphate in acid solution, which is represented by the equation: $\text{H}_2\text{O}_2 + 2\text{S}_2\text{O}_3'' + 2\text{H}^+ = \text{S}_4\text{O}_6'' + 2\text{H}_2\text{O}$, when calculated according to the velocity equation for bimolecular reactions:

$$dx/dt = k[(\text{H}_2\text{O}_2) - x][(\text{Na}_2\text{S}_2\text{O}_3) - x],$$

is found to be, as the average of a large number of determinations, $k = 1.53$. The reaction is accelerated by hydrogen ions. From these kinetic results, the conclusion is drawn that during the reaction there is an intermediate separation of electrically neutral S_2O_3 , which determines the velocity of the reaction. Iodine ions act catalytically on this intermediate stage of the reaction. The resulting acceleration, calculated according to the principle of co-existence from the separate, measurable parts of the reaction, is in good agreement with the experimental results. This constitutes the first case of the calculation of the catalytic acceleration of a reaction, which takes place even in the absence of a catalyst with measurable velocity.

The catalytic acceleration of the decomposition of hydrogen peroxide by iodine ions takes place, as was to be expected from theoretical considerations, in acetic acid solution, provided this contains sufficient acetate, in consequence of the diminished concentration of the hydrogen ions, and is in complete agreement with the results obtained by Bredig and Walton with neutral solutions.

The catalysis of the hydrogen peroxide-thiosulphate reaction also takes place equally well in acetic acid solution in presence of acetates. It follows (a) that the thiosulphate is oxidised with great velocity by hypiodite directly to tetrathionate according to the equation: $\text{IO}' + 2\text{S}_2\text{O}_3'' + 2\text{H}^+ = \text{S}_4\text{O}_6'' + \text{I}' + \text{H}_2\text{O}$; (b) that the catalysis of the hydrogen peroxide-thiosulphate reaction by iodine ions does not necessarily require the intermediate separation of iodine, cases possibly occurring in which the reaction leads directly to the

formation of the tetrathionate, that of the intermediate product, iodine, being completely suppressed, and (c) that the decomposition of hydrogen peroxide by the catalytic action of iodine ions is a catalysis of an intermediate reaction, the first stage being directly detected by the reaction with thiosulphate.

The addition of molybdic acid, even in the smallest concentrations, produces a far-reaching change in the nature of the reaction between hydrogen peroxide and thiosulphates. G. Y.

Esterification of Cinnamic and Hydrocinnamic Acids by Means of Alcoholic Hydrogen Chloride. ANTON KAILAN (*Monatsh.*, 1907, 28, 1137—1161. Compare Abstr., 1906, ii, 659; 1907, i, 849; ii, 158, 242, 243, 674, 675, 676, 853).—The velocity of esterification of cinnamic and hydrocinnamic acids by means of hydrogen chloride and alcohol, containing only small amounts of water, is proportional to the concentration of the hydrogen chloride. The relation of the velocity constants to the concentrations of the water and hydrogen chloride are expressed by the equations: for cinnamic acid, $1/k = 0.665 + 4.876/c - 1.678/c^2 + (2.911 - 3.212/c + 4.358/c^2)w + (-27.54 + 31.78/c - 2.284/c^2)w^2$, and for hydrocinnamic acid, $1/k = 0.0601 + 0.08337/c + 0.005244/c^2 + (-0.2169 + 0.2494/c + 0.03065/c^2)w + (-0.4866 + 0.4962/c)w^2$, which apply to solutions having the concentration of the water, $w = 0.3 - 1.3$, and of hydrogen chloride, $c = 0.15 - 0.66$. The esterification of cinnamic acid is greatly retarded by the α -ethylene linking, as is shown by the following values obtained for k . Cinnamic acid: $c = 0.1667$, $w = 0.052$, $k = 3.61$; $c = 0.333$, $w = 0.052$, $k = 3.41$; $c = 0.6667$, $w = 0.052$, $k = 3.52$. Hydrocinnamic acid, with the same values for c and w , has $k = 128.8, 132.2$, and 135.2 respectively.

In spite of the differences in velocity of esterification, the behaviour of cinnamic and hydrocinnamic acids is analogous to that of the acids previously studied. G. Y.

Esterification of Nitrocinnamic Acids by Means of Alcoholic Hydrogen Chloride. ANTON KAILAN (*Monatsh.*, 1907, 28, 1163—1186. Compare preceding abstract).—The velocity of esterification of *o*- and *m*-nitrocinnamic acids by means of hydrogen chloride in alcoholic solution, containing at most only small amounts of water, is found to be proportional to the concentration of the hydrogen chloride, but that of *p*-nitrocinnamic acid appears to increase more rapidly than the hydrogen chloride concentration. The last point, however, is doubtful, as the accuracy of the determination of the velocity of esterification cannot be altogether depended on in consequence of the sparing solubility of the *p*-nitro-acid. The esterification of the *m*-nitro-acid in presence of much water has also been studied, and the constant expressed as a function of the concentrations of the water and hydrogen chloride by the equation $1/k = 1.398 + 2.768/c + 1.04078/c^2 + (13.62 - 16.81/c + 5.469/c^2)w + (-28.38 + 32.42/c - 3.386/c^2)w^2$, which applies to solutions having the concentration of the water, $w = 0.02 - 1.3$, and that of the hydrogen chloride, $c = 0.16 - 0.66$.

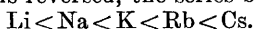
The introduction of the nitro-group into cinnamic acid accelerates the esterification to the smallest extent in the *m*-, and in the *o*-probably to a greater extent than in the *p*-position. At 25°, one litre of 99.97% alcohol dissolves 0.0107 gram-mol. of the *o*-, 0.0519 gram-mol. of the *m*-, and 0.0050 gram-mol. of the *p*-nitro-acid. G. Y.

Esterification of *p*-Mandelic Acid and Benzoylformic Acid. ANTON KAILAN (*Monatsh.*, 1907, 28, 1187—1209. Compare preceding abstract).—The velocity of esterification of mandelic acid by means of hydrogen chloride and alcohol at 25° increases approximately proportionally to the concentration of the hydrogen chloride if not more than traces of water are present, but more rapidly than the hydrogen chloride concentration in presence of much water. As ethyl mandelate is hydrolysed on titration with baryta, the method employed for the study of the velocity of esterification has in this case been modified by the use of ammonia instead of baryta for the titrations. The relation between the velocity constant and the concentrations of the water and hydrogen chloride are expressed by the equation: $1/k = 0.0999 + 0.1508/c - 0.003324/c^2 + (-0.2073 + 0.04395/c + 0.1236/c^2)w + (-0.7412 + 1.017/c - 0.0619/c^2)w^2$, which applies to solutions having $w = 0.01 - 1.3$ and $c = 0.16 - 0.71$. The constant for the velocity of esterification for mandelic acid in alcohol in absence of a catalyst increases with the mandelic acid concentration if calculated by means of the equation for unimolecular reactions, but decreases if calculated for a bimolecular reaction. It is shown, also, that, in absence of a catalyst, the addition of water has little effect on the velocity of esterification.

The constant of velocity of esterification of benzoylformic acid could be determined only approximately, as the ester is partially hydrolysed on titration with either baryta or ammonia; the results obtained show that the presence of a carbonyl group in the α -position has a much greater retarding influence on the esterification by means of hydrogen chloride and alcohol than has an α -hydroxyl.

The simultaneous esterification of benzoic and cinnamic acids by means of hydrogen chloride and alcohol has been studied. It is found that these two acids do not interfere with the velocity of esterification of each other. G. Y.

Action of Normal Salts. RUDOLF HÖBER (*Beitr. chem. Physiol. Path.*, 1907, 11, 35—64).—An examination of the effect of normal salts on the precipitation of egg-albumin, serum-albumin, and lecithin, and on the catalysis of methyl and ethyl acetates by acid and by alkali. The results obtained by catalysis are quite regular; for instance, the chlorides of the alkali metals accelerate the acid catalysis in the order of their atomic weights, LiCl being most, and CsCl least, active. The same applies to alkaline catalysis, except that the effect is a retardation, so that the order is reversed, the series becoming



The same applies to anions: in acid solution, $\text{SO}_4 < \text{Cl} < \text{Br} < \text{I}$; in alkaline solution, $\text{I} < \text{Br} < \text{Cl} < \text{SO}_4$.

These generalisations can be extended to the precipitation in colloidal systems, provided the reaction of the medium is either distinctly

acid or distinctly alkaline, the reversal of the reaction again bringing about reversal of the series. In neutral solution, however, the order of efficiency as precipitants becomes irregular, and depends simultaneously on both ions; for instance, egg-albumin is more readily precipitated by rubidium than by sodium when present as chloride, but less readily when present as sulphate. G. B.

Catalysis. JULIUS STIEGLITZ (*Amer. Chem. J.*, 1907, 38, 743—746).—It is claimed that the theory of catalysis put forward by Acree (Abstr., 1907, ii, 855) was first enunciated by the author in a paper published in 1904 (*Report Congress Arts and Sciences, St. Louis*, 2, 276—284). T. A. H.

Catalysis. VI. Bromination. SALOMON F. ACREE, J. M. JOHNSON, and SIDNEY NIRDLINGER (*Amer. Chem. J.*, 1907, 38, 746—748).—In view of the publication of a note by Cohen and Cross on the bromination of acylamino-compounds (*Proc.*, 1907, 23, 148), it is pointed out that the authors have been engaged in the investigation of such catalytic actions, and have discussed the processes by which they occur (Abstr., 1907, i, 506, 855), and that the isolation by Cohen and Cross of the intermediate compound, $C_6H_4Me \cdot NHBr_2Ac$, formed in the bromination of acetyl-*p*-toluidide, affords a confirmation of their views. One of the authors (Nirdlinger) has prepared the related substance, $C_6H_5 \cdot NMeBr_2Ac$, in an impure state. T. A. H.

Use of a Vacuum for Drying Salts Containing Water of Crystallisation. FRIEDRICH KRAFFT (*Ber.*, 1907, 40, 4770—4774).—A study of the behaviour of salts containing water of crystallisation in the vacuum of the cathode light, and a comparison of the results obtained with those originally observed by Graham (*Phil. Mag.*, 1835, [iii], 6, 333). It is shown that there is no essential difference between the so-called water of constitution and water of crystallisation, the former is lost in vacuum, but it requires a very much longer time. Barium oxide in powder is the drying agent generally employed, as sulphuric acid volatilises in this vacuum. The rate in which the water is eliminated depends on the state of division of the salt, the vacuum employed, and the temperature.

Zinc sulphate, $ZnSO_4 \cdot 7H_2O$, lost $6H_2O$ in summer during fifteen hours; in another experiment, sixty hours were required with larger crystals; the seventh molecule was only withdrawn after three weeks. In order to eliminate the last molecule quickly in vacuum, a temperature of 210° is necessary.

In the case of magnesium sulphate, a very finely-powdered specimen lost $6H_2O$ in fifteen hours, but the last molecule requires two hours' heating at 230° before expulsion. Graham stated that this salt retained $2\frac{1}{2}H_2O$ in vacuum over sulphuric acid; using barium oxide, instead, but otherwise adhering to Graham's conditions, during three weeks over 6 mols. were abstracted.

Ferrous, nickel, and cobalt sulphates lose $6H_2O$ during forty-five hours; the seventh molecule is eliminated at 280° . Copper sulphate,

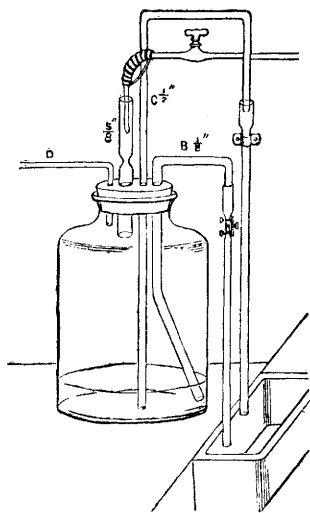
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, loses $4\text{H}_2\text{O}$ in a moderate vacuum over sulphuric acid in sixty hours; over barium oxide, more than $4\frac{1}{2}\text{H}_2\text{O}$ in ten days.

The loss of water from gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is scarcely noticeable at the ordinary temperature; at 100° , $1\frac{1}{2}$ mols. are lost, whilst at 150° the two are eliminated (compare Davis, Abstr., 1907, ii, 686).

The elimination of water from potassium alum is hastened in vacuum, and the following salts are quickly and completely dehydrated: sodium sulphate, sodium thiosulphate, manganese ammonium sulphate, copper chloride, strontium chloride, disodium hydrogen phosphate, sodium acetate, lead acetate, zinc lactate.

W. R.

A Simple Water-jet Blower. S. M. REVINGTON and J. G. RANKIN (*Chem. News*, 1907, 96, 259—260).—A large bottle of about 4 litres capacity is fitted with a cork carrying four tubes, *a*, *b*, *c*, *d*, the diameters of which are $\frac{5}{8}$ ", $\frac{1}{2}$ ", $\frac{3}{8}$ ", and $\frac{1}{4}$ " respectively. The tube *a*, which



passes just through the cork, has a sudden constriction immediately above the cork; into this tube, the water supply is delivered in such a way that the jet goes diagonally across the tube on to the side of the constricted part. The tube *b* is a syphon outlet reaching to the bottom of the bottle, and delivering into the sink at the other end; it is provided with a clip to regulate the outfall. The tube *c*, 2'5" in height, is a safety tube reaching nearly to the bottom of the bottle, and discharging at its upper bent end into a wide tube leading to the sink. The air blast is delivered through *d*, which passes just through the cork. To work the apparatus, the tube *d* is closed, and the water supply turned on; the pressure first starts the syphon and then air and water escape through *c*, and the pressure quickly reaches a maximum.

The tube *d* is now opened, when a steady blast of air is produced, which can be maintained for an indefinite time by regulating the water-jet and the clip so that the water does not rise in the bottle.

C. S.

Lecture Experiments with Inorganic Nitrogen Compounds. FRITZ RASCHIG (*Ber.*, 1907, 40, 4580—4588).—The author gives details of a number of lecture experiments to illustrate the preparation of various inorganic nitrogen compounds which have been described previously. Amongst the compounds in question, are salts of nitrilosulphonic acid, $\text{N}(\text{SO}_3\text{H})_3$, hydroxylaminedisulphonic acid, $\text{OH} \cdot \text{N}(\text{SO}_3\text{H})_2$, nitrosodisulphonic acid, $\text{NO}(\text{SO}_3\text{H})_2$, nitrososulphonic acid, $\text{OH} \cdot \text{NO} \cdot \text{SO}_3\text{H}$,

pernitric acid, HNO_4 , and chloroamine, NH_2Cl (*Chem. Zeit.*, 1907, 31, 126). The formation of hydrazine from ammonia and chloroamine is also described.

The yellow potassium nitrosodisulphonate, which yields violet solutions, is readily obtained by oxidising sodium hydroxylamine-disulphonate with ammoniacal potassium permanganate, filtering from manganese dioxide, and adding potassium chloride. A. McK.

Inorganic Chemistry.

The Development of Inorganic Chemistry in the last Forty Years. HANS LANDOLT (*Ber.*, 1907, 40, 4627—4637).—A lecture delivered before the German Chemical Society. W. H. G.

Activity of the Halogens: Chlorine, Bromine, and Iodine in Relation to Mercury. M. C. SCHUYTEN (*Chem. Zeit.*, 1907, 31, 1135. Compare *Abstr.*, 1896, ii, 524).—Even in the presence of an excess of the salt, the halogen in mercuric chloride, bromide, or iodide may be replaced by either of the other halogens, the only exception being the action of iodine on mercuric bromide; in this case, no bromine is displaced by the iodine. W. H. G.

New Polymorphous Form of Iodine. W. A. KURBATOFF (*Zeitsch. anorg. Chem.*, 1907, 56, 230—232).—When solutions of iodine in various solvents are evaporated to crystallisation, the element separates either as rhombic plates or as dendritic aggregates. The separation of a definite, crystalline form does not depend on the colour of the solution, but on the temperature, the common, rhombic, crystals being obtained at the higher temperatures. The transition temperature could not be determined by the usual thermal method, as there was no break in the cooling curve of iodine from 100—0°, but was established approximately by condensation on a glass surface kept at different temperatures; below 46—47°, the dendritic crystals were obtained, at higher temperatures the rhombic modification. G. S.

Action of Iodine on some Elements in Vacuum. MARCEL GUICHARD (*Compt. rend.*, 1907, 145, 807—808).—When a tube containing iron wire and iodine, separated by an asbestos plug, is evacuated, sealed, and heated in such a manner that the iron is kept at 500° and the iodine at 180°, ferrous iodide is formed and sublimes in the form of deep red crystals. Uranium and nickel also form iodides under similar conditions, the former as dark grey lamellæ. In the case of very volatile iodides, such as those of aluminium and silicon, it is necessary to keep the three portions of the tube (bent so that the middle portion is horizontal and the others pointing slightly downwards) at three different temperatures, the iodine at one end at 180°, the metal in the middle at 500°, and the other end (to receive the

iodide) at 15°. Otherwise the iodide formed remains mixed with the iodine vapour and retards the action. E. H.

Amorphous Sulphur. V. The System Sulphur-Iodine.

ALEXANDER SMITH and CHARLES M. CARSON (*Zeitsch. physikal. Chem.*, 1907, 61, 200—208. Compare Abstr., 1906, ii, 157; 1907, ii, 20).—The proportion of S_μ in the equilibrium mixture of S_λ and S_μ at a given temperature is raised by the addition of iodine. Thus, at 150° and in the absence of iodine, the percentage of S_μ in the equilibrium mixture is 6·7; when one part of iodine is present per one hundred parts of sulphur, the percentage of S_μ is 12·26; when five parts of iodine are present per one hundred parts of sulphur, the percentage of S_μ is 17·86. The effect of the presence of two parts of iodine per one hundred parts of sulphur at different temperatures is shown in the following table:

Temperature.....	150°	165°	220°	310°	448°
Percentage of					
insoluble	without iodine	6·7	14·0	29·4	32·6
sulphur		13·8	24·1	47·0	54·2
	with iodine.....	62·7			

A study of the freezing points of mixtures of sulphur and iodine shows that neither compounds nor solid solutions are formed (compare Boulouch, Abstr., 1903, ii, 538).

The authors reply to Hoffmann and Rothe (Abstr., 1907, ii, 539).

J. C. P.

Electro-Syntheses. SIMA M. LOSANITSCH (*Ber.*, 1907, 40, 4656—4666).—An investigation of the behaviour of various substances in a gaseous form, both when alone and mixed together, under the influence of a silent electric discharge. The apparatus and method employed have been described (Abstr., 1897, i, 179).

Sulphur dioxide is converted into sulphur trioxide with liberation of sulphur; in the presence of hydrogen or hydrogen sulphide, water is formed and sulphur liberated. Nitric oxide yields nitrogen and nitrogen peroxide; when mixed with hydrogen, it is reduced to nitrogen, the latter interacting with the water formed, yielding ammonium nitrite. A mixture of nitric oxide and hydrogen sulphide yields an aqueous solution of ammonium polysulphide.

Carbon disulphide vapour is converted into a *polymeride*, $(CS_2)_n$, an almost black substance, which decomposes into its components when strongly heated. A mixture of carbon disulphide and hydrogen or hydrogen sulphide yields a brown *substance*, $C_3H_2S_8$, previously inaccurately described as a polymeride of carbon monosulphide, $(CS)_n$ (*loc. cit.*), and by Berthelot (Abstr., 1899, i, 657) as a substance having the composition $C_2H_2S_4$. Carbon disulphide yields with carbon monoxide a brown, insoluble *substance*, $3CS_2, 2CO$; with ethylene, a brownish-yellow, insoluble *substance*, $5CS_2, 2C_2H_4$; with acetylene, an almost black, insoluble *substance*, $3CS_2, 2C_2H_2$.

Acetylene alone is converted into a viscid or solid mass containing (1) a fragrant, viscid *substance*, soluble in alcohol and ether, which rapidly absorbs oxygen from the air, forming a *substance*, $(3C_2H_2, C_2H_4, O)_5$;

(2) an insoluble *substance*, $C_{48}H_{46}$, yellowish-brown by reflected and yellowish-red by transmitted light, having an empyreumatic odour; it absorbs oxygen, forming the *substance*, $C_{48}H_{46}O_8$. These acetylene condensation products decompose at 100° ; they also evolve an emanation, which liberates iodine from potassium iodide and produces a reducing action through aluminium or gold leaf on a photographic plate; the emanation is not a radioactive emanation, the action produced being probably due to absorbed oxygen present in a labile state. The same substances are produced together with polymerised acetaldehyde when water is present with the acetylene. Equal volumes of acetylene and hydrogen or methane give a clear yellow product, containing a viscid liquid, soluble in ether, and an insoluble solid, of the formulæ C_6H_{10} and C_6H_8 respectively. Equal volumes of acetylene and ethylene yield (1) a *substance*, C_2H_2, C_2H_4 , obtained as a red, viscid, fragrant liquid; (2) a solid *substance*, $3C_2H_2, C_2H_4$, insoluble in all solvents, and decomposing when heated. Equal volumes of acetylene and hydrogen sulphide yield (1) a yellow *substance*, $C_8H_{14}S_2$, soluble in ether; (2) a yellow *substance*, $C_{10}H_{14}S_4$, insoluble in ether. Acetylene with carbon monoxide yields a yellowish-brown, insoluble *substance*, which absorbs oxygen rapidly, forming a *substance*, $4C_2H_2, CO, O_2$. Equal volumes of acetylene and sulphur dioxide condense with the formation of a dark brown, insoluble *substance*, C_2H_2OS .

Ethylene is converted into a yellowish-red, oily *substance*, soluble in alcohol; it absorbs oxygen, forming a viscid *substance*, $(C_{12}H_{22}O)_2$. Equal volumes of ethylene and methane yield a clear, yellow, viscid liquid, which absorbs oxygen, forming a viscid *substance*, $C_{22}H_{42}O_4$. Ethylene and hydrogen sulphide yield a *substance*, $(C_2H_4S)_6$, obtained as a viscid, yellowish-red liquid. It is probable that ethyl mercaptan is first formed, since this compound yields the same substance under the influence of a silent discharge. Ethylene and carbon monoxide yield (1) a *substance*, $(2C_2H_4, CO)_2$, obtained as a yellowish-red, viscid liquid, soluble in ether, &c.; (2) an insoluble *substance*, $(2C_2H_4, CO)_n$.

W. H. G.

Atomic Weight of Tellurium. WILLY MARCKWALD (*Ber.*, 1907, 40, 4730—4738).—Although both Staudenmaier and Mylius had drawn the conclusion from a series of fractional crystallisations that telluric acid is a uniform substance, these authors had not sufficiently considered the possibility of their having dealt with an isomorphous mixture which could be separated only by a systematic method of crystallisation. The author accordingly examined about 1500 grams of telluric acid from the latter standpoint, and, after several hundred crystallisations, obtained twenty fractions of about equal weights; between the first and last fractions, there was not, however, the slightest difference. There is no doubt as to the uniformity of tellurium.

For the determination of the atomic weight of tellurium, the author has modified the method of Staudenmaier, namely, the conversion of telluric acid into tellurium dioxide (*Abstr.*, 1896, ii, 97).

Crude tellurium, obtained from the Selmeczbanja mines, was converted into dioxide and separated from copper, lead, silver, &c.

The dioxide was then oxidised to telluric acid by means of chromic acid, and submitted to a prolonged series of crystallisations from water. The telluric acid used in the determinations was dried over phosphoric oxide in a vacuum. It is worthy of note that, when telluric acid is exposed over phosphoric oxide for two months in a vacuum, it remains practically constant in weight.

The method is based on the action as represented by the equation : $\text{H}_6\text{TeO}_6 = \text{TeO}_2 + \text{O} + 3\text{H}_2\text{O}$. The heating was conducted in a platinum vessel by means of an electrical oven, the temperature at the bottom of the vessel being measured through a Le Chatelier element by means of a millivolt meter. The temperature at the top of the platinum vessel was maintained lower than that at the bottom, in order to guard against volatilisation of the dioxide. The temperature was gradually raised in the course of two to three hours from 100° to 160° , and then gradually in the course of three to four hours more to 650° , which temperature was maintained for another hour. The residue was always white, and quite free from the trioxide. The weight did not alter on further heating for one hour.

The various precautions taken are indicated.

As a mean of six experiments, the value $126.85(\pm 0.02)$ was obtained on the basis of $\text{O} = 16$ and $\text{H} = 1.008$. This value is lower than that of iodine ($\text{I} = 126.97$).

A. McK.

Catalytic Synthesis of Ammonia from its Elements. LÉON BRUNEL and PAUL WOOD (*Compt. rend.*, 1907, 145, 922—924. Compare Woltreck, Abstr., 1904, ii, 115).—Attempts to effect the synthesis of ammonia by passing a mixture of pure hydrogen (3 vols.) and nitrogen (1 vol.) over a mixture of thorium and cerium oxides, palladinised pumice, quicklime, soda lime, calcium chloride, calcium molybdate, anhydrous barium or strontium oxide, manganese dioxide, aluminium phosphate, or magnesium phosphate at 15° to 350° were unsuccessful. The gaseous mixture reacts with nickel sesquioxide at 180° to 200° to form water and a trace of ammonia, but the reaction is fugitive. If, however, a mixture of air and excess of hydrogen is passed over heated nickel sesquioxide, the latter is alternately reduced and reoxidised, and the energy liberated by the reactions causes the formation of small quantities of ammonia; the reaction is continuous, provided that the nickel oxide is not allowed to become incandescent owing to the heat of the reaction. This is effected by suspending the tube containing the nickel oxide in a bath of petroleum, b. p. 200 — 246° .

M. A. W.

Boiling Point of Liquid Ammonia. EDWARD C. FRANKLIN (*Ann. Physik*, 1907, [iv], 24, 367—369).—A critical review of the determinations made by de Forcrand (*Ann. Chim. Phys.*, 1903, [vii], 28, 537), Gibbs (Abstr., 1905, ii, 570), Perman and Davies (Abstr., 1906, ii, 743), and Brill (Abstr., 1906, ii, 847) leads the author to the conclusion that Gibbs' value (-33.46°) is probably correct to within 0.1° .

J. C. P.

Formation of Nitric Oxide in High Tension Arcs. FRITZ HABER and ADOLF KOENIG (*Zeitsch. Elektrochem.*, 1907, 13, 725—743).—An alternating current was passed through mixtures of oxygen and

nitrogen under pressures varying from about 40 mm. to 200 mm. Electrodes of platinum, oxidised iron, and Nernst glowers were used. The gas was passed through water-cooled tubes of hard glass or quartz of 5 to 7 mm. bore, along the axis of which the discharge passed. At the lower pressures, the whole mass of gas in the tube glowed with a pink light, with the exception of a thin film next to the wall of the tube; at the higher pressures, the glowing column of gas tended to contract further from the walls. The best results are obtained when the gas does not flow over the electrodes, and when the latter are very hot. Electrodes of iron or Nernst filaments give the best results. The percentage of nitric oxide in the gas increases with the current up to a maximum which is not affected by further increase of current. The greatest concentration of nitric oxide is obtained with gas at 100 mm. pressure. The maximum percentage of nitric oxide obtained with each mixture was (at 100 mm.):

Percentage of oxygen in mixture	20.9	48.9	44.4	75.0	81.7	
Percentage of nitric oxide	9.8	14.4	14.3	12.77	12.1

Assuming that the formation of nitric oxide is a purely thermal phenomenon and using Nernst's determinations of the equilibrium concentrations, these results indicate that the temperature of the gas in the path of the arc was between 4300° and 5000° absolute.

From the thickness of the non-luminous film of gas between the luminous gas and the walls of the vessel, the authors calculate that the temperature of the hot gas could not have exceeded 3000°; further, the rate of cooling of the gas was small, so that nitric oxide formed by very high temperature alone would probably have been decomposed. The authors incline rather to believe that the temperature was low, and the high percentage of nitric oxide found was produced by collisions of electrons; owing to the low temperature, the nitric oxide thus formed escaped decomposition, which is not the case in the hotter flames produced in gases under atmospheric pressure. T. E.

Non-existence of a Common Solvent for White and Red Phosphorus. ALBERT COLSON (*Compt. rend.*, 1907, 145, 1167—1168).—Schroetter stated that red phosphorus is soluble in oil of turpentine; this statement has been contested, and the author shows that pure red phosphorus does not dissolve in oil of turpentine or in the polymerised products obtained by the action of heat on the solvent, even when heated at 270° in a sealed tube, provided that air is excluded. Further, red phosphorus is not altered when heated at 275—285° in a sealed tube containing a solution of phosphorus in turpentine.

There exists, moreover, no common solvent for white and red phosphorus, for Lemoine has shown that the two varieties have the same vapour density, corresponding with the molecule P_4 ; according to van't Hoff's hypothesis, therefore, the two varieties would become identical in a common solvent. M. A. W.

Action of Hydrogen Phosphide on Mercuric Chloride or Bromide, PHg_3Cl_3 and $P_2Hg_5Br_4$. PAUL LEMOULT (*Compt. rend.*, 1907, 145, 1175—1177)—H. ROSE (*Pogg. Ann.*, 1837, 40, 75, 87)

obtained a yellow, amorphous compound, $\text{PHg}_3\text{Cl}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, by the action of hydrogen phosphide on mercuric chloride, and an analogous compound of a brown colour when mercuric bromide replaced the mercuric chloride. The author finds, however, that mercuric chloride gives with hydrogen phosphide the anhydrous compound PHg_3Cl_3 , whereas mercuric bromide forms the compound, $\text{P}_2\text{Hg}_5\text{Br}_4$, according to the equations: I. $\text{PH}_3 + 3\text{HgCl}_2 = 3\text{HCl} + \text{PHg}_3\text{Cl}_3$; II. $2\text{PH}_3 + 5\text{HgBr}_2 = 6\text{HBr} + \text{P}_2\text{Hg}_5\text{Br}_4$. The presence of excess of hydrogen phosphide, even locally, as when the gas is bubbled through a solution of the mercuric halide, leads to a reduction of the salt with liberation of mercury, and the best results are obtained when an aqueous solution of hydrogen phosphide is carefully poured on to the surface of a concentrated solution of the mercuric halide and the corresponding potassium salt and the mixture suddenly shaken; the precipitate thus obtained is uniform in colour and of constant composition.

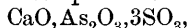
M. A. W.

Action of Arsine on Solutions of some Metallic Salts.

HANS RECKLEBEN, GEORG LOCKEMANN, and ALFRED ECKARDT (*Zeitsch. anal. Chem.*, 1907, **46**, 671—709).—Arsine is absorbed rapidly and completely by silver nitrate solution, but slowly by mercury, copper, lead, tin, and iron salt solutions; the latter solutions are useless for the quantitative absorption of arsine. The reaction with silver nitrate solution does not take place exactly according to Lassaigne's equation: $\text{AsH}_3 + 6\text{AgNO}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{AsO}_3 + 6\text{Ag} + 6\text{HNO}_3$, but, in part, according to the equation: $\text{AsH}_3 + 3\text{AgNO}_3 = \text{Ag}_3\text{As} + 3\text{HNO}_3$. The silver arsenide is not very stable in the presence of the nitric acid, and further action takes place: $\text{Ag}_3\text{As} + 3\text{AgNO}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{AsO}_3 + 6\text{Ag} + 3\text{HNO}_3$. In dilute ammoniacal silver nitrate solution, three reactions take place consecutively or simultaneously: (a) $\text{AsH}_3 + 3(\text{AgNH}_3)\text{NO}_3 = \text{Ag}_3\text{As} + 3\text{NH}_4\text{NO}_3$, (b) $\text{Ag}_3\text{As} + 3(\text{AgNH}_3)\text{NO}_3 + \text{NH}_4\text{OH} + \text{H}_2\text{O} = \text{NH}_4\text{AsO}_2 + 6\text{Ag} + 3\text{NH}_4\text{NO}_3$, and (c) $\text{NH}_4\text{AsO}_2 + 2(\text{AgNH}_3)\text{NO}_3 + 2\text{NH}_4\text{OH} = (\text{NH}_4)_3\text{AsO}_4 + 2\text{Ag} + 2\text{NH}_4\text{NO}_3$. Metallic arsenic, when warmed with ammoniacal silver nitrate solution, is oxidised, thus: $\text{As} + 5(\text{AgNH}_3)\text{NO}_3 + 3\text{NH}_4\text{OH} + \text{H}_2\text{O} = (\text{NH}_4)_3\text{AsO}_4 + 5\text{Ag} + 5\text{NH}_4\text{NO}_3$. In ammoniacal solution and in the presence of air, arsine is readily oxidised. It is also mentioned in the paper that finely-divided silver is not attacked by 6.3% nitric acid within four hours at the ordinary temperature, and *N*/10 nitric acid is only very slowly reduced at the ordinary temperature by arsenious acid.

W. P. S.

Compounds of Arsenic Sulphates with Potassium, Calcium, and Lead Sulphates. HUGO KÜHL (*Arch. Pharm.*, 1907, **245**, 377—379).—The crystalline compounds: $2\text{K}_2\text{O}, \text{As}_2\text{O}_3, 4\text{SO}_3$,



$\text{PbO}, \text{As}_2\text{O}_3, 2\text{SO}_3$ were obtained by dissolving arsenious oxide and potassium, calcium, or lead sulphate in concentrated sulphuric acid and driving off sulphuric acid by heating; with strontium and barium sulphates, similar compounds could not be obtained.

C. F. B.

Identity of Graphite and "Temper" Graphitic Carbon in Cast Irons. GEORGES CHARPY (*Compt. rend.*, 1907, 145, 1173—1174).—It was stated by Forquignon and Ledebur that the carbon (graphite) contained in cast iron that has been cooled gradually, differs from the carbon ("temper" carbon) that separates in rapidly-cooled cast iron, in that the latter is volatile and the former non-volatile when a stream of hydrogen or nitrogen is passed over the red-hot cast iron. Wüst and Geiger find, however (*Abstr.*, 1906, ii, 88), that pure hydrogen or nitrogen is without action on "temper" carbon or on graphite. The author has, therefore, examined the chemical behaviour of the free carbon obtained from two portions of cast iron, one of which had been cooled gradually, the other rapidly, cooled, and the results show that graphite and the so-called "temper" carbon are identical both with regard to the velocity with which they are oxidised to graphitic acid and to the rate at which they are completely eliminated in the gaseous form when a stream of pure hydrogen is passed over the cast iron at 1000°.

M. A. W.

Solubility of Potassium Iodide in Water, and of Water in Potassium Iodide at Low Temperatures. ROBERT KREMAN and F. KERSCHBAUM (*Zeitsch. anorg. Chem.*, 1907, 56, 218—222).—Meusser (*Abstr.*, 1905, ii, 317) has recently determined the complete solubility curves for water with potassium chloride and bromide respectively, and found no evidence of the formation of hydrates, but in the case of water and potassium iodide there was a break in the observations from 42.7% to 53.5% of the salt, the eutectic point being determined by extrapolation. The authors have now determined the complete curve, including observations within the limits indicated, and find no evidence of chemical combination; the eutectic point lies at -23.1° , the mixture containing 52.2% by weight of potassium iodide.

G. S.

Waterglass. VI. JOHN M. ORDWAY (*Amer. J. Sci.*, 1907, [iv], 24, 473—478).—In an earlier paper (*Amer. J. Sci.*, 1865, 40, 190), it has been shown that when alcohol is added to solutions of sodium and potassium silicates, basic silicates are precipitated.

On mixing strong solutions of sodium silicate and lithium chloride, precipitates are produced containing varying quantities of lithium and sodium silicates. By re-dissolving these precipitates and adding lithium chloride to the solutions, the proportion of lithium in the product can be gradually increased, but pure lithium silicate cannot be obtained in this manner. When, however, freshly-prepared silica is digested with lithium hydroxide solution at the ordinary temperature, a solution of lithium silicate, Li_2SiO_3 , is produced. On heating this solution, a precipitate is produced which re-dissolves on cooling.

Soluble rubidium silicates can be obtained of composition varying from $\text{Rb}_2\text{O}, \text{SiO}_2$ to $2\text{Rb}_2\text{O}, 9\text{SiO}_2$. In the case of the lithium silicates, the range is not so great.

When ammonia is added to a solution of a silicate containing a large proportion of silicic acid, a precipitate is usually produced.

E. G.

Ammonium Amalgam. G. MCPHAIL SMITH (*Ber.*, 1907, 40, 4893. Compare Abstr., 1907, ii, 615).—A reply to the criticisms of Travers (Abstr., 1907, ii, 865). It is argued that ammonium amalgam is completely analogous to sodium and potassium amalgams, which are regarded as solutions of NaHg_n or KHg_n in mercury.

E. F. A.

Amalgams. The Hydrargyrides of the Alkali and Alkaline Earth Metals. G. MCPHAIL SMITH (*Amer. Chem. J.*, 1907, 38, 671—683).—Further evidence in favour of the views expressed regarding the nature of amalgams in previous papers (Abstr., 1905, ii, 164, 450; 1906, ii, 673; 1907, ii, 462, 463, 615) is brought forward, and it is shown that, unlike the amalgams of the alkaline earth metals, those of the common alkali metals do not increase in stability with increase in the atomic weight of the alkali metal used (the order of stability being: Li, K, Na). The amalgams used were liquid, and were prepared by electrolysis of a solution of the chloride of the appropriate metal in presence of mercury.

The relative stabilities of the amalgams were tested (1) by the rate of decomposition on exposure to air, (2) by the capacity for decomposing water, (3) by the rapidity with which they were decomposed by ammonia solution, and (4) by the composition of the equilibrium amalgam obtained when the amalgam under investigation was acted on by an aqueous solution of sodium chloride and the chloride of its own metal.

By all four methods of investigation, it was found that the relative stabilities of the amalgams examined increased in the following order: K, Rb, Cs. The mercury compound of lithium is the least stable in the alkali metal group, whilst that of sodium is the most stable. Sodium amalgam also behaves in an exceptional manner; thus, on exposure to air, no sodium peroxide is formed, whereas the corresponding peroxide is formed in each case when an amalgam of potassium, rubidium, or caesium is exposed to air. The metals of the pairs, Cs, Na and Rb, Na, are, like most of the other metals of the alkali and alkaline earth groups, reversibly displaceable in aqueous solution in presence of mercury.

T. A. H.

Artificial Reproduction of Barytes, Celestine, and Anglesite, and Isomorphous Mixtures of these Substances. PAUL GAUBERT (*Compt. rend.*, 1907, 145, 877—879).—Behren's microchemical reaction for the detection of certain metals (Abstr., 1886, 917; 1891, 766) gives confused results in the cases of barium and strontium. By a modification of the method, the author has obtained crystals of the sulphates of barium, strontium, lead, or calcium similar to those of the natural minerals, and of such dimensions that the optic axial angles, which are characteristic for each substance, could be measured. The method consists in evaporating to dryness 100 c.c. of a saturated sulphuric acid solution of the metallic sulphate at the boiling point, or at a slightly lower temperature, and in the case of barium or strontium sulphate the crystals thus obtained were sufficiently large to admit of goniometrical measurement. Mixed

crystals of barium and strontium sulphate, or of either of these sulphates with that of lead, were prepared similarly. Calcium sulphate, not being isomorphous with the preceding sulphates, does not form with them mixed crystals, although the crystal forms of these sulphates are modified by the presence of calcium sulphate in the solution.

M. A. W.

Colloidal and Gelatinous Calcium and Magnesium Compounds. CARL NEUBERG [and, in part, B. REWALD] (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 820—822. Compare Neuberg and Neimann, *Abstr.*, 1906, ii, 753).—Calcium sulphate, calcium phosphate, and calcium oxalate are precipitated in a gelatinous form when sulphuric acid, phosphoric acid, and oxalic acid respectively are added to a methyl-alcoholic solution of calcium oxide. The clear, viscous, colloidal solution of calcium carbonate, obtained by passing a stream of carbon dioxide into a methyl-alcoholic solution of calcium oxide, may be evaporated, without undergoing decomposition, to a thick liquid which sets to a jelly. If a current of carbon dioxide is passed into a suspension of calcium oxide in methyl alcohol, the liquid after about five to six hours is transformed into a solid jelly, which dissolves slowly in methyl alcohol. The colloidal calcium carbonate is miscible with several organic solvents, for example, benzene, chloroform, and ether.

Analogous colloidal magnesium compounds may be similarly prepared from a methyl-alcoholic solution of magnesia.

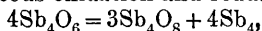
Analysis of the isolated gelatinous salts (sulphate, phosphate, and oxalate) of calcium and magnesium showed that they did not contain combined methyl alcohol.

W. H. G.

The Auto-reduction of some Metallic Oxides in the Vacuum of the Cathode Light and on the Volatility of the Corresponding Sulphides. F. DAMM and FRIEDRICH KRAFFT (*Ber.*, 1907, 40, 4775—4778).—The behaviour of oxides when heated is sometimes quite otherwise in a vacuum than under ordinary pressure. Thus cadmium oxide at 1000° decomposes into oxygen and cadmium, whereas in air it is completely stable. The experiments were carried out in quartz tubes heated in a Heraeus electric oven.

At 750°, lead oxide gives a metallic mirror, and bismuth oxide decomposes slowly at 650°.

Antimony oxide, volatile at about 700°, is not completely decomposed at 1050°. It is conjectured that the auto-reduction of the common metals may proceed in stages like that of antimony, consisting (1) of simultaneous oxidation and reduction:



and (2) conversion of a higher oxide into a lower.

The sulphides are more volatile than the corresponding oxides, cinnabar sublimes at 400° and cadmium sulphide very quickly at 770—780°, whereas lead sulphide volatilises at 600°; the sulphides of bismuth, antimony, and arsenic sublime at 740°, 530°, and 230° in the vacuum of the cathode light.

It is possible to separate by distillation, mixtures of arsenic and

antimony sulphides or mercury and lead sulphides under those conditions, as well as sulphur, selenium, and tellurium.

The sulphides of copper, tin, and silver are decomposed; the first two lose half their sulphur content, and the last is converted into metal and sulphur. W. R.

Solubility of Certain Lead Compounds in Water. MAX PREISSNER (*Chem. Zentr.*, 1907, ii, 1055—1056; from *Arb. Kais. Gesundheits.-Amt*, 1907, 26, 384—443).—This investigation was undertaken in connexion with the risk of contamination of water supplies by lead. Lead oxide and hydroxide, and the normal and basic carbonates, sulphates, and chlorides have been studied.

When hot solutions of lead salts are treated with alkali hydroxides, lead oxide, PbO , is precipitated, whilst from cold solutions, hydrated oxides separate. The lead oxide forms greyish-yellow scales with a metallic lustre, and gives a greenish-yellow powder. The same oxide is produced by the action of water containing much dissolved oxygen on lead, whilst by the action of water containing but little oxygen the hydrates are formed. A hydrate, $\text{Pb}_3\text{O}_2(\text{OH})_2$, has been identified, but higher hydrates probably exist, the solubility increasing with the degree of hydration. The oxide and its hydrates appear to dissociate, thus: $\text{Pb}(\text{OH})_2 \rightleftharpoons \text{Pb}(\text{OH})' + \text{OH}'$, the degree of dissociation in a solution saturated at 18° amounting to about 25%. The solubility of lead sulphate and chloride in water is diminished by the presence of sulphuric or hydrochloric acid, whilst that of the carbonate is increased by the presence of carbonic acid.

The following basic lead salts have been obtained, and their individuality established by application of the phase rule. $\frac{1}{3}$ -Basic lead carbonate, $\text{PbO}, 2\text{PbCO}_3, \text{H}_2\text{O}$; $\frac{1}{2}$ -basic lead sulphate and chloride, $\text{PbO}, \text{PbSO}_4$ and $\text{PbO}, \text{PbCl}_2, \text{H}_2\text{O}$; $\frac{2}{3}$ -basic lead sulphate and chloride, $3\text{PbO}, \text{PbSO}_4, \text{H}_2\text{O}$ and $3\text{PbO}, \text{PbCl}_2, \text{H}_2\text{O}$. These salts are less soluble in water than the corresponding normal salts.

The solubility (millimols. Pb per litre) and the specific conductivity of the saturated solutions, after deducting the value for the conductivity of the water, are as follows at 18° :

	PbO	$\text{Pb}_3\text{O}_2(\text{OH})_2$	PbCO_3	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$	PbSO_4
Solubility	0.31	0.45	0.0002	< 0.0002	0.126
Specific conductivity	19.5	27.3	—	—	33.9
	$\text{Pb}_2\text{O}(\text{SO}_4)$	$\text{Pb}_4\text{O}_2(\text{OH})_2(\text{SO}_4)$	PbCl_2	$\text{PbCl}_2(\text{OH})_2$	$\text{Pb}_4\text{Cl}_2\text{O}_2(\text{OH})_2$
Solubility	0.050	0.106	33.6	0.38	0.10
Specific conductivity	8.8	9.3	4512	68	19

E. G.

Aluminium Titanide. WILHELM MANCHOT and P. RICHTER (*Annalen*, 1907, 357, 140—144. Compare Manchot and Fischer, this vol., ii, 46).—Attempts to prepare double aluminium titanides with the object of investigating the capacity of titanium to form chains have resulted only in the formation of aluminium titanide,

Al_3Ti (Wöhler, *Annalen*, 1860, 113, 248; 115, 108). The titanide is best prepared by fusing 24 parts of potassium titanofluoride with 45.5 parts of aluminium, and gently heating the regulus with dilute sodium hydroxide. The product forms silver-white leaflets, D 5.5, is brittle, hardly scratches steel, glass, or fluorspar, contains trivalent titanium, since it forms a blue solution in hot dilute sulphuric acid, evolving twelve atomic proportions of hydrogen, and evolves thirteen atomic proportions of hydrogen when dissolved in aqueous potassium hydroxide. The titanide may have the double formula, $\text{Al}_3\text{Ti}\cdot\text{TiAl}_3$, but this cannot be decided. G. Y.

Manganese and the Periodic Law. HENRY REYNOLDS (*Chem. News*, 1907, 96, 260).—The author considers that manganese, which shows only the slightest resemblance to the halogens, should be placed in the eighth group with iron, nickel, and cobalt. It resembles these metals in physical properties, and in the formation of similarly constituted and isomorphous simple and double salts, $\text{M}''\text{SO}_4\cdot 7\text{H}_2\text{O}$ and $\text{R}_2\text{SO}_4\cdot \text{M}''\text{SO}_4\cdot 6\text{H}_2\text{O}$, alums, metallo- and metalli-cyanides. Moreover, potassium manganate and permanganate find a parallel in potassium osmite, potassium ruthenate, and per-ruthenate.

In many cases, a regular gradation of properties can be traced from manganese to cobalt, and a corresponding gradation from ruthenium to palladium, and from osmium to platinum. C. S.

[Determination of the] **Melting Points of the Iron Group Elements by a New Radiation Method.** GEORGE K. BURGESS (*Bureau Stand. Washington*, 1907, 3, (3), 345—355).—The m. p. of minute quantities of difficultly fusible substances have been determined by a method based on the measurement of the intensity of a particular monochromatic radiation from platinum (compare *Bureau Stand. Washington*, 1905, 1, 189; 1907, 3, 1). Within a blackened brass cylinder filled with hydrogen is a strip of platinum, $60 \times 4 \times 0.02$ mm., which is heated electrically to any desired temperature. On this strip is placed about 0.001 mg. of a metal or its oxide, which is watched through a mica window in the cylinder by one observer through a microscope, whilst simultaneously a second observer reads the temperature of the platinum strip by means of a Holborn-Kurlbaum optical pyrometer. The indications of the pyrometer are subject to two corrections, one for the reflection and absorption of the mica, the other for the selective emission of the platinum for the light used, red light, $\lambda = 0.66\mu$.

The following metals, in a state of maximum obtainable purity, have m. p.: iron, 1505° ; chromium, 1489° ; cobalt, 1464° ; nickel, 1435° ; manganese, 1207° . The m. p. of cobalt and nickel are correct to within 5° , those of the other three to within less than 10° . C. S.

Constitution of Roussin's Salts. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 658—660. Compare Abstr., 1907, ii, 960).—The simultaneous action on potassium heptanitrosulphide of mercuric cyanide, in amount equivalent to the sulphur present, and potassium cyanide in the quantity necessary for the complete formation of ferrocyanide, yields mercuric sulphide, alkali nitrite, and ferrocyanide,

as would be expected from the constitution attributed to Roussin's salts by the author (*loc. cit.*).

The phenomena observed in the precipitation of Roussin's salts by silver nitrate have led the author to assume that hyponitrous acid reduces ferric to ferrous salts. Preliminary experiments indicate that this reduction does not take place. The investigation is being continued. T. H. P.

1:2-Dichlorotetramminecobalt Salts; Ammonia-violet-Salts.

ALFRED WERNER (*Ber.*, 1907, 40, 4817—4825).—Numerous examples of stereoisomerism of cobalt salts containing organic amino-residues have been described (Jørgensen, *Abstr.*, 1898, ii, 226; Werner and others, 1901, i, 510, 512; 1907, i, 188, 290, 482, 590). Hitherto, the simplest tetramminecobalt salts, for example, the dichlorotetramminecobalt salts, $[\text{Cl}_2\text{Co}(\text{NH}_3)_4] \text{X}$, have been obtained in one form only, the so-called *praseo*-salts; a stereoisomeric series of salts, the *violeto*-salts, has now been prepared by the action of hydrochloric acid on octamminedioldicobalt salts (*Abstr.*, 1907, ii, 965). When concentrated hydrochloric acid is used at low temperatures, the reaction proceeds according to the equation: $[(\text{NH}_3)_4 \cdot \text{Co}(\text{OH})_2 \text{Co}(\text{NH}_3)_4] \text{X}_4 + 2\text{HCl} = [(\text{NH}_3)_4 \text{Co}(\text{OH})_2] \text{Cl}_3 + [\text{Cl}_2\text{Co}(\text{NH}_3)_4] \text{Cl}$, a mixture of 1:2-diaquotetramminocobalt chloride and 1:2-dichlorotetramminecobalt chloride being formed; the former is readily soluble in water, whereas the latter forms sparingly soluble, intensely blue crystals. The violeto-salt contains small amounts of the isomeric praseo-salt, from which it may be freed by conversion into the practically insoluble dithionate. The chloride can then be regenerated by rubbing the thionate with ammonium chloride. The following salts have been analysed: *chloride*, $\text{YCl}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$ [$\text{Y} = \text{Cl}_2\text{Co}(\text{NH}_3)_4$], *bromide*, *iodide*, and *nitrate*, all anhydrous, *dithionate*, $\text{Y}_2\text{S}_2\text{O}_6$, and *sulphate*, Y_2SO_4 . The chloride becomes anhydrous at 60° , and all are characterised by an intense, violet-blue colour. The aqueous solutions are somewhat less stable than those of the corresponding praseo-salts; even at 0° the solutions assume a reddish-violet colour owing to the formation of the chloroaquotetramminecobalt salts. When suspended in concentrated hydrochloric acid, the violeto-chloride is converted into the praseo-chloride. The violeto-salt is regarded as a *cis*-compound with the 1:2-constitution. J. J. S.

Complex Metal Ammonia Derivatives. VI. Octammine- μ -amino-ol-dicobalt Salts $\left[(\text{NH}_3)_4 \text{Co} \cdot \frac{\text{NH}_2}{\text{OH}_2} \cdot \text{Co}(\text{NH}_3)_4 \right] \text{X}_4$. ALFRED WERNER (*Ber.*, 1907, 40, 4605—4615. Compare *Abstr.*, 1907, i, 1012; ii, 965).—When an ammoniacal cobalt nitrate solution is oxidised by a slow current of air and an excess of sulphuric acid then added, Vortmann's insoluble sulphate separates. The author has shown previously (*Abstr.*, 1898, ii, 223) that this product is not homogeneous, since two compounds, a red and a green, can be separated from it, both of which belong to the class of complex cobalt salts. In the present paper, the constitution of the red salt is elucidated.

Salts of the types in question are decomposed by a mixture of hydrochloric and sulphuric acids into pentammine and tetrammine salts, from which it follows that 4 molecules of ammonia are attached

to each of the two cobalt atoms. The constitution of the red series of salts is discussed. The formula: $\left[(\text{NH}_3)_4\text{Co} \cdot \text{NH} \cdot \text{Co} \begin{smallmatrix} \text{OH}_2 \\ (\text{NH}_3)_4 \end{smallmatrix} \right] \text{X}_4$ is not favoured, because an imino-group could not be detected; no salt formation took place either with acetic acid or dilute mineral acids; no acetylation took place by the action of acetic anhydride, and no nitroso-compound resulted from the action of nitrous acid. Further, the compounds in question were neutral in aqueous solution and not acid, as would be the case if the formulation just stated were correct.

On the other hand, the formulation: $\left[(\text{NH}_3)_4\text{Co} \cdot \begin{smallmatrix} \text{OH} \cdot \\ \text{NH}_2 \end{smallmatrix} \cdot \text{Co}(\text{NH}_3)_4 \right] \text{X}_4$ accords with the experimental results. Since the cobalt atoms are saturated with respect to co-ordination numbers the fact that all the acid groups are inorganic in character is explained. The complex radicle contains no water, and the salts do not, consequently, give an acid reaction when dissolved in water. The amino-group behaves like ammonia in metal ammonia compounds, being indifferent towards chemical reagents in the cold. The hydroxyl group, also, does not have the property of adding on hydrogen ions. For those amino-groups which bind two metal atoms together, the author proposes the nomenclature " μ -amino."

Octammine- μ -sulphatoamino-dicobalt nitrate, obtained from Vortmann's sulphate, was shaken with concentrated hydrochloric acid until the reddish-violet tint of the salt had changed to brown. The product was washed with alcohol, and hydrochloric acid added to its aqueous solution, when the brownish-violet chloro-chloride separates. The following octammine- μ -amino-ol-dicobalt salts were prepared.

The *chloride*, $\text{YCl}_4 \cdot 4\text{H}_2\text{O}$ $\{\text{Y} = \left[(\text{NH}_3)_4\text{Co} \cdot \begin{smallmatrix} \text{NH}_2 \cdot \\ \text{OH} \end{smallmatrix} \cdot \text{Co}(\text{NH}_3)_4 \right]\}$, forms glistening, brownish-red prisms; by the action of hydrochloric acid, it is converted into pentammine and tetrammine cobalt salts. The *bromide*, $\text{YBr}_4 \cdot 4\text{H}_2\text{O}$, forms glistening, red scales. The *nitrate*, $\text{Y}(\text{NO}_3)_4$, forms dark red needles and scales. The *sulphate*, $\text{Y}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, forms brownish-red, silvery scales. The *dithionate*, $\text{Y}(\text{S}_2\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$, forms silvery, raspberry-coloured leaflets. The *thiocyanate*, $\text{Y}(\text{CNS})_4$, forms red crystals.

A. MCK.

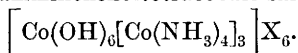
Complex Metal Ammonia Compounds. VII. Hexammine-trioldicobalt Salts. ALFRED WERNER [and, in part, EMIL BINDSCHIEDLER and ADOLF GRÜN] (*Ber.*, 1907, 40, 4834—4844. Compare *Abstr.*, 1898, ii, 223; 1899, ii, 658; 1907, i, 482, 1012; ii, 965, and preceding abstract).—*Hexamminetrioldicobalt salts* of the

type $\left[(\text{NH}_3)_3\text{Co} \cdot \begin{smallmatrix} \text{OH} \cdot \\ \text{OH} \end{smallmatrix} \cdot \text{Co}(\text{NH}_3)_3 \right] \text{X}_3$ may be prepared by the follow-

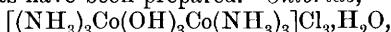
ing methods. 1. The chloride is obtained by the action of sodium hydroxide solution on dichloroaquotriammine cobalt chloride. 2. The sulphate by the action of sodium hydroxide solution on chlorodiaquotriammine cobalt sulphate. 3. The bromide by warming chlorobromoaquotriammine cobalt bromide with a little water at 60° . 4. The

sulphate by leaving chlorodiaquotriammine cobalt sulphate with potassium bromide solution for several days at the ordinary temperature.

When decomposed with halogen hydracids, the salts give quantitative yields of triamminecobalt salts, indicating that three ammonia residues are attached to each cobalt atom. The acid residues are readily ionised, as each salt can be transformed into the others by double decomposition. Their aqueous solutions are quite neutral to litmus, and hence the salts cannot be aquo-salts. They are isomeric with the black dodecamminehexoltetracobalt salts :



The following salts have been prepared. *Chloride*,



best obtained by rubbing the sulphate with ammonium chloride and water, brownish-red needles and prisms from dilute alcohol, decompose at 100°. *Bromide*, anhydrous, red, prismatic crystals, soluble in about thirteen times its weight of water at the ordinary temperature. *Nitrate*, red prisms containing $2\text{H}_2\text{O}$, becomes anhydrous when kept over sulphuric acid.

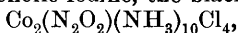
Sulphate, crystallises with $6\text{H}_2\text{O}$, pale red prisms, loses $5\text{H}_2\text{O}$ over phosphoric oxide and the last molecule at 77°.

Dithionate, $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]_2(\text{S}_2\text{O}_6)_3\cdot\text{H}_2\text{O}$, obtained by the action of a saturated solution of sodium dithionate on a solution of the bromide at 0°, dark red needles and prisms. *Thiocyanate*, anhydrous, dark red needles, soluble in 3 parts of water at the ordinary temperature.

J. J. S.

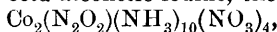
Pentamminecobalt Salts with Several Nuclei. JULIUS SAND and G. BÜCKMAN (*Ber.*, 1907, 40, 4497—4504).—Sand and Genssler have described two, a black and a red, series of pentamminenitrosocobalt salts (*Abstr.*, 1903, ii, 549; 1904, ii, 39). These salts, especially those of the black series, are characterised by their great reactivity. The present paper contains an account of the compounds obtained by the action of iodine on the black pentamminenitrosocobalt chloride and nitrate in alcoholic solution, and of the complex salts derived from these.

When boiled with alcoholic iodine, the black chloride,



yields the *chloride*, $[\text{Co}_3\text{ClI}_2(\text{NH}_3)_{15}(\text{H}_2\text{O})_2]\text{Cl}_6$, which, after being boiled with hydrochloric acid, separates from its ice-cold aqueous solution on addition of hydrochloric acid, potassium chloride or alcohol in green crystals; with v_{242} , has the molecular conductivity, $\mu = 731$, and gradually decomposes in aqueous solution at 25°, the conductivity increasing with the time. The action of potassium iodide on the chloride in ice-cold aqueous solution leads to the formation of the green, crystalline *iodide*, $[\text{Co}_3\text{ClI}_2(\text{NH}_3)_{15}(\text{H}_2\text{O})_2]\text{I}_6$, whilst the action of nitric acid leads to the formation of the *nitrate*, $[\text{Co}_3\text{ClI}_2(\text{NH}_3)_{15}(\text{H}_2\text{O})_2](\text{NO}_3)_6$. The solubility of these three salts decreases from the chloride through the nitrate to the iodide which is only very sparingly soluble.

When treated with cold alcoholic iodine, the black nitrate,



forms a green *substance*, which, when boiled with 20% nitric acid, yields the green complex salt, $[\text{Co}_3\text{I}_2(\text{NO}_3)(\text{NH}_3)_{15}(\text{H}_2\text{O})_2](\text{NO}_3)_6$. G. Y.

Equilibrium of the System Nickel-Bismuth. A. PORTEVIN (*Compt. rend.*, 1907, 145, 1168—1170).—The freezing-point curve of mixtures of nickel and bismuth consists of three branches, the points of intersection are given by the reactions $\text{Ni} + \text{Bi} \rightleftharpoons \text{NiBi}(\text{?})$ at 654° , and $\text{Ni} + \text{NiBi}(\text{?}) \rightleftharpoons \text{NiBi}_3$ at 462° . In neither case, however, is the reaction complete. M. A. W.

The Green Chromium Sulphates. ALBERT COLSON (*Ann. Chim. Phys.*, 1907, [viii], 12, 433—467).—A résumé of work already published (compare Abstr., 1905, ii, 94, 460, 592, 639; 1906, ii, 74, 233; 1907, ii, 177, 267, 356, 474, 780). M. A. W.

New Compound of Uranium, the Tetraiodide. MARCEL GUICHARD (*Compt. rend.*, 1907, 145, 921—922).—When iodine vapour is passed over uranium at 500° in sealed vacuum tubes (this vol., ii, 31), the *tetraiodide*, UI_4 , is formed as a crystalline sublimate, consisting of fine, black needles, m. p. about 500° , D^{15}_4 5.6. It is reduced when heated in hydrogen, decomposed by chlorine, yielding the chloride and iodine trichloride, readily oxidised by oxygen or air to form the oxide, U_3O_8 , and dissolves in water to form a green acid solution giving the characteristic reactions of uranium salts.

M. A. W.

Colloidal Hydroxides of Thorium, Zirconium, and Uranium. BÉLA SZILARD (*J. Chim. Phys.*, 1907, 56, 488—494).—The author considers that there are two distinct classes of colloids, those containing a little electrolyte, which are very stable, and those quite free from electrolytes, which are also fairly stable.

Colloidal thorium hydroxide, free from electrolytes, has been prepared by decomposing thorium nitrate with excess of dilute ammonia and washing the residue until free from ammonia, which takes three to six days. The product is a fine, milky suspension, in which the particles cannot be separated either by filtration or decantation; it is precipitated by electrolytes and by the carbon dioxide of the air. Colloidal zirconium hydroxide was prepared by the same method, and shows similar properties.

Colloidal thorium hydroxide, containing a little electrolyte, has been obtained by adding precipitated thorium hydroxide to thorium tetrachloride so long as the former is dissolved. This solution is much more stable than that free from electrolytes, is not affected by light or by boiling, and is not precipitated by small quantities of electrolytes or by weak acids (compare Müller, Abstr., 1906, ii, 762).

Colloidal uranyl hydroxide, containing a little electrolyte, has been prepared by the gradual addition of uranyl hydroxide to a dilute solution of uranyl nitrate as long as the former is dissolved; the solution thus obtained is orange-yellow in colour and very stable. The uranyl hydroxide for this purpose was obtained by exposing to light a mixture of uranyl acetate and ether and thoroughly washing the resulting precipitate. G. S.

Spitting of the Acid Vanadates of Univalent Metals. WILHELM PRANDTL and HANS MURSCHHAUSER (*Zeitsch. anorg. Chem.*, 1907, 56, 173—208).—In a previous paper (Abstr., 1905, ii, 170), it was shown that, when certain alkali acid vanadates, xM_2O, yV_2O_5 , are allowed to cool from high temperatures, a vigorous evolution of oxygen takes place on solidification, the mass spitting as solidifying silver does. On again heating in air, oxygen is absorbed, and the acid vanadates are regenerated. This phenomenon is due to the reversible change of the acid vanadates, xM_2O, yV_2O_5 , to vanadylvanadates, $xM_2O, (y-z)V_2O_5, zV_2O_4$, on solidification.

Only the oxides of the univalent elements of the first group in the periodic table give acid vanadates which spit on solidification. The respective oxides were mixed with vanadium pentoxide in varying proportions, and the composition of the mixtures which gave the highest proportion of oxygen determined; the results varied with the nature of the oxide, and were as follows: $Na_2O, 6V_2O_5$; $Ag_2O, 6V_2O_5$; $K_2O, 5V_2O_5$; $Rb_2O, 5V_2O_5$; $Cs_2O, 5V_2O_5$; $Li_2O, 2V_2O_5$. From mixtures of the same alkali oxide with varying proportions of vanadium pentoxide, the same vanadylvanadate is obtained, the composition of the four most important being as follows: $Na_2O, 5V_2O_5, V_2O_4$; $Ag_2O, 5V_2O_5, V_2O_4$; $2K_2O, 9V_2O_5, V_2O_4$; $4Li_2O, 7V_2O_5, V_2O_4$. The composition of these compounds was determined approximately by treating the mixtures containing them with boiling dilute ammonia, which dissolves unaltered V_2O_5 .

The amounts of oxygen evolved from solidifying sodium and silver vanadates correspond fairly closely with those calculated from the composition of the vanadylvanadates as determined above, so that the reaction is nearly complete, but in the case of the potassium, rubidium, caesium, and lithium vanadates the amounts of evolved oxygen are much less than the calculated values, showing that the decomposition on cooling is incomplete.

When mixtures of vanadium pentoxide and two alkali oxides are employed, the amount of oxygen evolved is approximately the mean of that obtained with the separate oxides.

The addition of boron trioxide in moderate amount to the mixtures does not affect the evolution of oxygen, but, when considerable amounts of phosphates are present, the fused mass solidifies without the liberation of oxygen, probably owing to the previous formation of vanadyl phosphate. G. S.

Silicon Chains. WILHELM MANCHOT and H. FISCHER (*Annalen*, 1907, 357, 129—139. Compare Manchot and Kieser, Abstr., 1905, ii, 165; 1906, ii, 83; Vigouroux, Abstr., 1906, ii, 30).—I. *Vanadium Aluminium Silicides*.—When heated together, potassium silicofluoride, aluminium, and ammonium metavanadate form three *vanadium aluminium silicides*, depending on the proportions of the mixture. In presence of an excess of vanadium and small amounts of silicon, the chief product is a silicide, crystallising in small, dark octahedra, together with small amounts of a silicide crystallising in large, hexagonal prisms. As the proportion of silicon is increased and that of vanadium diminished, the octahedra disappear and a silicide

crystallising in monoclinic leaflets is formed, becoming the chief product when the mixture contains a large excess of silicon. Of these vanadium aluminium silicides, only the hexagonal silicide, $V_8Al_2Si_{13}$, has been isolated. It crystallises in greyish-white, prismatic needles, D 4.3, hardness slightly above 5, and reacts with hydrofluoric acid with development of heat, forming, in absence of air, a reddish-violet solution containing *vanadium difluoride*, VF_2 , which on exposure to air in presence of excess of hydrofluoric acid evolves hydrogen and forms the green vanadium trifluoride solution. The hexagonal silicide is stable towards boiling concentrated hydrochloric, nitric, or sulphuric acid, *aqua regia*, or fused potassium chlorate, remains unchanged when heated in a current of oxygen over the bunsen flame, and is not attacked by chlorine at the ordinary temperature, but at a red heat is converted into volatile chlorides, and is dissolved by fused alkalis or alkali carbonates.

II. *Constitution of the Silicides*.—When treated with an excess of hydrogen fluoride, as was described in the case of the chromium salts (Abstr., 1906, ii, 63), the hexagonal vanadium aluminium silicide evolves seventy-four atomic proportions of hydrogen, whereas if the silicon were completely transformed into the fluoride eighty-two atomic proportions, including eight from the conversion of the difluoride into the trifluoride, should be evolved. It is considered that this points to linkings between silicon atoms which are not resolved by hydrofluoric acid. It is found impossible to construct a formula for the hexagonal silicide in which not more than eight of the thirteen silicon atoms are linked to form a chain.

G. Y.

Action of Sodium and Barium Peroxides on Gold. Aurates. FERNAND MEYER (*Compt. rend.*, 1907, 145, 805—807).—When precipitated gold is added to fused sodium peroxide, a vivid reaction takes place and sodium aurate is formed. A similar, but much less complete, reaction occurs with barium peroxide. From the aurate, auric hydroxide is prepared by means of sulphuric acid, adopting the precautions recommended by Fremy (*Ann. Chim. Phys.*, 1851, 31, [iii], 478). Analyses of the hydroxide, dried in a vacuum in the dark, agree with the formula $Au_2O_3 \cdot 3H_2O$, ordinarily written $Au(OH)_3$, but from analyses of the aurates the author proposes the formula $Au_2O_2(OH)_2 \cdot 2H_2O$. Krüss has described the hydroxide $Au_2O_3 \cdot H_2O$, which he writes $AuO \cdot OH$. The aurates of sodium (bright green needles) and potassium are prepared by treating a solution of the hydrate with the alkali in an atmosphere free from carbon dioxide, and evaporating in a vacuum in the dark. They have formulæ of the type $M_2(AuO_2)_2$. The salts of the alkali earth metals are obtained by treating solutions of their hydroxides with an alkali aurate solution. They form voluminous, light green precipitates which retain much water, are sensitive to light, and have the formula $M(AuO_2)_2$. The degree of hydration of the aurates is difficult to determine, but it tends towards the limit of $6H_2O$ for those of potassium, calcium, strontium, and barium, and $2H_2O$ for that of sodium. The aurates are stable towards heat when dry, but in

solution are decomposed by light or heat, giving a violet-black residue of aurous oxide, Au_2O .

Sulphur dioxide and alcohol (slowly) precipitate metallic gold from their solutions, which with dilute sulphuric and nitric acids form auric hydroxide and a sulphate or nitrate. Hydrochloric acid dissolves them, forming gold chloride and an alkali or alkali earth chloride. With organic matter, they form powders which detonate when heated.
E. H.

Gold Chromate. N. A. ORLOFF (*Chem Zeit.*, 1907, **31**, 1182).—A solution of *auric chromate*, $\text{Au}_2(\text{CrO}_4)_3$, is obtained by treating a large excess of freshly-precipitated silver chromate with a solution of auric chloride. On evaporation, the solution deposits at first gold, but subsequently the *chromate*, $\text{Au}_2(\text{CrO}_4)_3\text{CrO}_3$, crystallises from the red mother liquor.
W. H. G.

Mineralogical Chemistry.

Optical Activity of Mineral Oils in Connexion with the Question of their Origin. ROMAN ZALOZIECKI and H. KLARFELD (*Chem. Zeit.*, 1907, 31, 1155—1156, 1170—1172. Compare Kraemer and Spilker, *Abstr.*, 1900, i, 73, 333; Walden, *Abstr.*, 1906, ii, 368; Marcusson, *Abstr.*, 1907, i, 466; Neuberg, *Abstr.*, 1907, i, 577).—As a general rule, light-coloured Galician mineral oils are optically inactive, whereas the heavy, dark-coloured oils are optically active. Of the fractions obtained from the latter oils, only those boiling above, roughly, 200°/12—15 mm. are optically active. Since heavy, dark-coloured mineral oils contain a high proportion of asphaltic and resinous substances, the conclusion is drawn that the optical activity of these oils is almost entirely due to the presence of colophonic and terpene-like hydrocarbons. The authors discuss the several theories which have been advanced to explain the origin of mineral oils, and come to the conclusion that mineral oils are derived, not only from fats of higher animals, but also from substances of both animal and vegetable origin which do not readily putrefy, such as waxes, wax-fats, resins, gums, &c. W. H. G.

Enstatite-Augite in Diabase from Tasmania. ALFRED OSANN (*Centr. Min.*, 1907, 705—711).—Analysis I, by Dittrich, is of a pale-coloured pyroxene isolated from a medium-grained, fresh rock (anal. II) composed only of pyroxene and zoned plagioclase:

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	51·87	0·21	2·02	3·50	8·98	0·18	16·26	15·70	0·16	0·09	1·20	100·17
II.	52·49	0·62	16·44	2·60	5·30	trace	6·18	11·71	2·06	1·09	1·67	100·06*

* Also trace of P₂O₅.

The grains of pyroxene consist of an intergrowth of two optical varieties, differing in birefringence and in optical orientation (the optic axial plane being parallel to the plane of symmetry in one, and perpendicular to it in the other). An attempt to separate these two portions for analysis was not successful. In the low content of calcium and iron, and in the peculiar optical characters, this pyroxene resembles those of the enstatite-augite series of W. Wahl (*Tsch. Min. Mitt.*, 1907, 26, 1). The comparatively large amount of water is probably present as basic hydrogen.

L. J. S.

Physiological Chemistry.

Tension of Carbon Dioxide in Alveolar Air during Exercise.

BERTRAM J. COLLINGWOOD and H. L. F. BUSWELL (*Proc. Physiol. Soc.*, 1907, xxi—xxii; *J. Physiol.*, 36).—The method adopted for collecting alveolar air was rather different from that used by Haldane and Priestley, but the results, which show much greater variations than those given by the first-quoted authors, are stated to confirm their statement that the hyperpnœa of muscular work is due to a rise of carbon dioxide pressure in the respiratory centre. W. D. H.

Tension of Carbon Dioxide in Alveolar Air during Chloroform Narcosis. BERTRAM J. COLLINGWOOD and H. L. F. BUSWELL (*Proc. Physiol. Soc.*, 1907, xxiv—xxv; *J. Physiol.*, 36).—As anæsthesia advances, there is a well-defined rise of carbon dioxide tension in the alveolar air. Increased tension of the gas in the venous blood also occurs, which is due either to the slowing of the blood-stream, or to deficient lung ventilation. The experiments were made on cats. W. D. H.

Hypothermolysin. G. OLIVI (*Zeitsch. physiol. Chem.*, 1907, 53, 484—495).—Low temperatures (1° to 2°) alter the red corpuscles, so that their receptors are no longer able to unite with ordinary hæmolysin, but at the same time there is developed a specific anti-substance for the cooled corpuscles which is called *hypothermolysin*. The change produced by cooling is not total, a certain number of receptors remaining unchanged, and capable of uniting with normal hæmolysin. The bearing of this observation on the hæmolysis of paroxysmal hæmoglobinuria and rheumatism is discussed. W. D. H.

The Chemical Hæmolysins. III. ALBERT J. J. VANDELVELDE (*Bull. Soc. chim. Belg.*, 1907, 21, 373—380. Compare Abstr., 1907, ii, 792).—The paper is partly polemical against Führer (Abstr., 1907, ii, 631), and deals with the hæmolytic action of ethyl alcohol, digitalin, strophanthin, saponin, difluoroethyl alcohol, the three isomerides, *isopropyl* formate, methyl propionate, and ethyl acetate, the three compounds, *isobutyl* acetate, ethyl *isobutyrate*, and *isopropyl* propionate, the toluic acids, and the nitro-, hydroxy-, and amino-benzoic acids towards defibrinated ox-blood. The value 15.4888% by weight (Abstr., 1907, ii, 632) for the limiting hæmolytic value of ethyl

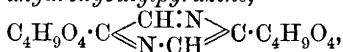
alcohol is confirmed. The critical coefficient (the ratio of isotoxic quantities of the substance and of ethyl alcohol, multiplied by 100) of digitalin (Merck) and of digitoxin (Merck) in alcoholic solution is 0.0036, in aqueous solution, 0.40. Comparison of these two figures gives further evidence that substances have a greater toxicity in alcoholic solution than when alone. The critical coefficient of strophantin or ouabain, and of saponin, in alcoholic solution is 0.13. Difluoroethyl alcohol has a critical coefficient, 92.92, showing that substitution of fluorine only slightly alters the toxic properties of ethyl alcohol (of which the critical coefficient is obviously 100). Comparison of the critical coefficients of isopropyl formate (5.67), methyl propionate (5.67), and ethyl acetate (11.31), and also of isobutyl acetate (4.34), ethyl isobutyrate (4.85), and isopropyl propionate (5.19), shows that the more symmetrical isomeride has the higher value. The values obtained for the critical coefficients of the substituted benzoic acids have already been described (Abstr., 1907, ii, 890).
E. H.

Nature of the Alkalinity of Intestinal Juice. EGIDIO POLLACCI (*Boll. Chim. Farm.*, 1907, 46, 789—791).—The alkalinity of intestinal juice is, at least partially, due to the presence of ammonia or an ammonium compound. The total volatile alkali evolved on heating 1000 grams of the fresh intestines of the hog amounts to 0.0268 gram of ammonia or 0.1513 gram of ammonium carbonate, or 0.531 gram of ammonium oleate.
T. H. P.

Animal Digestion. E. S. LONDON and W. W. POLOWZOWA (*Zeitsch. physiol. Chem.*, 1907, 53, 429—452).—From experiments on dogs with fistulae, the following conclusions are drawn; about 50% of the digested products are absorbed in the jejunum, and from 40—60% of the nitrogen. The concentration of protein cleavage products in the fluid to be absorbed is about 0.4%. By gastric digestion alone, the protein material passes into the intestine in an absorbable state. Glycine is absorbed in the same measure as the higher products of protein cleavage. The addition of the duodenal juices to the products of gastric digestion does not increase the rate of absorption. About 30% of the duodenal juices is absorbed in the jejunum. Aqueous solutions of monobutyryl and sodium oleate pass through the intestine more slowly than fluids which contain protein cleavage products. Sodium oleate is absorbed more slowly than monobutyryl and protein cleavage products; it causes increased secretion of intestinal juice. Solutions of sugar and dextrin are rapidly and completely absorbed in the jejunum. Dextrin solutions cause little or no secretion of bile, but an abundant secretion of pancreatic juice. All these statements are supported by figures, and details are added on rate of digestion *in vitro* with mixtures of juices.
W. D. H.

Behaviour of Glucosamine, and of the First Product of its Transformation, in the Animal Body. KARL STOLTE (*Beitr. chem. Physiol. Path.*, 1907, 11, 19—34).—Free glucosamine (chitosamine), dissolved in water or in methyl alcohol, is gradually changed, as was

shown by Lobry de Bruyn (Abstr., 1899, i, 732), into a substance which can also (and more readily) be obtained by the action of alcoholic ammonia on lævulose. The molecular weight of the acetyl derivative of this substance has now been determined, and shows that Lobry de Bruyn's formula must be doubled, so that it becomes $C_{12}H_{20}O_8N_2$. The acetyl derivative, $C_{23}H_{36}O_{16}N_2$, contains eight acetyl groups, and not four as supposed by Lobry de Bruyn. When oxidised with hydrogen peroxide, the substance is now found to yield pyrazine-2:5-dicarboxylic acid, previously described by Stöhr (Abstr., 1892, 507; 1893, i, 487). The transformation product of glucosamine and of lævulose, for which the name *fructosazine* is suggested, is therefore 2:5-ditetrahydroxybutylpyrazine,



and its formation from glucosamine would appear to take place according to the equation $2C_6H_{13}O_5N + O = C_{12}H_{20}O_8N_2 + 3H_2O$.

By means of intravenous injection into rabbits, the maximum dose of glucosamine was now determined which could be broken down by the organism without any of the substance passing into the urine. This dose was very small, 1/25 of the corresponding quantity of dextrose and of lævulose. A transformation into fructosazine in the organism could not be observed with certainty. Moderate doses of fructosazine, up to one gram, when given *per os*, were completely oxidised.

G. B.

Value of Ultimate Protein Cleavage Products in the Organism; Experiments on a Dog with Eck's Fistula. EMIL ABDERHALDEN and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1907, 54, 80—85. Compare Abstr., 1907, ii, 369, 892).—A dog with an Eck's fistula (a connexion between the portal vein and vena cava inferior, cutting out the liver from the portal circulation), not only remained in nitrogenous equilibrium, but retained nitrogen when fed on the ultimate cleavage products of protein (meat) for eight days. This result does not give support to the view that the liver plays an essential part in protein synthesis, but rather that this synthesis takes place in the intestinal wall.

G. B.

Comparative Study of Phenols as Agents in Parthenogenesis. YVES DELAGE and P. DE BEAUCHAMP (*Compt. rend.*, 1907, 145, 735—738).—Loeb's hypothesis that parthenogenesis is due to certain agents increasing the velocity of oxygen-transport is not supported by the present experiments; for substances such as catechol, quinol, and pyrogallol, which have this property in a high degree, are the least active in promoting parthenogenesis, whilst resorcinol and phloroglucinol are very active, although they possess little or no power of transporting oxygen. How these materials act, and how sugar acts as a favouring factor in their action, are subjects which are discussed, but not decided.

W. D. H.

Physical and Chemical Properties of Nerves. I. NATHANIEL H. ALCOCK and G. ROCHE LYNCH (*J. Physiol.*, 1907, 36, 93—103).—The average percentage of water in medullated nerves varies in differ-

ent species of animal; for instance, cat, 67·3; dog, 75·4, and horse, 69·3. The percentage in the non-medullated nerves of the horse is 81·2. There are also variations in the same species, and in different nerves of the same animal. Cats' nerves remain unchanged in weight in 1·16% sodium chloride solutions; in 1·17% solutions they lose weight, and in 1·46% solutions of potassium chloride, they gain weight. The average percentage of chlorine in medullated and non-medullated nerves of the horse is the same (0·23). The medullary sheath contains less water than the axis cylinder, but a not dissimilar amount of chlorine.

W. D. H.

Sulphur Compounds of the Nervous System. WALDEMAR KOCH (*Zeitsch. physiol. Chem.*, 1907, 53, 496—507).—The sulphur compounds of nervous tissue are divided into four groups: (1) that of lipoids, for example, protagon; (2) that of extractives soluble in 95% alcohol; (3) that of extractives insoluble in boiling alcohol and ether, but soluble in cold water; (4) that of proteins. The view is advanced that in so-called protagon, a sulphur compound acts as a link between lecithin and cerebrin. The sulphur compound under heading (2) consists as to one-tenth of its amount of inorganic sulphates, and the remainder of a taurine-like compound. Those under heading (3) consist mainly of inorganic sulphates, but the presence of protein-like sulphur compounds (gelatin?) is suggested. The protein sulphur (heading 4) is contained in neuro-keratin and nucleo-protein. The amount in albumin and globulin was not estimated. Estimation of these substances in grey and white matter shows that grey matter contains nucleo-protein, globulin, and neutral sulphur, and white matter contains the higher proportion of neuro-keratin and lipid-sulphur. The importance of the sulphur compounds for the oxidation processes in the brain is discussed; the brain has to be provided with excess of oxygen in order to perform its work. In *Dementia præcox* there is a marked lessening of the neutral sulphur (35% on the average; three cases), and a rise of inorganic sulphates; the lipid-sulphur is not altered. Interference with oxidation processes will explain some of the symptoms of this disease.

W. D. H.

Glycogen in Frogs during Inanition. EDUARD PFLÜGER (*Pflüger's Archiv*, 1907, 120, 253—289).—The author's previous work has shown that during inanition in dogs, glycogen does not entirely disappear from the body; in one animal, for instance, after a fast of twenty-eight days, the liver and muscles still contained fifty-two grams of glycogen. The present experiments on frogs confirm this. They were kept for months, from August onwards, in water renewed daily, no food was given; flies and other insects being kept out of the trough by a fine net. At intervals, ten frogs were taken and analysed by methods which are described in full. There is no accumulation of glycogen before the winter sets in; artificial warmth, like the summer, causes the glycogen to diminish, and a slight diminution was noticed in the first month. After this, the glycogen steadily increased from 47% to 56%. Indeed, the increase was almost as marked as in frogs freshly collected from time to time, in which case, of course, food was available.

W. D. H.

General Mechanism of the Transformation of Glycogen into Dextrose in the Muscles and Tissues. F. MAIGNON (*Compt. rend.*, 1907, 145, 730—732).—The muscles possess an amylase which is regarded as the agent which transforms glycogen into sugar. This occurs continuously in the normal state, but is exaggerated under certain influences; crushing accelerates it, because by that means the glycogen and the enzyme are brought more closely into contact.

W. D. H.

Creatine and Creatinine in Meat and Meat Extracts. A. D. EMMETT and HARRY S. GRINDLEY (*J. Biol. Chem.*, 1907, 3, 491—516. Compare Abstr., 1906, ii, 242).—With certain modifications, the Folin method is as applicable to meat and meat extracts as it is to urine. Creatine and creatinine together are present to the extent of 0.45% in meat, and from 1.4% to 6.5% in meat extracts. Hohner gives the latter number as 10—12%; his methods are criticised.

W. D. H.

Chemical Composition of Hair. THOMAS A. RUTHERFORD and PHILIP B. HAWK (*J. Biol. Chem.*, 1907, 3, 459—490).—The chemical composition of human hair is influenced by race, sex, age, colour of hair, and other factors. As judged by the numerous tables presented, the differences do not appear to be great. In different races, the sulphur-nitrogen ratio, for instance, varies from 1 : 3.2 to 1 : 2.9.

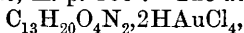
W. D. H.

Tissue Respiration in Perfused Kidneys. HORACE M. VERNON (*J. Physiol.*, 1907, 36, 81—92. Compare Abstr., 1907, ii, 111).—After perfusion of an excised mammalian kidney with Locke's solution for eleven hours, the gaseous metabolism falls to half its initial value. This does not occur if 2% of rabbit's serum is added; sheep's serum is less efficient, egg-white much less so, and milk is of no value at all. Witte's peptone (0.01% to 1%) is as efficient as serum proteins; diglycylglycine, glycine, and leucine have a slight sustaining influence, but urea produces a distinct improvement.

W. D. H.

Crab Extract. IV. D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. Nahr. Genussm.*, 1907, 14, 687—691).—In addition to the bases recorded previously (Abstr., 1907, ii, 283, 491) as being present in this extract, the following have been isolated: crangitine, methylpyridonium hydroxide, neosine, and crangonine.

Crangitine hydrochloride, m. p. 160°. The *aurichloride*,



forms short, pale yellow prisms, m. p. 162—165°. *Crangonine aurichloride* forms groups of short needles, m. p. 130—140° (not sharp). Neither base was obtained in the uncombined state.

W. P. S.

Spectroscopic and Chemical Behaviour of the Pigment Secretion of *Aplysia punctata*. RAFFAELE PALADINO (*Beitr. chem. Physiol. Path.*, 1907, 11, 65—70).—A table is given of the absorption spectra of the pigment in various solvents; the results differ not inconsiderably from those obtained by previous observers, such as MacMunn (Abstr., 1899, ii, 313). The chloroform extract of a solution of the

pigment in dilute acetic acid left, on evaporation, a partially crystalline substance, containing nitrogen and iron and, perhaps, traces of manganese. G. B.

Excretion of Creatine and Creatinine in Hepatic Disease. E. MELLANBY (*Proc. Physiol. Soc.*, 1907, xxiii; *J. Physiol.*, 36).—In ascitic fluid due to liver disease, no creatine or creatinine is found. In this condition, creatinine is diminished in the urine; this is attributed to circulatory disturbance and lessened hepatic functions. Creatine in the urine is increased in cancer of the liver (two cases); this is attributed to breakdown of muscle, failure to convert it into creatinine, or a direct production in the tumour. W. D. H.

Metabolism in Alcaptonuria. EMIL ABDERHALDEN and BRUNO BLOCH (*Zeitsch. physiol. Chem.*, 1907, 53, 464—483).—Administration of large amounts of water to a patient suffering from alcaptonuria caused a great increase in the excretion of nitrogen, but the quantity of homogentisic acid remained constant; the urinary ammonia was increased. The action of water is believed, not to be due to an increase of nitrogenous metabolism, but mainly to a washing out of the products readily. No conclusive answer was obtained to the question whether the urinary nitrogen comes chiefly from exogenous or endogenous metabolism; after inanition, however, the rise in excretion after giving nitrogenous food is very rapid. Some observations were also made on the value of gelatin and amino-acids in the diet. About half of the protein-nitrogen was replaceable by gelatin, but it is of importance not merely to examine the urine on the day of administration, as after effects are seen for some days later. Both gelatin and amino-acids increased the excretion of homogentisic acid. W. D. H.

Uroleucic Acid. ARCHIBALD E. GARROD and WILLIAM H. HARTLEY (*J. Physiol.*, 1907, 36, 136—142).—The existence of a second alcapton acid in cases of alcaptonuria has been mooted by several observers, who have named it, after Kirk, uroleucic acid. The present investigation lends no support to this idea; uroleucic acid is a residue consisting of homogentisic acid mixed with impurities. W. D. H.

Xanthine as a Cause of Fever. ARTHUR R. MANDEL (*Amer. J. Physiol.*, 1907, 20, 439—443).—In fever there is a distinct relationship between rise of temperature and the appearance of purine bases in the urine. The administration of xanthine or caffeine will effect a rise of body temperature in monkeys. This may be neutralised by the simultaneous administration of sodium salicylate. It is suggested (1) that in aseptic fever the fall in uric acid is due to lessened circulation through the kidneys owing to vaso-constriction; (2) that in surgical fever the purine bases are derived from crushed tissues; (3) that in septic fevers the action of toxins is to lessen the power of such tissues as muscle to oxidise xanthine to uric acid, and (4) that xanthine forms a combination with salicylic acid similar to diuretin (= caffeine + salicylic acid), thereby rendering it innocuous. W. D. H.

Action of Aconitine on Nerve Fibres. AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1907, xxx—xxxii; *J. Physiol.*, 36).—If a frog is chloroformed and then killed by aconitine, its nerves give no electrical response on excitation. If a normal frog's nerve is bathed in a solution of aconitine, it exhibits a peculiarity also produced by protoveratrine, namely, the response is persistent, and is not followed by an after effect in the opposite direction; the normal unfatiguability of a normal nerve is also abolished.

W. D. H.

Physiological Action of Adrenaline. W. KRETSCHMER (*Arch. exp. Path. Pharm.*, 1907, 57, 423—437, 438—440).—The administration of repeated doses of adrenaline in animals raises the blood-pressure until a maximum is reached, and it can be kept up by keeping up the injection. On cessation, the blood-pressure returns to normal, the rate of return being inversely proportional to the amount in the blood previously, and this gradually disappears. The rate of return is decreased by the administration of acids, the acid ions inhibiting the destruction of adrenaline in the blood and tissues.

W. D. H.

Hypnotic Action of the Valeric Acid Group. A. VAN DER ECKHOUT (*Arch. exp. Path. Pharm.*, 1907, 57, 338—357).—The recently-introduced narcotic *Bromoural* is monobromoisovalerylcarnamide, $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 149°. It is a pure narcotic, producing no primary excitation and no ill effects even in large doses in frogs, rabbits, and dogs. It acts rapidly, having a selective action on the cerebrum, and leaving the bulb and cord intact. It has no cumulative action. A large number of similar substances were investigated, and, as a rule, their activity is proportional to their solubility in fats. Chloroisovalerylcarnamide and α -bromo- α -methylbutyrylcarnamide are also narcotics; bromoisovalerylcarnamide is narcotic and toxic; iodoisovalerylcarnamide, bromobutyrylcarnamide, and bromobutyramide are toxic, and the following compounds are either very feeble narcotics or are inactive: bromovalerylcarnamide, isovalerylcarnamide, valerylcarnamide, bromoisobutyrylcarnamide, and bromoisobutyramide.

W. D. H.

Nitrite Poisoning after the Internal Administration of Bismuth Subnitrate. A. BÖHME (*Arch. exp. Path. Pharm.*, 1907, 57, 441—453).—The administration of large quantities of bismuth subnitrate in men leads to the formation of nitrous acid, and the consequence is methæmoglobinuria. The same follows *in vitro* in bacterial cultures, and is also produced by mixing fæcal matter with the salt. Similar results were obtained in experiments in animals.

W. D. H.

Cresol Poisoning. FERDINAND BLUMENTHAL and ERNST JACOBY (*Biochem. Zeitsch.*, 1907, 7, 39—44).—Whilst it is not denied that cresol affects many organs, such as the liver, injuriously, the principal cause of death is held to be the combination of the poison with the lipoids of the brain. Cresol readily forms compounds with fats and

fat-like substances. The amount found per gram of brain is very constant, whatever the dose of cresol given. If, however, the cresol is administered dissolved in olive oil, poisonous symptoms are not readily produced; it is absorbed slowly and excreted by the kidneys rapidly. In such cases, the amount in the brain is much less than when cresol is given in aqueous solution. Full protocols of experiments are given.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Chemistry of the Bacillus Coli Communis. MARY F. LEACH (*J. Biol. Chem.*, 1907, 3, 443—458, Compare Abstr., 1906, ii, 568).—By the action of sodium hydroxide and alcohol, part of the protein of the bacterial cells goes into solution in alcohol, and part remains undissolved. The solution contains the poison of the cell; the insoluble portion includes carbohydrate, nucleic acid compounds, and an immunising substance. Whether the immunising substance contains nucleic acid and depends for its action on this circumstance, is uncertain. W. D. H.

Formation of Glycogen by Yeast. FREDERICK W. PAVY and HUBERT W. BYWATERS (*J. Physiol.*, 1907, 36, 149—163).—Commercial (balloon) yeast contains 5% of glycogen, or 25% in the dry material. Incubation with water decreases the amount slightly, but with dextrose the amount is increased twice or thrice in as many hours. Beyond a certain point, however, increase in the concentration of the dextrose inhibits glycogen formation. Tartaric acid inhibits the process, and favours the disappearance of the glycogen. Sodium phosphate has no influence, but boiled yeast juice promotes glycogen production. The phenomena are due to increased cell growth, and not to simple accumulation of glycogen in pre-existing cells. W. D. H.

Assimilation of Carbon in Bacteria which Oxidise Hydrogen. A. F. LEBEDEF (*Biochem. Zeitsch.*, 1907, 7, 1—10).—Certain bacteria which can assimilate carbon from carbon dioxide liberate free oxygen, and this enables the oxidation of hydrogen to be carried out. The figures given are rather different from those which theory demands, an excess of hydrogen being always observed. The conclusion, however, is drawn that in all probability the chemistry of carbon assimilation in bacteria is not very different from what occurs in green plants. W. D. H.

Fixation of Nitrogen in Soil by Free Bacteria, and its Importance for the Nutrition of Plants. ALFRED KOCH, J. LITZENDORFF, F. KRULL, and A. ALVES (*J. Landw.*, 1907, 55, 355—416).—Assimilation of nitrogen in soils is increased by addition

of dextrose, sucrose, soluble starch, and probably cereal straw, the amount thus fixed being 8—10 mg. per gram of sugar. Frequent applications of sugar tend to diminish rather than increase the amount of nitrogen fixed. The best results in relation to the amount of sugar were obtained with one application of 2%.

Fixation of nitrogen was increased by superphosphate, basic slag, and iron sulphate, and retarded by lime, potassium sulphate and chloride, carbon disulphide, and, perhaps, by magnesium sulphate.

N. H. J. M.

Biological Succession of Mineral Substances in Marine Algæ.

FRANCESCO SCURTI and S. CALDIERI (*Chem. Zentr.*, 1907, ii, 1089; from *Staz. sperim. agrar. ital.*, 1907, 40, 225—233).—In continuation of the work of Scurti (*Abstr.*, 1907, ii, 122), it has been found that the elements contained in the marine algæ can be arranged in two groups. Those of the first group, including chlorine, calcium, magnesium, potassium, sodium, and silicon, gradually increase in quantity during the formation of the spores, whilst, after their appearance, these elements gradually decrease. The second group embraces iodine and phosphorus. The behaviour of iodine has already been recorded (*loc. cit.*). Phosphorus is absorbed during the production of the spores, but, unlike the elements of the first group, it still further increases in amount after maturation is at an end, and thus reaches its maximum in winter.

E. G.

Application of Bio-chemical Methods for the Detection of Sugars and Glucosides in Plants of the Tribe Taxææ. CHARLES LEFEBVRE (*Arch. Pharm.*, 1907, 245, 493—502. Compare *Abstr.*, 1907, i, 864).—Indication of the presence of various sugars and glucosides in extracts of plants, &c., may be obtained by treating these extracts with enzymes, such as invertase and emulsin. The change in the optical rotatory power of an extract of young twigs of *Taxus baccata* on treatment with invertase appeared to point to the presence of sucrose, but practically the same change is observed on treating raffinose with invertase. However, by treatment with barium or strontium hydroxide and fractional precipitation with alcohol were obtained, besides raffinose (compare *Abstr.*, 1907, ii, 715), crystals of sucrose and indications of the presence of a levorotatory sugar which does not reduce Fehling's solution. Investigation of twigs of *Taxus baccata* gathered at various times of the year showed that the quantity of sugars present does not vary considerably, whilst the quantity of taxicatin present is greatest in the autumn and winter and smallest from April to July.

The leaves and twigs of *Cephalotaxus drupacea*, *Cephalotaxus pedunculata*, *Podocarpus Chinensis*, and *Torreya myristica* all contain sugars, glucosidic substances hydrolysed by emulsin, and ferments similar in action to invertase and emulsin.

W. H. G.

Causes of the Displacement of Absorption Bands in the Leaf. D. IWANOWSKI (*Ber. deut. bot. Ges.*, 1907, 25, 416—424).—In the investigation of the well-known difference between the spectrum

of a living leaf and that of an alcoholic chlorophyll solution, the spectro-photometric method is preferable to the spectroscopic. By means of the former method, the leaf-spectrum is found to differ from that of the solution in having a much greater absorption at the red end (a—B), and in having both the principal absorption bands somewhat displaced towards the red. This difference has generally been attributed to the chlorophyll of the chloroplasts being in the solid state. Solid solutions of chlorophyll in gelatin and in paraffin-wax were, however, found to have a spectrum differing but slightly from that of an alcoholic solution.

By adding a little neutral salt (for example, MgSO_4) to a concentrated alcoholic chlorophyll solution greatly diluted with water, the author obtained a fine suspension, which had a spectrum very similar to that of the living leaf. This similarity is attributed to the circumstance that in both cases the spectrum is largely due to the reflected light, whereas in the case of an alcoholic chlorophyll solution it is wholly formed by transmitted light. G. B.

Fruit of *Celestrus scandens* and *Solanum Dulcamara*. A. A. WELLS and GRANT S. REEDER (*Chem. News*, 1907, 96, 199—200).—Berries of *Celestrus scandens* were found to contain lævulose, tartaric acid, and gallic acid. The seeds contain palmitic acid, and an oil which yields olein and a small amount of palmitin when hydrolysed. Berries of *Solanum Dulcamara* contain tartaric and citric acids and fructose. N. H. J. M.

Supposed Toxicity of Hungarian Haricots. LÉON GUIGNARD (*Compt. rend.*, 1907, 145, 1112—1118).—A reply to Evesque, Verdier and Bretin (*Abstr.*, 1907, ii, 912). The author has examined a sample of the Hungarian haricots stated by Evesque, Verdier and Bretin to contain 0.342 gram of hydrogen cyanide per kilo., and finds that, in common with all the specimens of Hungarian haricots that he has examined (*Abstr.*, 1906, ii, 301), they do not contain a trace of hydrogen cyanide. He also shows that the method of macerating the beans with water containing tartaric acid, preliminary to estimating the hydrogen cyanide, is untrustworthy, as the tartaric acid exercises a paralysing effect on the ferment (emulsin) that causes the hydrolysis of the cyanogenetic glucoside. M. A. W.

Chemistry of Mistletoe (*Viscum album*). M. LEPRINCE (*Compt. rend.*, 1907, 145, 940—941).—The author has obtained 1.6 grams of a crystalline hydrochloride of a base from 25 kilos. of dry mistletoe plant; the crystalline *platinichloride*, $(\text{C}_8\text{H}_{11}\text{N})_2\text{H}_2\text{PtCl}_6$, decomposes at 250°. M. A. W.

Inosites of Mistletoe. GEORGES TANRET (*Compt. rend.*, 1907, 145, 1196—1198).—The fresh ripe berries of mistletoe contain in addition to dextrose, lævulose, and sucrose, *i*-inosite and *r*-inosite; 12 grams of the former and 4 grams of the latter being obtained from 1 kilo. of the fresh fruit, or four times these quantities from 1 kilo. of dry fruit. Up to the present, the leaves of the walnut tree have

formed the chief source of *i*-inosite (Tanret and Villiers, Abstr., 1877, ii, 304; 1878, 390; Maquenne and Tanret, Abstr., 1890, 471), but the yield is only one-sixteenth of that afforded by mistletoe. The isolation of *r*-inosite from mistletoe is important as affording the first instance of the separation of a racemic sugar from a living organism. The leaves of the mistletoe plant also contain the inosites, probably in the form of some compound, because the author could only isolate 0.50 gram from 1 kilo. of dry leaves. M. A. W.

Lippia scaberrima (Beukess Boss). FREDERICK B. POWER and FRANK TUTIN (*Arch. Pharm.*, 1907, 245, 337—350; *Amer. J. Pharm.*, 1907, 79, 449—462).—Dried stems and leaves of this South African plant were examined. In addition to resins and other amorphous products, the following substances were isolated. (1) An aromatic essential oil (0.25%), b. p. 220—230°, D_{15}^{25} 0.950, $n_D^{20} + 7.36'$ (100 mm. tube). (2) Heptacosane, $C_{27}H_{56}$, m. p. 59°. (3) Hentriacontane, $C_{31}H_{64}$, m. p. 68°. (4) A paraffin, m. p. 80°, in very small amount. (5) A phytosterol, $C_{27}H_{46}O$, m. p. 134°. (6) Unsaturated alcohols, probably of the general formula, $C_nH_{2n-4}O$, and containing one double linking. (7) Formic and butyric acids in the uncombined state. (8) Esters of various acids, including formic, butyric, valeric, arachic, and linoleic. (9) *Lippianol*, $C_{25}H_{36}O_4$, a colourless, crystalline substance, having the properties of a monohydric alcohol; m. p. 300—308° (decomp.), $[\alpha]_D^{20} + 65^\circ$ in 0.5% alcoholic solution. (10) Minute quantities of two yellow, crystalline substances, m. p. 267° (approx.), and a trace of a colourless, crystalline substance, m. p. 123°. (11) Dextrose (mainly in the inactive form). A glucoside-like substance was also present, but was not isolated; it yielded on hydrolysis dextrose and other products which were not identified.

C. F. B.

The Fruit of Styra Obassia. Y. ASAHINA (*Arch. Pharm.*, 1907, 245, 325—328).—By extracting the husks with 60% alcohol, *styracitol* was obtained in yield equal to 10% of the drug. This crystalline substance, $C_6H_{12}O_5$, m. p. 155°, $[\alpha]_D^{20} - 71.72^\circ$, is very readily soluble in water, sparingly so in strong alcohol; reduces ammoniacal silver nitrate, but not Fehling's solution, even after boiling with dilute mineral acids, although it does so after oxidation with sodium hypobromite or nitric acid; does not form a compound with phenylhydrazine acetate or with benzaldehyde when shaken with the latter and 50% sulphuric acid; yields no crystalline acetyl or benzoyl derivative; forms β -hexyl iodide when distilled with hydriodic acid and yellow phosphorus.

The kernels yielded 18% of fatty oil when extracted with ether. The oil expressed from the seeds had D_{15}^{25} 0.974°, acid number 9, saponification number 180, iodine number (Hübl) 127, Hehner's number 91.

C. F. B.

Physico-chemical Processes in the Production of Soil. PAUL ROHLAND (*Chem. Zentr.*, 1907, ii, 724; from *Landw. Jahrb.*, 36, 473—483).—The colloids present in soils are derived from feldspar by

the action of water and carbon dioxide. Their coagulation by electrolytes probably depends on the simultaneous separation of hydroxyl ions from the alkali. Soils containing colloidal hydroxides at a constant temperature take up or lose water until the vapour tension of the colloid equals the surrounding vapour tension. Alterations in temperature continuously alter the amount of water.

Adsorption is attributed partly to chemical actions, partly to adsorption, and is perhaps also due to catalytic influences. N. H. J. M.

Protective Action of Colloids on Clay Suspensions. GUSTAV KEPPELER and ALBERT SPANGENBERG (*J. Landw.*, 1907, 55, 299—300).—Fickenberg (*ibid.*, 1906, 343) showed that much greater amounts of alkali are required to flocculate suspensions of natural clay soil than in the case of kaolin, and attributes his results to a protective action exercised by the humus.

Determinations of the amounts of alkali required for flocculation showed that varying results are obtained with different soils, and it is found that the amounts depend on the quantity of humic acid in the soil. N. H. J. M.

Movement of Ammoniacal Nitrogen in Nature. PAUL EHRENBURG (*Chem. Zentr.*, 1907, ii, 723—724; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1907, 4, 1—254).—Loss of ammonia by evaporation from soils is only to be expected in the case of sandy soils containing much calcium carbonate and deficient in zeolitic compounds and humus, and then only at the highest summer temperatures, when the soil is dried up, and when there has been a heavy application of nitrogenous manure. Even then the loss is extremely small.

Ammonium salts are undoubtedly directly utilised by plants. With the exception, however, of plants utilising acids, the amount of nitrogen so taken up is insufficient, and for satisfactory growth nitrification is essential. N. H. J. M.

Influence of Plant Constituents on the Physical and Chemical Properties of Soils. VIKTOR ZAILER and LEOPOLD WILK (*Chem. Zentr.*, 1907, ii, 732—734; from *Zeitsch. Moorkultur u. Torfverwert.*, 1907, 1—109).—The physical properties of peat, especially when only slightly decomposed, which vary distinctly when the peat is derived from only very distantly related plants, are coherence, density, capacity for holding water, hygroscopicity, and absorptive power; other physical properties seem to depend less on botanical composition. Hygroscopicity decreases as decomposition proceeds, notwithstanding the increase of humus substances. Absorption of ammonia depends chiefly on free humic acid and related colloids.

The amount of ash in peat is generally higher than would be indicated by the botanical composition. Potassium and sodium salts are almost completely washed out, and phosphoric acid to a considerable extent, whilst calcium and iron remain almost unchanged in quantity. The amount of nitrogen depends mainly on the amount originally present in the plants, and to a less extent on chemical processes and chitinous remains. N. H. J. M.

Fallow. WILHELM KRÜGER and BERTHOLD HEINZE (*Chem. Zentr.*, 1907, ii, 726 ; from *Landw. Jahrb.*, 36, 383—423).—During a fallow the amount of soluble forms of nitrogen, especially nitrates, increases. The number of micro-organisms increases at first, and then gradually diminishes. The total nitrogen seemed to increase, but this requires confirmation. N. H. J. M.

Manurial Experiments with Different Kinds of Nitrates. JOHN SEBELIEN (*Landw. Versuchs-Stat.*, 1907, 55, 293—297).—Pot experiments with white mustard, grown in poor sandy soil, showed that the yield when manured with calcium nitrate and with “sulphate-nitrate” respectively was about five times as great as with sodium nitrate, and that far greater amounts of these manures may be applied without injury as compared with the ordinary inorganic nitrogenous manures.

“Sulphate-nitrate” [$\text{CaSO}_4 + 2(\text{NH}_4)_2\text{NO}_3$] is prepared by mixing calcium nitrate with ammonium sulphate (equal mols.), the idea being to avoid the difficulty in the use of calcium nitrate due to its deliquescence.

Further experiments with oats grown in sandy soil and in loam showed that sodium and calcium nitrates had about equal effects.

N. H. J. M.

Is a Favourable Stimulating Effect on the Development of Crops by Small Amounts of Manganese Salts Observable in the Field? HJALMAR VON FEILITZEN (*J. Landw.*, 1907, 55, 289—292).—The soil on which the experiment was made consisted chiefly of slightly decomposed sphagnum peat, and has been under cultivation since 1894, when sand and lime were applied, as well as artificial manures which have been applied each year since.

An application of 10 kilos. of magnesium sulphate per hectare was found to have no effect on oats.

N. H. J. M.

Leucite and its Application as a Manure. UGO ALVISI and DOMENICO VENDITORI (*Gazzetta*, 1907, 37, ii, 379—383).—No action takes place between leucitic materials and superphosphates when these are applied together as manures, so that the value of the superphosphate remains uninjured.

T. H. P.

Analytical Chemistry.

Improvements in Hemple's Gas-Analysis Apparatus. GEORGE DE VOLDERE (*Chem. Zentr.*, 1907, ii, 1113—1114; from *Zeitsch. chem. Apparatenkunde*, 1907, 2, 344—346).—The levelling tube is replaced by a levelling reservoir fitted with a side tube having the same diameter as the burette. The burette is constructed as recommended by Pfeiffer

(Abstr., 1907, ii, 194), but the capillary tube between the first enlargement and the stopcock has been omitted, and a four-way cock has been put instead, whilst a second tube serves for the purpose of applying suction or pressure. The chief advantage of this arrangement is that the burette can be fixed firmly by means of a clamp. The U-tube in the pipette has been also replaced by a four-way stopcock. For further details, the illustrations in the original article should be consulted.

A convenient apparatus is also described for the combustion of gases by means of palladium asbestos. L. DE K.

Use of Chloral Hydrate, Chloral Alcoholate, and Bromal Hydrate Solutions in Chemical, Microscopic, and Microchemical Investigations. EDUARD SCHAEER (*Ber. deut. pharm. Ges.*, 1907, 17, 407—413).—Aqueous and alcoholic solutions of chloral hydrate and bromal hydrate dissolve a large number of inorganic and organic substances which have no other common solvent. Where complete solution of a mixture is necessary or advantageous as a preliminary step to the detection or separation of its components, the employment of 60% to 80% aqueous or alcoholic chloral hydrate solutions as the solvent is recommended. The value of chloral hydrate as a clearing agent for microscopic preparations depends on its penetrating power, as also on its action as a solvent for the cell contents which render the preparation opaque. In many cases, the best results are obtained by successive treatment with concentrated aqueous and alcoholic solutions. In microchemical analysis, it has been found possible with the aid of chloral hydrate solutions of the alkaloid reagents to determine the location of alkaloids in plant structures. G. Y.

Isolation of Traces of Mineral Substances from Saline Mixtures. Application to Medical Chemistry, Toxicology, and Hydrology. G. MEILLÈRE (*J. Pharm. Chim.*, 1907, [vi], 26, 443—450).—A summary of the methods used in analysis for concentrating small quantities of substances which might otherwise escape detection. For instance, traces of lead in water are carried down completely by adding a little copper sulphate before passing hydrogen sulphide, and phosphoric and arsenic acids are precipitated completely in presence of ferric hydroxide. In some cases, extraction by means of an immiscible solvent in a suitable apparatus gives good results. Strong hydrochloric acid extracts lithia from alkali chlorides, &c. L. DE K.

Addition of Indigo in Titrations with Methyl- or Ethyl-orange. ROBERT LUTHER (*Chem. Zeit.*, 1907, 31, 1172. Compare Kirschnick, Abstr., 1907, ii, 910).—Solutions of indigo-carmin and methyl-orange are mixed in such proportions that, when added to a saturated solution of carbon dioxide in water, a neutral grey tint is obtained (compare Küster, Abstr., 1897, ii, 74). When such a mixture of methyl-orange and indigo-carmin is used, the change of colour during the titration of an alkali with acid is as follows: yellow,

green, colourless (or grey if a large quantity of indicator is taken), violet. The change from green or violet to the neutral grey or colourless stage is said to be very decided and sharp. The addition of indigo to solutions which are tinted yellow is also advantageous. W. H. G.

Behaviour of Chlorates and Perchlorates during Reduction.

DOMENICO VENDITORI (*Gazzetta*, 1907, 37, ii, 383—386).—In presence of sulphuric acid, finely-divided aluminium reduces chloric acid completely to hydrochloric acid, but has no reducing action on perchloric acid. Chloric acid may hence be estimated by converting it into hydrochloric acid and then estimating the latter by Volhard's method. T. H. P.

Detection of Fluorine Compounds in Wines.

L. VANDAM (*Ann. Chim. anal.*, 1907, 12, 466—468; *Rev. intern. Falsif.*, 1907, 20, 147—148).—Two hundred c.c. of the sample are mixed with a few drops of a 20% solution of sodium sulphate and then with 10 c.c. of a 10% solution of barium acetate. After twelve hours, the bulk of the liquid is poured off, and the precipitate collected on a filter, washed, dried, and ignited in a platinum crucible. After moistening with a drop of water, a little sulphuric acid is added and the crucible is at once fitted with an india-rubber ring supporting a paraffin-coated watch-glass, the convex part of which carries an inscription made with a soft point. The watch-glass is kept cold by a current of cold water. After heating the crucible for half an hour on a boiling water-bath, the watch-glass is gently heated to melt the paraffin coating and wiped with a soft linen cloth. If the sample is pure, no inscription will be visible, or at most but very faintly on breathing on the glass, but a visible etching is noticed even when there is as little as 10 mgs. of ammonium fluoride per litre. L. DE K.

Estimation of Sulphur Dioxide in Wines.

CARLO MENSIO (*Gazzetta*, 1907, 37, ii, 344—355).—The maximum amount of total sulphur dioxide per litre of wine permitted in Italy is 0.2 gram, of which not more than 0.02 gram should be in the free state. According to the official method of estimation, sulphur dioxide, which is evolved from wine on boiling, is regarded as existing in the free state in the wine. The author shows that this view is inaccurate, since compounds such as that formed by sodium hydrogen sulphite with acetaldehyde give up from 30% to 75% of their sulphur dioxide when boiled in aqueous solution and from 90% to 95% when boiled with wine.

The most accurate method of estimating the total sulphur dioxide in wine consists in acidifying with phosphoric acid and distilling in a current of carbon dioxide, the distillate being collected in iodine solution, in which the sulphur dioxide may be estimated either by titration of the excess of iodine with sodium thiosulphate or by Haas's method (*Abstr.*, 1882, 773). None of the methods given for estimating free sulphurous acid in a wine yields accurate results.

As the experiments of Franz and Rost (*Abstr.*, 1904, ii, 632) indicate that the toxic action of combined sulphur dioxide is not greatly dissimilar from that of the uncombined, and as the presence

of the latter in a wine is detectable by the taste, the fixing of a limit to the proportion of free sulphur dioxide should be abolished.

T. H. P.

Digestion of Urine in the Estimation of Nitrogen by the Kjeldahl Method. PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1907, 29, 1634—1637).—The nitrogen in urine may be estimated equally well by digestion with sulphuric acid and copper sulphate, sulphuric acid and metallic mercury, or sulphuric acid, metallic mercury and potassium sulphate added towards the end. In any case, the boiling should be continued for at least thirty minutes.

L. DE K.

Alkalimetric Estimation of Phosphoric Acid by Neumann's Method. J. P. GREGERSEN (*Zeitsch. physiol. Chem.*, 1907, 53, 453—463. Compare Abstr., 1903, ii, 243; 1905, ii, 68).—As the result of numerous series of experiments, the conclusion is drawn that Neumann's method gives excellent results when the following precautions are taken. In the destruction of the organic material and the formation of ash, 20 c.c. of Neumann's acid mixture should be used, and during the process concentrated nitric acid, and not the mixed acids, should be dropped in. In the precipitation, 250 c.c. of liquid should be used, and this should contain 15% of ammonium nitrate, only a slight excess of ammonium molybdate being employed; thus, for 10—15 mgs. phosphorus, 4 grams of molybdate suffice. In the final titration, it is advisable to add a slight excess of standard acid, to boil, in order to remove carbon dioxide, and then to titrate back with 0.5*N* sodium hydroxide.

J. J. S.

Estimation of Phosphoric Acid in Basic Slags by Grete's Method. C. H. KETNER (*Chem. Weekblad.*, 1907, 4, 757—764).—Grete's method (titration with gelatin-molybdenum solution until no further precipitate is formed) has been applied successfully in the Dutch agricultural stations, but for soluble phosphoric acid only. The author has tried to use it for total phosphoric acid also, and after some trials has succeeded by working as follows.

Ten grams of the basic slag are powdered, moistened with a little water, and then heated in a 500 c.c. Jena flask with 50 c.c. of sulphuric acid for about half an hour and until white fumes are formed. When cold, water is added, and, when again cooled, water is added up to the mark, and the whole is thoroughly shaken and filtered. Twenty-five c.c. of the filtrate are neutralised with ammonia, 20 c.c. of ammonium nitrate solution (1 : 2), a teaspoonful of powdered potassium nitrate, and 15 c.c. of nitric acid, D 1.2, are added, and the solution is then heated to boiling and titrated. In standardising the gelatin-molybdenum solution as usual with dihydrogen potassium phosphate in presence of the above substances, there should also be added 16 c.c. of 10% ammonia previously neutralised with dilute sulphuric acid.

L. DE K.

Estimation of Arsenic by the Gutzeit Method. CHARLES R. SANGER and OTIS F. BLACK (*J. Soc. Chem. Ind.*, 1907, 26, 1115—1123).—The modification suggested by the authors in order to

make the Gutzeit method quantitative, consists in allowing the arsine to pass over the surface of a strip of paper impregnated with mercuric chloride. The band of colour thus obtained is compared with a series of bands prepared from known amounts of arsenic. The sensitised paper is inserted in the form of a strip in a horizontal delivery tube leading from the evolution flask. The exact method of carrying out the estimation is given at length in the original paper, together with remarks on the precautions to be observed, and on the influence of certain interfering substances.

W. P. S.

Estimation of Arsenic in Urine. CHARLES R. SANGER and OTIS F. BLACK (*J. Soc. Chem. Ind.*, 1907, 26, 1123—1127; *Zeitsch. anorg. Chem.*, 1907, 56, 153—157).—The evaporated urine is distilled with hydrochloric acid, the distillate is oxidised with nitric acid, the latter is removed by heating with sulphuric acid, and the remaining solution is used for the estimation of the arsenic. About 200 c.c. of the urine are evaporated to a volume of 35 c.c. and then introduced into a distillation flask. One hundred c.c. of pure hydrochloric acid are added, and the mixture is distilled, the distillate being collected in a receiver containing 25 c.c. of concentrated nitric acid. When about 100 c.c. have distilled over, the distillate is treated with a further 25 c.c. of nitric acid and evaporated to a small bulk; 5 c.c. of sulphuric acid are next added, and the heating continued until the nitric acid has been expelled. The residue is diluted with water to a definite volume, and a part of it employed for the estimation of the arsenic, the Marsh-Berzelius method being used for the latter purpose.

W. P. S.

Estimation of Hydrofluosilicic Acid. SAMUEL HÖNIG (*Chem. Zeit.*, 1907, 31, 1207—1208).—The process is based on the fact that 1 mol. of hydrofluosilicic acid is neutralised by 2 mols. of sodium hydroxide when using methyl-orange as indicator, whereas 6 mols. are required if phenolphthalein is the indicator.

Twenty-five c.c. of the sample are titrated with *N*-sodium hydroxide in presence of methyl-orange. The result equals hydrofluosilicic acid and any other mineral acid present. The liquid is now heated to boiling, and titrated while hot with phenolphthalein as indicator. Four mols. of sodium hydroxide now represent 1 mol. of hydrofluosilicic acid. The method is not strictly accurate, owing to the slight dissociation of the sodium silicofluoride formed, but this does not interfere with its technical application.

L. DE K.

The Carrasco-Plancher Method of Estimating Carbon and Hydrogen in Organic Substances. WILHELM LENZ (*Zeitsch. anal. Chem.*, 1907, 46, 557—565).—The results of a number of estimations of carbon and hydrogen in salicylic acid by this method (*Abstr.*, 1906, ii, 201) are given. Whilst in some cases the quantities of carbon and hydrogen found agreed with those required by theory, in others the carbon was as much as 3.5% too low. The loss was due to the formation of carbon monoxide; the quantity of the latter produced appeared to depend on the speed at which the combustion was carried out, the

longer the time taken for the estimation the greater the amount of carbon monoxide formed.

W. P. S.

Estimation of Carbon Monoxide in Atmospheric Air. J. LIVINGSTON R. MORGAN and JOHN E. MCWHORTER (*J. Amer. Chem. Soc.*, 1907, 29, 1589—1592).—The air is passed first through tubes containing sulphuric acid and potassium hydroxide. If it is desired to estimate also the carbon dioxide, another tube containing standard barium hydroxide is placed in front of the sulphuric acid tube. The carbon monoxide is then absorbed in a U-tube containing iodine pentoxide and heated at 150° in a glycerol-bath. The products of the reaction, free iodine and carbon dioxide, are passed through a tube containing potassium iodide solution, and the iodine is afterwards titrated with *N*/1000 thiosulphate by way of a check. The carbon dioxide is absorbed in standard barium hydroxide, the excess of which is then titrated as usual with standard oxalic acid.

In estimating carbon monoxide by passing it over iodine pentoxide, the ends of the U-tube should be sealed off after filling, so as to avoid traces of greasy matter from the lubricant used with glass stoppers.

L. DE K.

Volumetric Estimation of Potassium as the Cobaltinitrite. W. A. DRUSHEL (*Amer. J. Sci.*, 1907, [iv], 433—438; *Zeitsch. anorg. Chem.*, 1907, 56, 223—329).—A modification of the method proposed by Adie and Wood (*Trans.*, 1900, 77, 1076). The solution is mixed with excess of sodium cobaltinitrite and a little acetic acid, and evaporated to a pasty condition on a water-bath. The residue is treated with cold water, and the precipitate collected and washed on an asbestos filter. The filter and contents are then heated with excess of *N*/10 permanganate for some five minutes, when excess of dilute sulphuric acid (1:7) is added, and the whole heated short of boiling until the manganese precipitate has completely dissolved. The excess of permanganate is estimated as usual by first bleaching with *N*/10 oxalic acid and then titrating with permanganate. Working in this manner, 1 c.c. of *N*/10 permanganate = 0.000856 gram of K₂O.

The process is suitable for the estimation of potash in manures, not being interfered with by the presence of phosphoric acid. L. DE K.

New Volumetric Method of Estimating Sodium Sulphide. E. PODRESCHETNIKOFF (*Zeitsch. Farb. Ind.*, 1907, 6, 388).—The new method permits of the estimation of both sodium hydroxide and sodium sulphide, owing to the latter undergoing complete hydrolysis in dilute solution according to the equation: $\text{Na}_2\text{S} + \text{H}_2\text{O} = \text{NaHS} + \text{NaOH}$. On titrating a very dilute solution of the sulphide with *N*/10 sulphuric acid in the presence of phenolphthalein as indicator, the quantity of sodium sulphide plus the free hydroxide is obtained. The amount of sulphide alone is then determined by adding a slight excess of formaldehyde, and titrating by means of the acid, the sodium hydroxide liberated according to the equation: $\text{NaHS} + \text{CH}_2\text{O} + \text{H}_2\text{O} = \text{NaOH} + \text{OH}\cdot\text{CH}_2\cdot\text{SH}$. The results obtained by this method are quite accurate.

W. A. D.

Biological Method for Estimating Alkali Carbonates in Soils. HARALD R. CHRISTENSEN (*Centr. Bakt. Par.*, 1907, ii, 19, 735—736).—It was shown previously that azotobacter is unable to utilise calcium in the form of sulphate, chloride, and tribasic phosphate. It is now shown that some soils, deficient in calcium, in conjunction with mannitol and potassium phosphate, will develop a growth of azotobacter when supplied with calcium sulphate similar to that obtained when calcium carbonate is added. Such soils show almost invariably an alkaline reaction, and the conclusion is drawn that an alkali carbonate is present which interacts with the calcium salt to form calcium carbonate.

It is proposed to utilise the different behaviour of calcium sulphate in different soils for ascertaining the amounts of alkali carbonates present.

N. H. J. M.

Volumetric Estimation of Magnesium. LEOPOLD ROSENTHALER (*Zeitsch. anal. Chem.*, 1907, 46, 714—716).—The magnesium salt is dissolved and treated with a measured volume (an excess) of potassium hydrogen arsenate, KH_2AsO_4 , solution (containing about 9 grams per litre). The mixture is then diluted to a known volume with 10% ammonia and mixed. After three hours, the solution is poured through a filter, and a portion of the filtrate, say 100 c.c., is evaporated to dryness on the water-bath. The residue is dissolved in a very little water, the solution is transferred to a stoppered flask, the basin is rinsed out with a little concentrated hydrochloric acid, which is also added to the flask, and the acid solution is then treated with concentrated potassium iodide solution. If a precipitate forms, a little more water is added; if not, hydrochloric acid is added before adding the water. The liberated iodine is then titrated back with thiosulphate solution. The difference between the amount of potassium hydrogen arsenate added and that found in excess represents the quantity precipitated with the magnesium; 1 c.c. of $N/10$ thiosulphate solution corresponds with 0.002018 gram of magnesia (MgO).

W. P. S.

Detection of Small Quantities of Zinc by Electrochemical Means. WALTER NEUMANN (*Zeitsch. Elektrochem.*, 1907, 13, 751—752).—The solution to be tested, containing sufficient potassium hydroxide to render it, roughly, $N/10$, is electrolysed, using a small platinum bead as anode, and a brightly polished, thin copper wire as cathode. Should zinc be present, the copper becomes coated with a bright white deposit of zinc, which may be removed by dipping the wire in $2N$ potassium hydroxide solution. It is possible by this method to detect zinc in 0.1 c.c. of a $N/40,000$ solution of the metal. The solution to be tested must not contain chloride or nitrate.

W. H. G.

A Method of Estimating very Small Quantities of Zinc. GABRIEL BERTRAND and MAURICE JAVILLIER (*Compt. rend.*, 1907, 146, 924—926).—The method described previously (*Abstr.*, 1907, ii, 53) of precipitating small quantities of zinc in the form of hydrated calcium zinc oxide can be employed for the estimation of the metal in solutions containing 0.1 mg. of zinc in 3 litres in the presence of tin, antimony,

arsenic, copper, cadmium, cobalt, lead, silver, iron, manganese, aluminium, barium, calcium, magnesium, sodium, and potassium as carbonates, chlorides, sulphates, nitrates, phosphates, silicates and sulphides. For details of the separation, the original must be consulted.

The final separation of the zinc from the calcium in the hydrated calcium zinc oxide is best effected by dissolving in hydrochloric acid, evaporating to dryness, precipitating the zinc as sulphide in the presence of sodium acetate, and weighing as the sulphate. M. A. W.

Rapid Estimation of Zinc by Electrolysis. FRANCIS C. FRARY (*J. Amer. Chem. Soc.*, 1907, **29**, 1596—1603).—A solution containing about 8 grams of sodium hydroxide and 0.1 gram of zinc deposits all the metal on a nickel gauze in thirty minutes with electromagnetic rotation (*Abstr.*, 1907, ii, 649) and a current of 4.5 amperes. The temperature should be as low as possible. For quantities of zinc up to 0.2 gram, the strength of the current should be 4.5 amperes for fifteen minutes and then 1.5 amperes for twenty minutes. It is advisable always to test the electrolysed liquid to see whether the precipitation has been complete. L. DE K.

Estimation of Zinc. A. R. THORNEWELL (*Chem. Zentr.*, 1907, ii, 1269; from *Chemist and Druggist*, 1907, **71**, 413).—The solution should be perfectly neutral to methyl-orange and contain about 0.3 mg. of zinc per c.c. Two hundred c.c. are mixed with 25 c.c. (or more) of *N*-sodium hydroxide previously saturated with hydrogen sulphide, and the whole is diluted to 250 c.c. and well shaken. Twenty-five c.c. of the clear supernatant liquid are then mixed with 25 c.c. of *N*/10 sulphuric acid, the hydrogen sulphide is expelled by boiling, and when cold the excess of acid is titrated with *N*/10 sodium hydroxide, using methyl-orange as indicator. The zinc is then calculated from the amount of alkali absorbed. L. DE K.

Volumetric Estimation of Lead. H. BOLLENBACH (*Zeitsch. anal. Chem.*, 1907, **46**, 582—588).—In the process described, the lead solution is titrated with permanganate in alkaline solution. Sodium hydroxide is added to the lead solution until the precipitate which at first forms is redissolved, and the whole is then diluted to a known volume. Fifty c.c. of this solution are run from a burette into a measured excess of potassium permanganate solution, placed previously in a 500 c.c. flask together with 300 c.c. of hot water and 5 c.c. of *N*/2 sodium hydroxide solution. The addition of the lead solution is accompanied with constant agitation of the permanganate mixture. After the lead solution has been introduced, the solution is cooled, diluted to 500 c.c., and the excess of the permanganate estimated, either iodometrically or by the use of a lead solution of known strength. The permanganate solution should contain 3.2 grams of the salt per litre, and be titrated against the standard lead solution. The reaction takes place according to the formula: $2\text{KMnO}_4 + 6\text{Pb}(\text{ONa})_2 = 2\text{MnO}_2 + 3\text{Pb}_2\text{O}_3 + \text{K}_2\text{O} + 6\text{Na}_2\text{O}$. The presence of chlorides, bromides, and sulphates has no influence on the results obtained by the method, but iodides, and substances which reduce permanganate, should not be present. W. P. S.

Red Leads and their Examination. ALFRED PARTHEIL (*Arch. Pharm.*, 1907, 245, 519—528).—According to the *Deutsche Arzneibuch*, IV, the purity of red lead may be tested by adding 2·5 grams of the material mixed with 0·5 gram of oxalic acid to 10 c.c. of hot nitric acid, and then adding gradually 25 c.c. of hot water; not more than 0·035 gram should remain undissolved. It is shown that this test is quite useless, owing to the formation of insoluble basic lead oxalates, lead oxalonitrate, &c. The following method is said to give better results: 10 c.c. of water, 5 c.c. of lactic acid, and 10 c.c. of 25% nitric acid are added to 2·5 grams of the red lead; a violent reaction takes place, after which the insoluble residue is weighed. W. H. G.

Colorimetric Estimation of Copper. JAROSLAV MILBAUER and VLADIMÍR STANĚK (*Zeitsch. anal. Chem.*, 1907, 46, 644—656).—The well-known blue coloration produced when copper sulphate solution is treated with ammonia has not always the same intensity for equal quantities of the metal. Increasing quantities of ammonia or ammonium chloride diminish the depth of colour, whilst ammonium carbonate has the opposite effect, the maximum coloration obtained with ammonia and copper sulphate being increased by one-third on the addition of ammonium carbonate. Potassium hydroxide, in the presence of amines, gives with copper sulphate a coloration varying from 56% to 66% of that obtained with ammonia. Many other instances are given, but in each the coloration is less than that yielded by ammonia. An ammoniacal copper solution has a coloration one hundred and fifty times more intense than a copper sulphate solution containing the same quantity of copper. W. P. S.

Estimation of Mercury by Reduction with Hydrogen Peroxide. A. KOLB and A. FELDHOFFEN (*Zeitsch. angew. Chem.*, 1907, 20, 1977—1980).—Twenty-five c.c. of mercuric chloride solution, containing about 0·1 gram of mercury, are mixed with 25 c.c. of 2*N* hydrochloric acid and 25 c.c. of 10% tartaric acid solution. The liquid is neutralised with ammonia, and again faintly acidified with tartaric acid. The whole is heated on the water-bath, and 10 c.c. of hydrogen peroxide are added, and then from time to time another 5 c.c., so that 25—30 c.c. are used in the space of forty-five minutes. The precipitated calomel may be collected and weighed, or, better, titrated iodometrically.

The process is also useful for the separation of mercury from arsenic, antimony, tin, cadmium, and bismuth. L. DE K.

Detection of very Small Quantities of Mercuric Chloride. K. KOF and HUGO HAEHN (*Arch. Pharm.*, 1907, 245, 529—533).—The vapour arising from a mercuric chloride solution can not only be caught on a photographic plate (compare *Abstr.*, 1907, ii, 732), but also on moist filter paper. A moistened filter paper resting on a thin glass slide, and placed for one hundred and sixty-five hours at a distance of about 1 cm. above the surface of a 2% aqueous solution of mercuric chloride, turns dark when treated with hydrogen sulphide, except where it has been protected by the strip of glass. The photographic effect may be employed

for the detection of small quantities of mercuric chloride. A distinct, white patch is obtained on developing a photographic plate which has been kept at a distance of 2 to 3 mm. from one drop of a 0.01% solution of mercuric chloride for twenty-four hours. The same effect on the plate is produced if, instead of the drop of mercuric chloride solution, one drop of the distillate, obtained by steam-distilling 100 c.c. of a 0.01% mercuric chloride solution until 100 c.c. of distillate are obtained, is employed.

W. H. G.

Acidimetric Assay of White Precipitate. ERWIN RUPP and F. LEHMANN (*Pharm. Zeit.*, 1907, 52, 1014).—0.2–0.3 Gram of the powdered sample is dissolved in 50 c.c. of water and 2–3 grams of potassium iodide, and the ammonia and potassium hydroxide liberated in the reaction are titrated with *N*/10 hydrochloric acid with 1–2 drops of 0.2% alcoholic methyl-orange solution as indicator. 0.2 Gram of the commercially pure article requires 15.6–16 c.c. of *N*/10 acid.

L. DE K.

Complete Analysis of Mercury Cyanides. ERWIN RUPP and F. LEHMANN (*Pharm. Zeit.*, 1907, 52, 1020).—One gram of the compound is dissolved, and the solution made up to 100 c.c. In order to estimate the mercury, 20 c.c. are placed in a flask, and, after adding 1–2 grams of potassium iodide and 3–5 c.c. of official potassium hydroxide, the mercury is reduced to the metallic state by adding 2–3 c.c. of official formaldehyde previously diluted with 20 c.c. of water. After shaking thoroughly for two minutes, a slight excess of acetic acid is added, and then 25 c.c. of *N*/10 iodine. When, after repeated shaking, the mercury has redissolved, 10 c.c. of dilute sulphuric acid are added, and the excess of iodine is titrated with *N*/10 thiosulphate. In order to estimate the cyanogen, 10 c.c. of the solution are mixed with a little water and 5–10 c.c. of official sodium hydroxide, and 25 c.c. of *N*/10 iodine are added slowly with constant agitation. The whole is allowed to remain for two to three hours, or else heated for twenty to thirty minutes in the water-bath. The liquid is diluted to 100 c.c., acidified with about 25 c.c. of hydrochloric acid, and titrated with thiosulphate; 0.1 gram of mercury cyanide = 15.87 c.c. of *N*/10 iodine.

L. DE K.

Borax Bead Test for Praseo- and Neo-dymium Salts. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1907, 46, 657–658).—The following colorations are obtained when these salts are heated in the usual way on a borax bead. Neodymium: in oxidising flame, no colour; in reducing flame, violet, if sufficient of the salt is used. Praseodymium: oxidising flame, yellowish green; reducing flame, green. The colorations are seen only when the bead is cold. Beads consisting of phosphates may be employed in place of borax.

W. P. S.

Detection and Estimation of Small Quantities of Manganese. MAURICE DUYK (*Ann. Chim. anal.*, 1907, 12, 465–466).—A pink or red coloration is obtained when a trace of manganese salt is heated with moderately alkaline potassium hypochlorite solution (10%)

to which has been added 1 drop of copper sulphate solution (10%). A precipitate of cupric oxide is produced, and the coloration is observed in the supernatant liquid. The reaction may be made quantitative by comparing the coloration obtained with that produced by known amounts of manganese.

W. P. S.

Modification of Volhard's Method of Estimating Manganese. ERWIN W. MAYER (*Zeitsch. angew. Chem.*, 1907, 20, 1980—1981).—Four modifications of the process are described, of which the following two are the most suitable for technical purposes. (1) One gram of ferromanganese, 4 grams of pig-iron, or 8 grams of steel are dissolved in nitric acid (D 1.2); the solution is evaporated to a small bulk, diluted with water, introduced into a litre-flask, and mixed with a sufficiency of zinc oxide emulsion to precipitate the iron. The whole is then diluted to 1 litre, and in 250 c.c. of the filtrate, the manganese is titrated with standard permanganate. (2) The sample is dissolved as before in nitric acid, but, before boiling down, a few drops of hydrochloric acid are added.

L. DE K.

Clay Analysis. Residue Left After Volatilisation of the Silica with Hydrofluoric and Sulphuric Acids. W. R. BLOOR (*J. Amer. Chem. Soc.*, 1907, 29, 1603—1606).—Experiments showing that the residue obtained on heating the separated silica with hydrofluoric and sulphuric acids does not consist of iron and aluminium oxides only, but contains also the other constituents of clay, such as calcium and magnesium oxides, also titanium.

L. DE K.

Precipitation of Iron by Ammonia in Presence of Tartaric Acid. WILHELM STRECKER (*Chem. Zeit.*, 1907, 31, 1217. Compare Grossmann and Schück, *Abstr.*, 1907, ii, 819).—Ferric hydroxide is precipitated completely on addition of ammonia to a solution containing 0.1110 gram of iron in the ferric state and 0.1911 gram of tartaric acid in 53 c.c. If a larger proportion of tartaric acid is present, the precipitation is incomplete, and is finally inhibited. Attempts to isolate a complex compound from the resulting red solution containing excess of tartaric acid have been unsuccessful, as the products obtained do not have a constant composition (compare Méhu, *Jahresber. Chem.*, 1873, 569).

G. Y.

Colorimetric Comparison of Copper and Nickel Solutions. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1907, 46, 656—657).—Nickel salts when treated with ammonia give a similar blue coloration to that obtained with copper salts. The author finds that one part of copper gives a coloration equal to that yielded by eighteen parts of nickel, and this fact renders the test of little use in testing very small quantities of the latter metal. In fact, a N/100 ammoniacal nickel solution is practically colourless, whilst a copper solution of equivalent concentration has a marked blue colour.

W. P. S.

Brunck's Dimethylglyoxime Process for the Estimation of Nickel. HERRMANN GROSSMANN and BERNHARD SCHÜCK (*Zeitsch. angew. Chem.*, 1907, 20, 1981—1982).—A reply to Brunck (*Abstr.*,

1907, ii, 989) in which the authors uphold the accuracy of their own dicyanodiamidine process.

L. DE K.

Volumetric Estimation of Bismuth. RICHARD EHRENFELD (*Zeitsch. anal. Chem.*, 1907, 46, 710—711).—The process consists in precipitating the bismuth with excess of sodium phosphate, and afterwards titrating back this excess. The bismuth solution is acidified with nitric acid to prevent the formation of basic salt, a known excess of sodium phosphate solution is added, and the mixture is diluted to a known volume. After filtration or settling, the excess of phosphate is titrated in a portion of the clear solution; uranium acetate solution is used for the titration, and sufficient sodium acetate is added to the solution to be titrated in order to remove the free nitric acid (compare Abstr., 1906, ii, 55; 1907, ii, 403).

W. P. S.

Apparatus for the Prevention of Acid Fumes in Gold and Silver Assaying. DARD (*Ann. Chim. anal.*, 1907, 12, 425—426).—A portable apparatus which may be placed in front of any kind of chimney. The hydrochloric or nitrous vapours are made to traverse a layer of fragments of white marble, and the carbon dioxide liberated is carried off by a central chimney-funnel, which will act readily owing to the heat given off by the burners. Several assays can be made simultaneously without suffering from irritating fumes.

L. DE K.

Refractometric Analysis of Organic Mixtures. ADOLF BEYTHIEN and R. HENNICKE (*Pharm. Zentr.-h.*, 1907, 48, 1005—1013).—The composition of a mixture containing any two of the following substances may be ascertained from its refractive index, the constants taken being: acetone, n_D^{15} 1.3620, n_D^{20} 1.3590; carbon disulphide, n_D^{15} 1.6315; oil of turpentine, n_D^{20} 1.4690; carbon tetrachloride, n_D^{20} 1.4630; xylene, n_D^{15} 1.49680; ethyl bromide, n_D^{15} 1.42540; chloroform, n_D^{15} 1.4466. Mixtures containing three of these substances may be analysed in the same way if one of the constituents can be estimated by a separate method.

W. P. S.

Reaction of Phloroglucinol-Hydrochloric Acid with Essential Oils. KARL KOBERT (*Zeitsch. anal. Chem.*, 1907, 46, 711—714).—The author finds that only those essential oils which contain an allyl-group give a red coloration when treated with a hydrochloric acid solution of phloroglucinol. A red coloration is obtained with the essential oils of mustard, cloves, pimento, dill, orange-blossom, jaborandi leaves, tarragon, basil, bay, lavender, Peru balsam, geranium, parsley, and sassafras.

W. P. S.

Detection of Methyl Alcohol in Fermented Liquids. JULES WOLFF (*Ann. Chim. anal.*, 1907, 12, 470—471).—Any alcoholic liquid containing sucrose, invert-sugar, or caramel should be redistilled before testing it for methyl alcohol by means of chromic acid, &c. (formation of formaldehyde polymerides). These substances yield formaldehyde

when thus tested, and, consequently, methyl alcohol may be stated to be present in a spirit when such is not the case. W. P. S.

Normal Tubes for the Polarimetric Estimation of Sucrose. H. ROUSSET (*Ann. Chim. anal.*, 1907, 12, 468—470).—The use of tubes 179.2 mm. and 358.4 mm. in length is recommended for the estimation of sucrose by means of Laurent and Duboseq's or Vivien's polarimeters. The weight of the sample taken is 20 grams in 100 c.c. of water, and the percentage of sucrose is obtained without calculation. W. P. S.

Estimation of the Most Important Acids that Occur in Wine in Presence of Alcohol and Glycerol. A. HEIDUSCHKA and GEORGE QUINCKE (*Arch. Pharm.*, 1907, 245, 458—461).—The method described was tested with a mixture of acetic, lactic, tartaric, malic, and succinic acids with alcohol and glycerol (and water), and found to give good results. Of such a mixture, 50 c.c. are neutralised with aqueous barium hydroxide and evaporated to 15 c.c., care being taken to keep the liquid neutral. The residue is rinsed with a little hot water into a measuring cylinder, and mixed with so much alcohol that the mixture contains 80% (by volume) of the latter. The precipitate of barium tartrate, malate and succinate is collected on a filter and washed with 80% alcohol. The filtrate, which contains barium acetate and lactate and glycerol, is freed from alcohol by evaporation, and diluted to a known volume. An aliquot portion is distilled under diminished pressure, the distillate is diluted to a known volume, an aliquot part of it is oxidised with a large excess of potassium dichromate and dilute sulphuric acid (say 5 c.c. with 50 c.c. *N*/10 dichromate solution and 50 c.c. 20% sulphuric acid) by heating for one hour in a pressure-bottle in the water-bath, and the excess of dichromate is estimated by adding potassium iodide and titrating with *N*/10 sodium thiosulphate solution; in this way, the glycerol is determined. An aliquot portion of the filtrate is oxidised in the same way without being distilled first; in this way, the sum of the glycerol and the lactic acid is determined ($C_3H_6O_3$ requires 2O).

The precipitated barium salts, with the filter, are brought into a measuring cylinder, stirred with 20 c.c. of water containing some sulphuric acid, diluted with alcohol to 100 c.c., and filtered. Of the filtrate, 80 c.c. are mixed with 0.5 c.c. of 20% potassium acetate solution, 15 grams of powdered potassium chloride, and 2 c.c. of acetic acid, and allowed to remain for twelve hours; the precipitated potassium hydrogen tartrate is then filtered off, and its amount determined by titration. The filtrate is freed from alcohol by evaporation, mixed with 50 c.c. of dilute sulphuric acid, and titrated with *N*/10 potassium permanganate solution; in this way, the malic acid is determined ($C_4H_6O_5$ requires 6O). The oxidised liquid is evaporated to dryness with quartz sand, the residue is extracted with ether, the extract is evaporated, and the succinic acid left is weighed.

The alcohol is estimated by neutralising another portion of the original mixture, distilling off the alcohol, and oxidising a portion

of the distillate with dichromate and sulphuric acid as described above (C_2H_6O requires 20).

The acetic acid is estimated by distilling another portion of the original mixture, and titrating the distillate. C. F. B.

Estimation and Colour Reactions of Glycuronic Acid.

K. U. LEFÈVRE and BERNHARD TOLLENS (*Ber.*, 1907, 40, 4513—4523; *Zeitsch. Ver. deut. Zuckerind.*, 1907, 57, 1097—1110. Compare Neuberg and Neimann, *Abstr.*, 1905, ii, 426; Tollens, *ibid.*, 559).—When boiled with hydrochloric acid, glycuronic acid yields furfuraldehyde and carbon dioxide (Günther and Tollens, *Abstr.*, 1890, 1352; Chalmot and Tollens, *Abstr.*, 1891, 568; Mann and Tollens, *Abstr.*, 1895, ii, 335). On this reaction, the authors have based two methods of estimating glycuronic acid; in the first, the furfuraldehyde is converted into, and weighed as, its phloroglucide; in the second, the carbon dioxide evolved is absorbed and weighed. The weight of the phloroglucide is one-third and that of the carbon dioxide one-quarter of the glycuronic acid. Details are given of estimations with glycuronic acid, euxanthic acid, magnesium euxanthate, and sodium urochloralate in which the error does not exceed 1—1.5%. By the first method, piuri (Indian-yellow) is found to contain 18% to 19.5% of glycuronic acid, equivalent to 43.1% to 46.7% of euxanthic acid; Graebe, Aders, and Heyer (*Abstr.*, 1902, i, 39) found piuri to contain 39% to 46% of euxanthic acid. To estimate pentoses and glycuronic acid in presence of each other, the amount of glycuronic acid is determined by the carbon dioxide method and one-third of its weight subtracted from the phloroglucide, the remainder of this being equivalent to the pentoses.

Piuri is found to contain 1.39% of nitrogen which is only partly accounted for by the presence of small amounts of hippuric acid, and a substance which is probably *m*-toluic acid; another specimen contained benzoic acid.

Contrary to Bial's (*Abstr.*, 1902, ii, 703) and Sachs's (*Abstr.*, 1907, ii, 135) statements, glycuronic acid reacts with Bial's orcinol reagent, but more slowly than the pentoses and only on continued heating of the reaction mixture. The green coloration can be detected with 0.0025 mg. of xylose, 0.005 mg. of arabinose, and 0.025 mg. of glycuronic acid. With phloroglucinol in presence of ferric chloride, glycuronic acid forms a dirty red, turbid solution, which gives a spectrum with a band at the *D*-line less marked than the band lying to the right of the *D*-line in the pentose-phloroglucinol spectrum.

G. Y.

Detection and Estimation of Benzoic Acids in Ketchups, Fruits, and Ciders. HARRY S. REED (*J. Amer. Chem. Soc.*, 1907, 29, 1626—1629).—The sample is acidified with sulphuric acid, the benzoic acid is extracted with chloroform, and the latter is evaporated in a current of air in a special apparatus. The residue is then heated at 260° in a current of air, and the volatilised benzoic acid absorbed in aqueous sodium hydroxide. From this, it is recovered by acidifying

the solution and shaking with chloroform, and the residue left on evaporation is then tested for benzoic acid by converting it first into *m*-dinitrobenzoic acid and this into ammonium diaminobenzoic acid, which has a characteristic appearance.

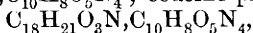
The quantitative estimation is based on the fact that calcium benzoate is fairly soluble in cold water. The chloroform residue of the acid is treated with a definite amount of milk of lime, and the benzoic acid is calculated from the amount of calcium found in the solution after allowing for dissolved calcium oxide, as found by a blank experiment.

L. DE K.

Estimation of Fat in Skimmed Milk. R. LEZÉ (*Compt. rend.*, 1907, 145, 817—818).—Three litres of the skimmed milk are heated to a temperature of 40° and treated with 60 c.c. of a solution prepared by dissolving 20 grams of sodium hydroxide in 180 c.c. of ammonia and diluting to a volume of 250 c.c. The treated milk is then subjected to centrifugal action, a small apparatus being used, and the cream thus separated is used for the analysis, the estimation of the fat being made by Gerber's process.

W. P. S.

Estimation of Some Alkaloids by Means of Picrolonic Acid. HERMANN MATTHES and O. RAMMSTEDT (*Zeitsch. anal. Chem.*, 1907, 46, 565—574).—Cotarnine, codeine, and morphine give insoluble precipitates when treated with picrolonic acid, and this reaction may be used for the estimation of these alkaloids in preparations such as tablets, powders, &c. A tablet, or a quantity of the powder, equivalent to about 0.05 gram of alkaloid is dissolved in 10 c.c. of water, the solution is filtered, and, after washing the filter and insoluble residue, the filtrate is treated with 2.0 c.c. of *N*/10 alcoholic solution of picrolonic acid. The mixture is placed aside for fifteen hours at the ordinary temperature, after which time the precipitate is collected on a weighed filter, washed with water, dried at 110°, and weighed. The precipitates have the following formulæ: cotarnine picrolonate, $C_{12}H_{15}O_4N, C_{10}H_8O_5N_4$; codeine picrolonate,



and morphine picrolonate, $C_{17}H_{19}O_2N, C_{10}H_8O_5N_4$ (compare Abstr., 1907, ii, 592).

W. P. S.

Estimation of Cystine in Urine. J. F. GASKELL (*J. Physiol.*, 1907, 36, 142—149).—The addition of acetone renders the acetic acid method of estimating cystine a trustworthy one. In five cystine calculi, cystine crystallised in hexagons, but it may crystallise in other forms. The specific rotation of cystine dissolved in ammonia is -97.5° , and dissolved in hydrochloric acid -223° . Hair-cystine and calculus-cystine are identical.

W. D. H.

Estimation of Indigotin in Indigo-yielding Plants. CYRIL BERGTHEIL and RICHARD V. BRIGGS (*J. Soc. Chem. Ind.*, 1907, 26, 1172—1174).—The modifications of the persulphate and isatin methods suggested by Orchardson, Wood, and Bloxam (*Abstr.*, 1907, ii, 415) are considered by the authors to be useless in ordinary practice, both

leading to untrustworthy results unless the exact indican-content of the sample is known previously and the methods adjusted accordingly.

W. P. S.

Analysis of Indigo (III) and of the Dried Leaves of Indigofera Arrecta and Indigofera Sumatrana. R. GAUNT, F. THOMAS, and W. POPPLEWELL BLOXAM (*J. Soc. Chem. Ind.*, 1907, 26, 1174—1182).—As the result of continued use of the tetrasulphonate method, the authors consider that the claims for accuracy made for this process (Abstr. 1906, ii, 819) are fully substantiated. For the analysis of the leaf, the isatin method is, at present, the only trustworthy one; the product obtained from it has been proved to be almost chemically pure indirubin. As the formation of indirubin can only originate from the indoxyl liberated from the indican on hydrolysis, the quantity of indirubin obtained must be a true expression of the amount of this substance which is present.

W. P. S.

Titration of Tannin by Means of Iodine. FERDINAND JEAN (*Ann. Chim. anal.*, 1907, 12, 426—427).—A reply to Cormimbœuf (Abstr., 1907, ii, 994). The author states that the iodine process is trustworthy, but the titration should take place in a solution containing excess of sodium hydrogen carbonate.

L. DE K.

Vanillin-Hydrochloric Acid as a Test for Albumin and Tryptophan. LEOPOLD ROSENTHALER (*Chem. Zentr.*, 1907, ii, 946; from *Apoth. Zeit.*, 1907, 22, 678).—Winckel has shown (*Apoth. Zeit.*, 1905, 22, 209) that several fruit juices and substances containing ferments give a violet coloration with vanillin and hydrochloric acid, and has concluded that this is a characteristic reaction of ferments. In the present paper, it is pointed out that albumin, globulin, and casein give a violet coloration with vanillin and hydrochloric acid; likewise also tryptophan, but not phenylalanine, tyrosine, histidine, or pyrrolidine-2-carboxylic acid.

W. H. G.

Estimation of Pepsin by Means of Edestin. ERNST FULD and LOUIS A. LEVISON (*Biochem. Zeitsch.*, 1907, 6, 473—501).—The method is based on the principle that edestin (the crystalline protein from hemp seeds) is precipitated by sodium chloride from its solution in 0.3% hydrochloric acid, but that the products of its digestion are not so precipitated. Accordingly, the minimum quantity of gastric juice is found, which, when added to a definite volume of the edestin solution, prevents the formation of a precipitate when solid sodium chloride is added after half an hour's incubation.

G. B.

General and Physical Chemistry.

Influence of Temperature on the Optical Properties of Dissolved Substances. C. CHÉNEVEAU (*Compt. rend.*, 1907, 145, 1332—1334. Compare Abstr., 1907, ii, 920).—The index of refraction of a dissolved substance varies slightly with the temperature; the variation of the optical constant K [$K = \Delta/c$, where $\Delta = n_s - 1$ or $(n_s^2 - 1)/(n_s^2 + 2)$, and c is the concentration in grams per litre] with the temperature is due to the change of volume of the solution, and the relation is expressed by the equation $K'_t = K_t [1 + m(t' - t)]$, where m is the mean coefficient of expansion of the solution. The calculated and observed values of the optical constant in the cases of solutions of sodium chloride, potassium chloride (Bender, Abstr., 1900, ii, 461; 1902, ii, 437), potassium nitrate, and chloral hydrate are tabulated in the original. M. A. W.

Rotatory Power in Solutions. THOMAS S. PATTERSON (*Ber.*, 1908, 41, 113—120).—Polemical. A reply to Walden's criticisms (Abstr., 1907, ii, 519) of Patterson and Thomas (Abstr., 1907, ii, 322). See also Walden (Abstr., 1906, ii, 209). E. F. A.

Origins of Stereochemistry. EMANUALE PATERNÒ (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 717—719).—A question of priority. T. H. P.

Optical Properties and Electron Theory. H. ERFLE (*Ann. Physik*, 1907, [iv], 24, 672—708*).—The dispersion of benzene, α -bromonaphthalene, and methyl iodide has been measured for wavelengths in the visible spectrum. The results are discussed in reference to Drude's theory of dispersion, according to which it is possible to calculate a limiting value (p) for the number of freely vibrating electrons in the molecule, this value depending on the composition and constitution of the molecule in the same way that the refraction equivalent does. The values of p are calculated for a large number of compounds, the dispersion of which was measured by Landolt, Brühl, and others, and, from these molecular values, constants are deduced which represent the values of p for various atoms and radicles, and also for double and triple linkings and for the benzene and naphthalene rings. In aliphatic compounds, the various atoms have the same value of p as they have in aromatic compounds when directly attached to the benzene ring. When present in aromatic compounds and not directly attached to one of the six carbon atoms of the ring, the values of p are different. In nitrogen compounds, the values of p for carbon, hydrogen, and oxygen are different from the values found in compounds not containing nitrogen. Between 10° and 30°, the numbers are independent of the temperature.

H. M. D.

* And *Zeitsch. physikal. Chem.*, 1907, 61, 399—421.

Spectra of the Alkali [Metals]. CARL RUNGE (*Physikal. Zeitsch.*, 1908, 9, 1—2).—It is pointed out that the new series of lines observed by A. Bergmann (*Diss.*, Jena, 1907) in the ultra-red region of the emission spectra of potassium, rubidium, and caesium are similarly related to the lines in the first subsidiary series as the lines in the principal series are to those in the second subsidiary series.

H. M. D.

The Variations of the Absorption Bands of Didymium and Erbium Salts in a Magnetic Field. JEAN BECQUEREL (*Compt. rend.*, 1907, 145, 1412—1415. Compare Abstr., 1906, ii, 317, 421; 1907, ii, 147).—The author has extended his investigation on the variations of the absorption bands of rare earth salts in a magnetic field at low temperatures (this vol., ii, 3), and in the present paper the results obtained with didymium chloride and nitrate and mixtures of the two, didymium sulphate oxalate, and fluoride and erbium chloride are recorded. The soluble salts were dissolved in alcohol, and the insoluble salts suspended in alcohol and solidified by means of liquid air. With the exception of the oxalate and fluoride of didymium, the absorption bands of all these salts suffered displacement when placed in a magnetic field, and the author draws the conclusion that the influence of the magnetic field on the change of period of the corpuscles producing a band is independent of the temperature, and also of other conditions which tend to modify the band; the amount of displacement of a band in a magnetic field of known strength appears to be a characteristic property of the oscillating system.

The author is of opinion that it is premature to put forward any hypothesis in explanation of the curious result that rays which are circularly polarised in the same direction are not all displaced in the same sense by a magnetic field.

M. A. W.

Influence of Temperature Changes on the Absorption in Solid Substances. JEAN BECQUEREL (*Physikal. Zeitsch.*, 1907, 8, 929—942).—The author has investigated the changes which take place in the absorption bands of certain crystals containing rare earths (xenotime, tysonite) when these are subjected to different temperatures. The bands were examined in most cases at $+25^{\circ}$ and at -188° .

In general, the absorption bands are shifted towards the smaller wave-lengths when the temperature is lowered, although certain bands move in the opposite direction. The width of the bands diminishes with fall of temperature, and in most cases the intensity of the absorption increases. If the widths of the bands are measured by the distances between the two points which correspond with maximum disturbance on the curve of dispersion, it is found that these are proportional to the square root of the absolute temperature.

Some observations on the emission spectra of phosphorescing substances at the temperature of liquid air indicate that similar temperature effects are to be met with in this case.

H. M. D.

Cause of the Emission of the Principal Series Lines of the Alkali Metals and the Doppler Effect in Canal- and Anode-Rays. CARL FREDENHAGEN (*Physikal. Zeitsch.*, 1907, 8, 927—929).—Another explanation is given of the experimental observations which have led Gehrcke and Reichenheim (*Verhandl. Phys. Ges.*, 1906, 8, 559, and 1907, 9, 76) to the view that the *D*-lines are emitted by positively charged sodium atoms. The facts also agree with the view that collisions between sodium and oxygen atoms are the cause of the *D*-line emission. This theory derives strong support from the experimental observation that, whilst the intensity of the anode-ray emission from anodes containing sodium compounds increases as the exhaustion becomes more complete, the *D*-line emission decreases in intensity. It is also consistent with Lenard's observation that the *D*-lines are due to electrically neutral particles.

H. M. D.

Reactions in Ultra-violet Light. HERMANN THIELE (*Ber.*, 1907, 40, 4914—4916).—In the experiments described, the source of light was a mercury lamp constructed of quartz; the vessels were likewise composed of quartz. Hydrogen peroxide is formed in small quantities when water is exposed to the ultra-violet rays, but a 0.3% solution of hydrogen peroxide is decomposed quickly. Formic acid is decomposed into carbon dioxide, carbon monoxide, and an inflammable gas. The formation of water from hydrogen and oxygen, of carbon dioxide from carbon monoxide and oxygen, of chlorine from hydrogen chloride and air (Deacon's process), and of nitrite from *N*/10 potassium nitrate are accelerated when exposed to ultra-violet rays.

W. R.

Phosphorescence at Low Temperatures. JOSEPH DE KOWALSKI (*Compt. rend.*, 1907, 145, 1270—1272).—The phosphorescence excited by ultra-violet light in alcoholic solutions of the nitrates of the rare earths and of phenanthrene, anthracene, and anthraquinone, when cooled in liquid air, and its persistence after extinction of the exciting light, has been studied. When the solutions (which have solidified) of the nitrates of the rare earths are exposed to the light from a mercury arc lamp (taking a current of 4 amperes at 25 volts), they become phosphorescent, and the phosphorescence has a relatively long duration (five minutes) after extinction of the lamp. The phosphorescence of the erbium solution is green, of the samarium greenish-yellow, and of the neodymium violet, but, except in the case of samarium, the intensity is too small to permit measurement of the emission spectra. The latter for samarium is composed of a series of fine lines. The solidified solution of phenanthrene has a greenish-yellow, of anthracene a blue, and of anthraquinone a bright green phosphorescence. The phosphorescence of these solutions is sufficiently intense for spectroscopic examination, and their spectra are found to consist of thin bands and fine rays. Apparently clearness and fineness of the bands are characteristic of phosphorescence emission spectra at low temperatures.

The intensity of the phosphorescence varies with the concentration of the solution; saturated solutions exhibit very little phosphorescence, probably owing to crystallisation of the solute when the solution

solidifies. The intensity of the phosphorescence of solutions of anthraquinone and anthracene diminishes gradually with their concentration, but that of phenanthrene solution reaches a maximum at a concentration of about 0.2%. The non-observance of a maximum intensity in the first two cases is perhaps due to the slight solubility of anthracene and anthraquinone in alcohol. E. H.

Measurement of the Absorption Coefficients of Radium Emanation in Solutions and Mixtures. MARTIN KOFLER (*Physikal. Zeitsch.*, 1908, 9, 6—8).—The influence of foreign substances on the solubility of radium emanation in water at 18° has been examined. Metallic salts and sucrose diminish the solubility, the diminution being greater the greater the concentration of the dissolved substance. When the absorption coefficients for solutions of different metallic salts of the same density are compared, it is found that the coefficient increases as the molecular weight of the dissolved substance increases. The solubility of the emanation in ethyl alcohol-water mixtures increases rapidly with the proportion of ethyl alcohol in the mixture. H. M. D.

Radioactivity of Air Over the Open Sea. CARL RUNGE (*Chem. Zentr.*, 1907, ii, 1353; from *Nachr. K. Ges. Wiss. Göttingen*, 1907, 211—229).—A wire, 18 metres long, charged to a very high negative potential, was fixed to the mast of a vessel on the open sea. After thirty hours, it was wound on a small frame, and its activity measured by the electroscope. The cause of the activity cannot be due only to radium emanation, because a noticeable activity remained after that induced by radium must have disappeared. The values obtained do not agree with the rate of decay of activity induced by thorium. Comparative experiments with radium emanation performed in the laboratory indicate that over the open sea some other source of radioactivity must exist; the curve of decay, logarithmically plotted, resembles somewhat that of the activity induced by radium, but is at first steeper and finally flatter.

The presence of radium and thorium emanations alone serves to account for the activity induced in a wire on the Hainberge near Göttingen. C. S.

Specific Radioactivity of Uranium. HERBERT N. MCCOY and W. H. ROSS (*J. Amer. Chem. Soc.*, 1907, 29, 1698—1709).—The values of the specific activity of uranium in pure uranium compounds and in minerals which have been obtained previously have been determined from measurements with a distance of 3.5—4.5 cm. between the active film and the charged electrode. Since it has been shown by Bragg and Kleeman (*Phil. Mag.*, 1905, [vi], 10, 318) that the ranges of radium-A and radium-C both exceed 4.5 cm., it follows that the value given for the specific radioactivity of uranium in minerals is too low. Measurements have now been made with a new form of gold-leaf electroscope, which allows a distance of 8.5 cm. between the active film and the electrode. With this instrument, the activity of a pure uranium compound was the same at 4.5 cm. as at 8.5 cm. from the

electrode, but the film of a uranium mineral was about 4% more active at 8.5 cm. than at 4.5 cm. For these determinations, the films were deposited on perfectly flat surfaces, and the observed activity was corrected for deficiency due to loss of emanation.

The specific activity of uranium in minerals is 3616, and in pure uranium compounds 796. Hence, for equal uranium content, minerals free from thorium are 4.54 times as active as pure compounds. The relative activity of equilibrium amounts of uranium and radium in a mineral is 1.87. The range of uranium is about 3.4 cm., and it is considered probable that there is a uranium product which emits α -rays with a range of 3.25 cm.

It is suggested that the supposed genetic relationship of actinium to uranium is due to the disintegration of uranium-*X* in two ways, one giving β -rays and the inactive product which finally produces radium, and the other, a much slower change, giving α -rays and actinium. E. G.

Specific Radioactivity of Thorium and the Variation of the Activity with Chemical Treatment and with Time. HERBERT N. MCCOY and W. H. ROSS (*J. Amer. Chem. Soc.*, 1907, 29, 1709—1718).—In an earlier paper (Abstr., 1906, ii, 415) on the radioactivity of thorium minerals, it was shown that, after deducting the activity due to uranium from the total activity, the residual activity was proportional to the percentage of thorium present. The same conclusion has been arrived at by Boltwood and by Dadourian (Abstr., 1906, ii, 415).

Determinations of the specific activity of thorium have been made with films deposited on flat plates and under such conditions that all the α -rays reach their maximum ranges in air (compare preceding abstract), and the value 1009 has been obtained.

Experiments have been carried out with the object of finding a method of separating radiothorium from thorium by chemical means, but without success. The reduction in the activity of thorium which is effected by certain chemical processes is due to the removal of mesothorium and the consequent gradual decay of the radiothorium. If all the mesothorium is removed in the preparation of pure thorium dioxide, the activity of the latter will fall to a definite minimum. From the activity of a specimen supposed to have reached this minimum, it has been calculated that the period of mesothorium is 5.5 years; the quantitative changes of activity with time of a number of samples of the oxide have been found to agree with the values calculated on this assumption. E. G.

Wehnelt Cathode in High Vacua. FREDERICK SODDY (*Physikal. Zeitsch.*, 1908, 9, 8—10).—Wehnelt has shown that currents of considerable intensity can be passed through a highly exhausted tube containing a platinum cathode coated with a layer of calcium oxide heated to a temperature of 1300—1400°. Experiments have been made to ascertain whether this phenomenon is, as generally assumed, independent of the degree of exhaustion of the apparatus.

A tube containing a Wehnelt cathode and a calcium anode was filled with oxygen in order to remove argon, and then, by connecting the

tube with an apparatus containing strongly heated calcium, a high degree of exhaustion was produced. The electrodes were then connected with a battery of 250 volts, and a current of 1.2 amperes was passed intermittently in order to allow the gases evolved by the heated cathode and the tube to be absorbed by the heated calcium anode. The current was finally allowed to pass continuously, whereby the calcium anode was heated to its vaporisation temperature. At this point, the current ceased to pass through the tube, and, although a feeble intermittent glow was subsequently evident, the discharge was insufficient to affect the amperemeter. By means of an induction coil, it was found possible to pass a current between the heated cathode and a second anode, and when this became hot by the continued passage of the current from the coil, a sufficient quantity of gas was evolved within the tube to enable the large current of 1.2 amperes to pass again from the cathode to the first anode.

These facts indicate that the phenomenon associated with the Wehnelt cathode cannot be observed in very high vacua. In contrast to the view that the large currents obtainable with this electrode are carried entirely by the emitted electrons, the author maintains that the observed facts indicate that these currents are to be referred almost exclusively to the residual gas, a very small fraction only being carried by the electrons as such.

H. M. D.

Electrochemical Equivalent and Temperature. FRIEDRICH KOHLRAUSCH and RUDOLF H. WEBER (*Ber. deut. physikal. Ges.*, 1907, 5, 681—696).—Experiments are recorded the object of which was to ascertain if temperature has any measurable influence on the value of the electrochemical equivalent. The method of experiment consisted in passing a current through a solution contained in a U-tube, the lower part of which was kept cool by immersion in ice-cold water, whilst the solution in the upper portions of the two limbs was heated by the current passing through it. If the electrochemical equivalent varies with the temperature, then at the surface of separation of the hot and cold solutions ions should be set free, and these may be recognised if suitable indicators are present in the solution. To prevent the disturbances resulting from convection currents at the surface of separation, it was found necessary to gelatinise the solutions by the addition of arrowroot.

The solutions examined were 40% sodium nitrate, 40% sodium chlorate, 30% potassium bromide, and 26% potassium iodide, litmus being added to the first three solutions to indicate the liberation of alkali metal or acid ions at the surface of temperature change. The starch in the gelatinised solution furnishes the indicator for any liberated iodine ions in the potassium iodide solution.

The results obtained are in all cases negative, and indicate that, if the electrochemical equivalent varies with the temperature at all, the variation must be less than one-millionth per 1° in the case of sodium nitrate, sodium chlorate, and potassium bromide, and less than one ten-millionth per 1° in the case of potassium iodide. If there should be a temperature-coefficient common to all electrolytes, then this is presumably smaller than the lowest observed maximum value

($<1 \cdot 10^{-7}$). To this extent, the electrochemical equivalent may be regarded as independent of the temperature. H. M. D.

Emission of Negative Ions by Heated Metals and by Heated Calcium Oxide. FRITZ DEININGER (*Ber. deut. physikal. Ges.*, 1907, 5, 674—680 *).—The emission of negative ions by heated platinum, carbon, tantalum, and nickel, and by the same elements when covered by a layer of calcium oxide, has been investigated by measuring the saturation currents at a series of temperatures. In all cases, Richardson's formula expresses the relationship between the saturation current and the temperature of the heated material. The number of ions emitted by the uncovered elements increases in the order: nickel, platinum, tantalum, carbon. When the heated wires are coated with a thin layer of calcium oxide, the differences disappear, the number of ions emitted, although very much greater, being in all cases the same.

The author concludes that the emission of negative ions by heated metals depends very much on the nature of the metallic surface, and the frequently observed irregularities are to be attributed to variation in the nature of the surface layers. H. M. D.

Measurement of the Variation of Specific Heat with Temperature. ERNST LECHER (*Ber. deut. physikal. Ges.*, 1907, 5, 647—656).—A new method of measuring specific heats of metals at high temperatures is described. The metal, in the form of a wire 3—4 mm. in diameter, is contained in an evacuated porcelain tube heated in an electric furnace. A measured, alternating electric current is passed for a known interval of time through the wire, and the rise of temperature thereby produced is measured by means of a thermoelement in contact with the metal under examination. Although the method only yields relative specific heat values, it is particularly suitable for the determination of the variation of the specific heat with the temperature, for it gives relative specific heats at definite temperatures, whereas ordinary calorimetric methods give only mean specific heat values over considerable ranges of temperature.

The results obtained for nickel and iron are recorded in the form of curves. From these, it appears that the specific heat of nickel rises with the temperature and attains a maximum at 320° . A similar maximum is found for iron at about 740° . In a footnote, the author alludes to the possibility that the observed maxima may be connected with molecular changes in the metals, and prefers to regard the measured quantities as the total quantities of heat required for the change in state (*Erwärmungsenergien*). H. M. D.

Apparatus for Distillation in High Vacua. H. BÜLLER DE FLORIN (*Chem. Zeit.*, 1908, 32, 56).—In the apparatus, which is described and figured, the side tube of the distilling bulb is fused into the receiver, thus doing away with cork or rubber connexions, and is surrounded by an extension of the air-bath in which the bulb is heated. The receiver is jacketed, and may be heated with water or steam to assist in the removal of solidified distillates. G. Y.

A Water Thermostat for the Normal Temperature of 15° . PODA (*Zeitsch. angew. Chem.*, 1907, 20, 2245—2247).—The

* And *Ann. Physik*, 1908, [iv], 25, 285—308.

author has devised an arrangement for maintaining a water-bath at 15°, the variations in temperature amounting to less than 0.1 of a degree. For details, the description and diagram in the original must be consulted. G. Y.

New Vapour Pressure Interpolation Formula. EMIL BOSE (*Physikal. Zeitsch.*, 1907, 8, 944—951).—The relationship between vapour pressure and temperature is accurately represented by the equation $\log p = A + B.1/T + C.1/T^2 + D.1/T^3$ if low values of the absolute temperature, T , are excluded. The experimentally determined vapour pressure values for eight substances (ethyl alcohol, water, fluorobenzene, methyl acetate, ethyl formate, *n*-pentane, chlorine, and ethyl ether) at temperatures from -20° to +140° are compared with the requirements of this formula, and also with those of the Nernst formula: $\log p = A + BT + C \log T + D.1/T$. The mean relative deviations of the experimental vapour pressure values for these eight substances from those calculated are smaller in the case of the exponential formula than in that of Nernst's formula if ethyl ether is excepted. If curves representing the deviations as a function of the temperature are plotted, the closer agreement of the experimental values with those calculated from the new formula is strikingly evident. This is particularly the case for water, fluorobenzene, methyl acetate, and ethyl formate, the deviations being, not only small, but quite irregular and attributable to small errors in the determination of the vapour pressures. The exponential formula is more accurate for extrapolation to higher temperatures, but for extrapolation to low temperatures the values calculated from Nernst's formula are more accurate. H. M. D.

Thermodynamics of Non-homogeneous Mixtures. II. EMIL BOSE [with MISS B. MAY CLARK] (*Physikal. Zeitsch.*, 1907, 8, 951—957).—A further theoretical consideration of the relationship between the vapour pressures of partially miscible liquid mixtures and the heat change which takes place on mixing the two liquids.

Measurements of the heat change on mixing *isobutyl* alcohol and water have been made at three different temperatures. At 20.76°, the two liquid phases contain respectively 10% and 83% of *isobutyl* alcohol; at 50.74°, 8% and 82%, and at 60.72°, 6.5% and 81%. The heat change which accompanies the formation of 1 gram of saturated solution of *isobutyl* alcohol in water is at the three temperatures, +2.85, +0.44, and -0.13 cal. respectively. The heat change accompanying the formation of 1 gram of saturated solution of water in *isobutyl* alcohol at the same three temperatures is -1.97, -3.61, and -4.36 cal. respectively.

The partial pressures of the two components are calculated from the thermal measurements, and it is found that the sums of the partial pressures are in close agreement with the total vapour pressures determined experimentally by Konowaloff. H. M. D.

Molecular Attraction. VII. Examination of Seven Esters. JAMES E. MILLS (*J. Physical Chem.*, 1907, 11, 594—622. Compare Abstr., 1907, ii, 226).—The validity of the equation $(L - E)/(\sqrt[3]{d} - \sqrt[3]{D}) = \text{constant}$ is further tested by reference to experimental data available for propyl formate, ethyl acetate, methyl propionate, propyl

acetate, ethyl propionate, methyl butyrate, and methyl *isobutyrate*. The results are very favourable, and therefore furnish additional support to the view that the attraction between the molecules of a liquid varies inversely as the square of their distance. Crompton's formula for the heat of vapourisation has been further examined; the values given by this formula are uniformly too high at low vapour pressures, but at high vapour pressures in the vicinity of the critical temperature the formula is accurate.

Some relations at the critical temperature, already discussed in earlier papers, are confirmed for the seven esters which have been examined. J. C. P.

Thermochemical Data relating to the Chlorinated Compounds derived from Millon's Base. H. GAUDECHON (*Compt. rend.*, 1907, 145, 1421—1425. Compare *Abstr.*, 1907, ii, 621, 667).—The monohydrate of dimercuriammonium chloride, $(\text{NHg}_2\text{Cl})_2 \cdot \text{H}_2\text{O}$ (compare André, *Abstr.*, 1899, 837), prepared either by neutralising the base, $(\text{NHg}_2)_2\text{O} \cdot 4\text{H}_2\text{O}$, with $N/2$ HCl or by dehydrating the dihydrate, $(\text{NHg}_2\text{Cl})_2 \cdot 2\text{H}_2\text{O}$, or by the limited action of boiling water on the compound $\text{NHg}_2\text{Cl} \cdot \text{NH}_4\text{Cl}$ or $\text{NHg}_2\text{Cl} \cdot 3\text{NH}_4\text{Cl}$, is a yellow, amorphous substance. The dihydrate, $(\text{NHg}_2\text{Cl})_2 \cdot 2\text{H}_2\text{O}$, prepared by the action of ammonia on mercuric chloride or on the compound $3\text{HgO} \cdot \text{HgCl}_2$, is also amorphous. From the determination of the heat of neutralisation of the base, $(\text{NHg}_2)_2\text{O} \cdot 4\text{H}_2\text{O}$, with $N/2$ HCl, and the heat of solution of the salt, $2\text{NHg}_2\text{Cl} \cdot \text{H}_2\text{O}$ or $2\text{NHg}_2\text{Cl} \cdot 2\text{H}_2\text{O}$, in potassium cyanide, the heat of formation of the salt, $2\text{NHg}_2\text{Cl}$ (solid), from the base $(\text{NHg}_2)_2\text{O}$ (solid), and hydrochloric acid (dissolved) is 50.9 Cal.; the corresponding values in the case of potassium hydroxide, barium oxide, and silver oxide are 27.4 Cal., 27.7 Cal., and 41.2 Cal. respectively, and this explains why Millon's base can displace potassium, sodium, and barium from solutions of their chlorides.

The heat of formation of the compound $\text{NHg}_2\text{Cl} \cdot \text{NH}_4\text{Cl}$ or $\text{NHg}_2\text{Cl} \cdot 3\text{NH}_4\text{Cl}$ (solid) from the salt, NHg_2Cl (solid), is 15.6 Cal. or 18.4 Cal. respectively, and is comparable to the heat of formation of such complex salts as the platinichlorides, platinibromide, or mercuricyanides. M. A. W.

Density of Liquids below Zero. J. TIMMERMANS (*Bull. Soc. chim. Belg.*, 1907, 21, 395—402).—The author has studied the variation of density (compared with that of water at 4°) with change in temperature of the liquids, methyl and ethyl alcohols, ethyl ether, acetone, *isobutyric* acid, ethyl acetate, acetonitrile, ethyl bromide, chloroform, *isopentane*, toluene, chlorobenzene, and pyridine, below 0°. The liquids were repeatedly distilled, using a Young column, until their boiling points were constant to 0.01°, and were finally distilled from a powerful dehydrating agent. The variation in density was determined by a dilatometer method, temperatures being measured by a Callendar platinum resistance thermometer. The results obtained are subject to a maximum error of ± 0.0005 . For the liquids studied, the density below 0° varies directly with the temperature (below zero). A table is given showing the temperature interval studied, the density of the liquid at 0° (D_4^0), the coefficient

of increase in density per degree lowering of the temperature, and the densities (1) found experimentally, (2) calculated by the author's formula, and (3) calculated by Young's formula at a definite temperature arbitrarily chosen for each liquid. In no case was a maximum density observed. E. H.

Vapour Density Determinations at very High Temperatures. H. VON WARTENBERG (*Zeitsch. anorg. Chem.*, 1907, 56, 320—336. Compare Abstr., 1906, ii, 161; Nernst, Abstr., 1903, ii, 636).—The vapour densities of a number of elements, mainly metals, have been determined in the neighbourhood of 2000° by Nernst's method (*loc. cit.*). Some slight modifications of the earlier arrangements are described; in particular, the iridium bulb was coated inside and outside repeatedly with a paste of magnesia and magnesium chloride, and heated strongly after each addition. This coating proved much more satisfactory than that used previously. Argon or nitrogen was used for filling the bulb. In addition to the measurements in the neighbourhood of 2000°, some experiments were made at lower temperatures, the temperatures up to 1600° being determined by means of a thermocouple in the bottom of the bulb.

The apparent average molecular weights at the temperatures indicated are as follows: bismuth, 224 at 2070°; antimony, 128 at 2070°; selenium, 200 at 1850°, 120 at 2100°; tellurium, 160 at 2100°; lead, 225 at 1600—1870°; thallium, 220 at 1320—1690°; zinc, 72 at 1200—2070°; sulphur, 50 at 2070°. The agreement of separate observations with the same substance is only moderate.

The results show that all the metals so far investigated are monatomic in the state of vapour at the highest temperatures.

From the temperatures at which rapid volatilisation of the metals takes place, the following boiling points have been estimated approximately: thallium, 1280°; lead, 1580°; silver, 2050—2100°. Tin, gold, copper, magnesium, and aluminium boil above 2200°.

The results obtained by the author and by previous observers for the dissociation of the elements of the sulphur and phosphorus groups are tabulated. By means of Nernst's equation connecting equilibrium and temperature, the energy required for the dissociation of a diatomic into a monatomic molecule is estimated at 90,000 Cal. for the elements of the sulphur group, and 80,000 Cal. for those of the phosphorus group.

Incidentally, it is shown that, contrary to the statement of Cooke (Abstr., 1906, ii, 539), the density of zinc is the same in argon as in nitrogen, so that the suggestion of this observer, that zinc may form a compound with argon, is incorrect. Attempts to obtain argon in combination with aluminium or magnesium were unsuccessful, neither did argon combine with iridium under the conditions of the experiments. G. S.

Application of the Method of Limiting Densities to Organic Vapours. PHILIPPE A. GUYE (*Compt. rend.*, 1907, 145, 1330—1331).—Using the experimental values obtained by Ramsay and Steele (Abstr., 1903, ii, 635) for the densities and compressibilities of the vapours of the organic compounds, ethyl ether, hexane, methyl

alcohol, diisobutylbenzene, *n*-octane, and toluene, the authors have calculated the corresponding values of the gas constant R from the relation $R = M/L(1 - A_0^1)$. The results show that the values of R are not constant, but decrease as the critical temperatures of the vapours under consideration increase; and the author concludes, provisionally, that the extrapolation methods which give the coefficient A_0^1 are insufficient (compare Berthelot, *Abstr.*, 1898, ii, 502; 1907, ii, 154).

M. A. W.

Viscosity of Solutions. I. CLERK RANKEN and WILLIAM W. TAYLOR (*Trans. Roy. Soc. Edin.*, 1906, 45, 397—406).—The viscosity of aqueous solutions of potassium chloride, chlorate, ferrocyanide and ferricyanide, of ammonium iodide, mercuric chloride and cyanide, and of carbamide has been determined for a series of concentrations and temperatures. In regard to the dependence of the relative viscosity on the concentration, the results indicate that the relative viscosity of all solutions passes through at least one minimum, the position of this being determined by the nature of the dissolved substance and the temperature.

For all the solutions examined, with the exception of mercuric cyanide, the relative viscosity increases with rise of temperature. For electrolytes, the rate of increase is very much greater than for non-electrolytes; in this respect, mercuric chloride, which is but slightly ionised, ranges itself with the non-electrolytes.

At low temperatures, aqueous solutions of carbamide exhibit "negative viscosity," and thus furnish an exception to the general rule that this is only exhibited by aqueous solutions of electrolytes.

The effect of the addition of an electrolyte or non-electrolyte to pure water, and, on the other hand, to a solution which has the same viscosity as pure water, is found to be the same if the quantities added are small.

H. M. D.

Viscosity and Conductivity. KURT ARNDT (*Zeitsch. Elektrochem.*, 1907, 13, 809—812).—The rule which says that the product of maximum equivalent electrolytic conductivity and viscosity is independent of the temperature and of the nature of the solvent is tested for fused sodium metaphosphate and mixtures of it with boron trioxide. Between the melting point and about 900°, the viscosity diminishes very rapidly, whilst the conductivity is a linear function of the temperature; the rule is therefore not even approximately true; above about 900°, however, the viscosity diminishes more slowly, and the rule holds good. It is also shown that above 900° the product of viscosity and equivalent conductivity is constant for mixtures containing from 100% to 0.5% of sodium metaphosphate. If the dissociation of the metaphosphate increases with dilution, the more dilute solutions should be relatively better conductors than the more concentrated ones; since this is not the case, the author draws the conclusion that the salt is completely dissociated even in the pure state at 900°.

T. E.

Spectrophotometry, Viscosimetry, and Electric Signs of Solutions. CHARLES HENRY (*Compt. rend.*, 1907, 145, 1415—1417).—The results obtained by Mayer, Schaeffer, and Terroine (this vol., ii, 24) on the effect of traces of acids and alkalis on the size of colloidal granules are in agreement with those observed by the author on the effect of traces of chlorine water on solutions or colloidal suspensions of dyes (auramine, crystal-ponceau, or methylene-blue). In the case of the solutions, the molecular aggregates are increased in size, and the viscosity of the solution is diminished, and in the case of the colloidal suspensions the granules are diminished in volume and the viscosity of the solution is increased by the addition of chlorine water. M. A. W.

Permeabilities of Collodion, Gold-beaters' Skin, Parchment Paper, and Porcelain Membranes. S. LAWRENCE BIGELOW (*J. Amer. Chem. Soc.*, 1907, 29, 1675—1692).—In an earlier paper (Bigelow and Gemberling, *Abstr.*, 1907, ii, 933), the results of experiments on the permeability of collodion membranes under pressures varying from 50 mm. to 250 mm. and at temperatures between 1° and 35° were recorded. Apparatus is now described by means of which determinations have been made through a much greater range of pressure and temperature on the rate of the passage of water through collodion, gold-beaters' skin, parchment paper, and porcelain. The permeabilities of the different membranes are compared. The results show that the rate of passage of water through the molecular interstices of these membranes conforms to the laws regulating the rate of passage of liquids through capillary tubes. E. G.

Diffusion of Electrolytes in Aqueous Solution. B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 696—702. Compare this vol., ii, 20).—Into aqueous solutions of alkali haloid and silver nitrate the author dips the two vertical ends of a horizontal capillary tube filled with water. The length of the tube beneath the surface must be the same for the two solutions, which must stand at the same level and have the same sp. gr. The position at which the silver haloid is deposited in the capillary is then noted. It is found that, in the same time, potassium chloride, bromide, and iodide traverse almost equal paths in the capillary tube. The positions of the layers of precipitate formed can be calculated approximately by assuming that the molecules of both the silver and alkali salts move with velocities equal to the means of the velocities of migration of their respective ions. T. H. P.

Crystal-Systems and Optical Interference-Figures of Liquid Crystals. DANIEL VORLÄNDER (*Zeitsch. physikal. Chem.*, 1907, 61, 166—170).—Liquid crystals of ethyl azoxybromocinnamate were observed to have the form of tetragonal bipyramids with straight edges. Interference figures in convergent polarised light were seen with liquid crystals of several substances, and are best shown by ethyl anisylideneaminocinnamate. All liquid crystals are optically uniaxial. L. J. S.

Velocity of Crystallisation of Isomorphous Mixtures. MAURICE PADOA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 695—696).—Bogojawlenski and Sacharoff's investigations on the velocities of crystallisation of mixtures of isomorphous substances (Abstr., 1907, ii, 751), although extending over a greater range of concentrations than the author's experiments (Abstr., 1904, ii, 390), are in accord with the latter, and hence lead to the conclusions drawn by the author (*loc. cit.*). With some of the substances examined by the author, the maximum velocity of crystallisation was only maintained over a very small temperature interval, whilst in other cases, this maximum could not be attained practically. In these instances, the velocities of crystallisation of the pure substances and of their mixtures were compared at equal degrees of supercooling. This procedure the author defends, as his results were only qualitative. T. H. P.

Solution in a Dissolved Solid. CHARLES L. PARSONS (*J. Physical Chem.*, 1907, 11, 659—680).—The explanation suggested (this vol., ii, 105) for the solubility of glucinum hydroxide in glucinum sulphate is capable of a wider application. The assumption of a complex in cases where the freezing point of a solution of two solutes is abnormally high is not always necessary, for a dissolved solid may itself act as a solvent. Camphor dissolved in aqueous acetic acid raises the freezing point of the latter and lowers its conductivity, and yet no assumption of complexes is made here. So, also, it is possible that iodine dissolves readily in potassium iodide solution, not because a complex is formed, as is generally assumed, but because iodine is soluble in potassium iodide just as iodine is more soluble in aqueous alcohol than it is in water. The author's view is supported by the observation that the iodine and potassium iodide can be partially separated by dialysis, whereas in cases of undoubted complex formation, for example, in potassium silver cyanide solutions, no such separation by dialysis takes place. The dialysis experiments with potassium silver cyanide solutions show that the formation of any other complex than $KAg(CN)_2$ is highly improbable. Further dialysis experiments with boric acid dissolved in borax solutions show that the boric acid is to be regarded as mixed with the borax rather than combined with it as a polyborate; there is no need in this case to assume the existence of complex molecules. J. C. P.

Adsorption and the Behaviour of Casein in Acid Solutions. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1908, 4, 35—44).—It is questioned whether adsorption or mechanical affinity exists at all, and the theory that proteins form adsorption compounds is considered to be premature and unproved. W. D. H.

Influence of Acids and Bases on the Absorption of Acidic and Basic Dyes by Wool. LOUIS PELET-JOLIVET and N. ANDERSEN (*Compt. rend.*, 1907, 145, 1340—1341).—The authors have determined the amount of crystal-ponceau and methylene-blue absorbed by wool in the presence of varying amounts of hydrochloric, sulphuric, or phosphoric acids, or of sodium hydroxide. The amount

of crystal-ponceau absorbed increases with the increasing acidity of the bath, the greatest absorption taking place with hydrochloric acid and the least with phosphoric acid, whilst the amount of methylene-blue absorbed diminishes under the same conditions. In an alkaline bath, almost no crystal-ponceau is absorbed, but methylene-blue shows a maximum absorption.

These results are in accordance with the colloidal theory of dyeing (compare this vol., ii, 18). M. A. W.

Physico-chemical Researches on Lecithin and Cholesterol. OTTO PORGES and E. NEUBAUER (*Biochem. Zeitsch.*, 1907, 7, 152—177. Compare Abstr., 1903, i, 301).—An investigation of the properties of emulsions prepared by adding an ethereal solution of lecithin or an acetone solution of cholesterol to distilled water, and subsequently removing the organic solvent. The suspension of lecithin is homogeneous and stable; it can be filtered, and resembles a colloidal solution; the cholesterol suspension is not very stable by itself, but becomes so in the presence of albumin or of lecithin.

The general conclusion arrived at is, that lecithin is a "hydrophilous" colloid, and cholesterol a "suspension" colloid (these terms are from Hüber's "Physikalische Chemie der Zelle und Gewebe." Hydrophilous colloids increase the viscosity of the solvent, and suspension colloids do not. Solutions of the former approximate more closely to true solutions).

In comparing the efficiency of various salts of the alkali metals as lecithin precipitants, the anions and cations are found to be in the same order as that observed by Pauli for the precipitation of albumin (Abstr., 1903, i, 299; 1904, i, 356). Lecithin solutions are peculiar in not being precipitated by concentrated (nor by very dilute) solutions of salts of the alkali metals, but only by solutions the concentration of which lies between certain limits. The precipitation of lecithin by salts of other metals is also, for the most part, closely analogous to the precipitation of albumin (Pauli). With several salts of the heavy metals, the phenomenon is complicated by the occurrence of two precipitation zones, separated by a region of intermediate concentrations in which no precipitation occurs. The precipitation reactions of cholesterol are much more uniform than those of lecithin, and show great similarity to those found by Buxton and Shaffer for mastic suspensions (Abstr., 1906, ii, 839).

Lecithin and cholesterol suspensions are precipitated by acids and dissolved by alkalis, indicating anodic convection. Accordingly, both are precipitated by cathodic colloids at a certain optimal concentration. Cholesterol can, for instance, be precipitated by albumin (at a certain relative concentration and in neutral solution), but not by mastic, which, like cholesterol, is electro-negative. Lecithin and cholesterol form a colloidal compound with each other, since the former protects the latter against precipitation by salts.

The biological application of the results is also discussed. G. B.

Colloidal, Amorphous, and Crystalline States. P. P. VON WEIMARN (*Chem. Zentr.*, 1907, ii, 1293—1294; from *Zeit. chem. Ind. Kolloide*, 1907, 2, 76—83).—The observation that the appearance and

structure of the precipitate of barium sulphate, obtained by the reaction between manganese sulphate and barium thiocyanate in aqueous solution, depend essentially on the concentrations of both of the participating salts, led the author to extend his researches, with the following results. Equal volumes of normal solutions of different salts, which yield very sparingly soluble precipitates, are mixed at various dilutions, and the precipitates examined macroscopically, microscopically, and ultramicroscopically. Gelatinous precipitates are formed at concentrations so much the smaller the less soluble the precipitate, the more viscous the solutions, and the more complex the reacting substances. Precipitates such as the hydrated oxides of aluminium or silicon are obtained gelatinous on account of their slight solubility; they can be obtained in crystals by a very slow reaction in very dilute solution. Moreover, numerous crystalline substances have been obtained in a gelatinous or quasi-gelatinous state by the addition of substances which lower the solubility (for example, alcohol in the case of the sulphates of calcium, strontium, barium, and lead), or by increasing the concentration (easily applicable with very viscous salt solutions, or with substances the solubility of which does not exceed 10^{-2} per 100 grams of water).

When a proportionality exists between the solubility and the concentration at which a precipitate separates in the gelatinous state, conclusions can be drawn as to the order of magnitude of the solubility of the precipitate, that of aluminium hydroxide being 10^{-8} to 10^{-9} per 100 grams of water at the boiling point, and those of the hydroxides of iron and silicon in water, and of barium sulphate in alcohol, being still smaller.

By continuously increasing the concentrations of the reacting solutions, the average size of the resulting crystals increases from the invisibly minute, through those of ultramicroscopic dimensions (crystalline suspensions, sols), to those of microscopic magnitude; the last reach a maximum (microcrystalline precipitates), and then the size of the crystals, still with solutions of increasing concentration, begins to diminish, until, finally, invisibly minute crystals are again obtained (undifferentiated, transparent jellies).

The crystalline nature of precipitates formed at very small or at very great concentrations cannot be proved optically; nevertheless, the characteristic properties of flocculent and gelatinous precipitates (such as increased solubility and vapour tension, lower melting point, and increased absorptive capacity), as well as their conversion into distinctly microcrystalline precipitates, can be attributed to the properties of crystalline substances in an exceedingly minute state of division.

The author states the following conclusions: (1) the so-called colloidal, amorphous, and crystalline states are general properties of matter; (2) colloidal and amorphous states are modifications of the crystalline. Irreversible sols represent suspensions of very finely-divided, crystalline substances which have lost the power of cohering to form larger aggregates in consequence of the too slight mobility of the crystalline particles and the too great viscosity of the medium. Sols of complex, reversible colloids, such as gluten, are limit cases of

true solutions; their coagulation by cooling is identical with the ordinary phenomenon of crystallisation, but the crystals do not attain visible magnitudes because they have lost the power of coherence in consequence of the complexity of the molecule. A gelatinous substance consists of a crystalline, sponge-like framework, which is impregnated with the solution of the substance existing before, or produced by, a reaction. The size of the crystals varies according to the conditions of formation, from the ultramicroscopically invisible to the microscopically visible; so-called amorphous precipitates are crystalline particles of distinctly greater dimensions than those of typical gelatinous substances; (3) the fundamental, and possibly the sole, cause of the formation of amorphous and gelatinous precipitates, as opposed to crystalline, is found in the different conditions of their formation, which is influenced by, or is dependent on, the relative velocity of formation of the substance in the solution, the complexity of the substance, and the viscosity of the medium; (4) in markedly gelatinous media, the velocity of diffusion and of reaction is small, and often practically nil; (5) crystalline structure is conditioned by the internal symmetry of the elementary crystalline particles of substances; this symmetry is not destroyed by the passage into the liquid and gaseous phases. The increase in mobility causes the particles to deviate from directions parallel to their elements of symmetry. The viscosity of very concentrated solutions, or of molten substances near the solidifying point, is caused by the striving of the particles to move parallel to one another, a striving which cannot be fulfilled under the given conditions of temperature and pressure. Identical conditions must hold for the transformation from the liquid to the solid, and from the gaseous to the liquid, states. C. S.

Possibility of Determining the Mass of Suitable Precipitates by Observation of their Rates of Settling. S. KOHN (*Chem. Zeit.*, 1907, 31, 1287).—An attempt to determine the mass of a precipitate by comparing its rate of settling when suspended in a liquid with the rates observed for known masses of the same substance. The method employed is to shake the washed precipitate with a liquid in which it is insoluble in a measuring cylinder, and to observe the times in which the upper surface of the precipitate falls through equal intervals; the results are compared with the rates of settling of two precipitates of known mass, one of greater, the other of less, mass than that to be determined. Details quoted of experiments with barium carbonate and ferric hydroxide show that the rate of settling of a precipitate is only approximately proportional to its mass; hence the error of the method diminishes with the differences between the masses of the three precipitates. The observations for the first two, or even three, intervals must be discarded as abnormal in consequence of the persistence of the movement of the liquid after the mixing. The rates of settling of different precipitates are comparable, of course, only when all the conditions of their precipitation and subsequent treatment are the same. G. Y.

Equilibrium Relations of Chromates in Solution. MILES S. SHERRILL (*J. Amer. Chem. Soc.*, 1907, 29, 1614—1675).—The con-

ductivity determinations of solutions of chromates, dichromates, and chromic acid carried out by Walden (Abstr., 1888, 1008) indicate that chromic acid exists in solution as H_2CrO_4 dissociating into



or, as Ostwald (Abstr., 1888, 1009) has suggested, as $\text{H}_2\text{Cr}_2\text{O}_7$ dissociating into $2\text{H}^+ + \text{Cr}_2\text{O}_7''$. The latter view has been generally accepted, whilst the possible existence of the HCrO_4' ion has been overlooked. It is pointed out that both of these reactions must be taken into account in studying the constitution of chromic acid solutions. The relative amounts of the HCrO_4' and $\text{Cr}_2\text{O}_7''$ ions present depend on the concentration and the equilibrium constant of the reaction $2\text{HCrO}_4' = \text{H}_2\text{O} + \text{Cr}_2\text{O}_7''$.

[With F. MALCOLM EATON.]—Cryoscopic determinations have been made with dilute solutions of chromic acid and potassium dichromate. The depression of the f. p. in the most dilute solutions was greater than that which would correspond with complete ionisation into $\text{Cr}_2\text{O}_7''$ and H or K ions, and the presence of an appreciable quantity of HCrO_4' ions was indicated. The values of the equilibrium constant for the second reaction, that is, of the hydration constant,

$$K_H = \text{Cr}_2\text{O}_7'' / (\text{HCrO}_4')^2,$$

were calculated and found to be 61 from the potassium dichromate and 27 from the chromic acid experiments.

[With ALDEN MERRILL.]—Determinations of the hydrolysis of ammonium chromate in dilute solutions were made by measuring the increase of conductivity produced by the addition of sufficient ammonia to drive back the hydrolysis completely; the value of the ionisation constant, $K_A = \text{H}^+ \times \text{CrO}_4' / \text{HCrO}_4'$, at 18° was found to be 5.7×10^{-7} .

[With DONALD E. RUSS.]—By means of distribution experiments, the concentration of the ammonia in chloroform was determined which is in equilibrium with the ammonia produced by hydrolysis in dilute ammonium chromate solutions. From the results, the ionisation constant, $K_A = \text{H}^+ \times \text{CrO}_4' / \text{HCrO}_4'$, was found to be 6.2×10^{-7} at 18° and 7.4×10^{-7} at 25° , and is thus about 1/30 of that of acetic acid.

Determinations were made of the solubility of silver chromate in dilute ammonia at 25° , and the value of the solubility product,

$$(\text{Ag}^+)^2 \times \text{CrO}_4'',$$

was calculated and found to be 9×10^{-12} , the corresponding silver-ion concentration in the saturated aqueous solution being 2.5×10^{-4} mols. per litre. Experiments on the solubility of silver chromate in dilute nitric acid showed that, in acid solutions of greater strength than $0.075N$, silver chromate is decomposed with separation of silver dichromate as a solid phase. Silver dichromate is decomposed by water or nitric acid solutions of lower concentration than $0.06N$ with separation of silver chromate. From these results and the solubility product of silver chromate, the hydration constant, K_H , the ionisation constant, K_A , and the solubility product, $K = (\text{Ag}^+)^2 \times \text{Cr}_2\text{O}_7''$, for silver dichromate were found to be 75, 8.4×10^{-7} , and 2×10^{-7} respectively. This value of the solubility product is equivalent to a concentration of 7.3×10^{-3} mols. Ag per litre.

The results of this work indicate that in a solution of potassium

dichromate containing 0.1 mol. per litre, about 15% of the salt exists as KHCrO_4 and 85% as $\text{K}_2\text{Cr}_2\text{O}_7$, whilst in a solution of concentration 0.01 mol. per litre, approximately 45% is present as KHCrO_4 .

It is shown that the results obtained are in accord with those of Whetham (Abstr., 1903, ii, 405) on the conductivity of potassium dichromate solutions, and of Spitalsky (Abstr., 1907, ii, 695) on the catalytic decomposition of ethyl diazoacetate by chromate solutions, but indicate that Spitalsky's conclusion that dilute solutions of chromic acid and potassium dichromate do not contain any considerable quantity of HCrO_4 ions is incorrect. E. G.

Equilibria in Ternary Systems. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 691—694).—In the case when the freezing-point curve of a binary system does not exhibit a maximum, it may give indications of the formation of an additive product, although no conclusion can be drawn with regard to the proportions in which the two components combine. In general, it is theoretically possible to find a third substance capable of bringing the maximum temperature corresponding with the additive compound below that at which this compound decomposes. This substance should have no action on, and should not be isomorphous with, either of the two components or the additive compound. It is best to employ a third substance of such a nature that the freezing points of the two components are lowered considerably, whilst the eutectic points of the three binary systems formed by the third substance with the two components and the additive compound respectively lie near to the freezing point of the third substance itself. These theoretical considerations are to be tested experimentally. T. H. P.

Hydrolytic Fission of Acetylated Hydroxycarboxylic Acids. JULIUS RATH (*Annalen*, 1907, 358, 98—125).—Anschütz and Bertram found that the action of water on the acetyl derivatives of lactic and glycollic acids leads to the formation of acetic acid and the hydroxy-acid, the hydrolysis taking place slowly at the ordinary, more quickly at the higher, temperature (Abstr., 1906, i, 966, 990). In continuation of this work, the present author has studied the influence of concentration and temperature on the velocity of the hydrolysis of a number of acetoxy-acids. In each case, the velocity constant does not vary with the time only when calculated according to the equation for unimolecular reactions. This reaction between acetoxy-carboxylic acids and water must therefore be intermediate between Ostwald's autocatalysis and true catalysis; although both the original substance and the reaction products act catalytically, the amount of the catalyst, that is of the hydrogen ions which accelerate the hydrolysis, must remain approximately unchanged throughout the reaction. The influence of the concentration on the rate of hydrolysis varies with the acid; in most cases, the velocity increases with the concentration, but in some the rate of hydrolysis is almost unaltered by changes in the concentration, whilst the constant for acetylcitric acid diminishes with increasing concentration. Of the following

values for k obtained for the acids named, the first is with $v=9$, the second with $v=54$, at 100° , or for acetylcitric acid at 50° .

Acetyl-lactic acid, 0.05011, 0.02548; acetylglycollic acid, 0.06483, 0.04001; diacetyltartaric acid, 0.16149, 0.11128; acetylmalic acid, 0.10467, 0.09209; acetylsalicylic acid, 0.17842, 0.16976; acetyl-mandelic acid, 0.04423, 0.02548; acetylcitric acid, 0.12414, 0.27512.

The relation of the velocity constant to the temperature is represented by the expression: $\log K = a + bt$; the value $b = 0.02713$ is obtained for diacetyltartaric acid; the temperature-coefficient for intervals of 10° has the normal value 1.87.

Whilst the abnormal behaviour of acetylcitric acid points to a relation between the velocity constant and the constitution of the acetoxy-acid, the data are as yet insufficient to allow of any definite conclusion. G. Y.

Velocities of Catalytic Reactions in Heterogeneous Systems. Decomposition of Hydrogen Peroxide by Means of Platinum Foil Compared with Catalysis by Colloidal Platinum. I. S. TELETOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1358—1379).—In order to determine whether Nernst's hypothesis regarding the velocity of reaction in a heterogeneous system is also applicable to catalytic processes (compare Nernst, *Abstr.*, 1904, ii, 315), it is necessary that both the surface of the catalyst and the rate of stirring of the reacting substance should be determined readily. These conditions are fulfilled by the decomposition of hydrogen peroxide by platinised platinum foil. Ordinary platinum foil does not produce decomposition. The thickness of the layer of platinum-black has no influence on the reaction, but in the presence of platinum poisons, such as hydrogen sulphide, carbon disulphide, &c., its activity is destroyed; the activity can be restored by treating the plate with concentrated sulphuric acid at 150 — 200° . The reaction is unimolecular, and the thickness of the layer surrounding the plate, in this case probably pure water, through which the hydrogen peroxide diffuses, can be calculated from the formula $\delta = D \cdot 0.0^{0.4343} / (0.4343K) \cdot v$ (where δ = thickness of layer, D = the diffusion of hydrogen peroxide in c.c. per minute, O = surface of plate, and v = volume of the solution). For $v = 900$ c.c. and $O = 20$ c.c., $0.4343K = 0.004$ at 25° and 250 revolutions per minute, and thus $\delta = 0.014$ mm., which agrees closely with Brunner's results (*Abstr.*, 1904, ii, 315). Contrary to Henri's statement (*Abstr.*, 1906, ii, 13), calculating δ from Bredig's results, it is found to be 0.065 mm. Towards the end of the reaction, especially in concentrated solutions, K diminishes, owing to the growing passivity of the plate, the activity of which cannot be restored by sulphuric acid; it is probable that an intermediate oxidation product of platinum is formed analogous to the one already isolated for mercury. In acetic acid solution, the reaction is slower, but it is still unimolecular. In sodium hydroxides, it is also unimolecular, and K rises to a maximum in solutions containing 50—100% of the alkali. In this, as in many other respects, the behaviour of the platinum is analogous to that of ferments. Both in the case of the platinum plate and in that of colloidal platinum, K rises 28% for every 10° rise in temperature. In

the latter, an ultramicroscopic examination has shown that the velocity of the platinum particles varies in the same degree. In both cases (but especially for colloidal platinum), the velocity of the reaction is largely diminished when the viscosity of the reacting solution is increased by addition of sugar. The following relations for reactions in the presence of a platinum plate are also deduced: $K_1/K_2 = O_1v_2/O_2v_1 = C_1/C_2$ and $K_2 = K_1(n_2/n_1)^{\frac{1}{2}}$ (where C_1, C_2 = the concentration of the catalyst, and n = number of revolutions of the stirrer in the given time). Z. K.

Evolution and Devolution of the Elements. A. C. and A. E. JESSUP (*Phil. Mag.*, 1907, [vi], 15, 21—55).—A theory of evolution of the elements based on astro-physical observations is put forward. According to spectroscopic evidence, matter in the nebulous stage consists of only four elements, two of which are unknown, the third being hydrogen, and the fourth helium. These original elements are termed protons, and are supposed to be formed from primary corpuscles (which at one time represented the only form of matter) by an aggregation into stable integral systems. By a process of condensation of corpuscles round the proton groups, other atoms are supposed to be formed, the various elements representing groupings of maximum stability in a gradual and continuous process.

The authors consider that evolution takes place both along the vertical groups of the periodic table and along the horizontal series. The improbability of the existence of more than four original elements, considered in conjunction with the apparent existence of considerably more groups, leads to the hypothesis that at least one of the protons has given rise to more than one product of evolution. The alkali metal group, the alkaline earth-metal group, and the group of inert elements are supposed to have been evolved respectively from the first (hydrogen), the second (proto-glucinum), and the fourth (helium) protons. From the third proton (proto-boron), the tervalent elements, boron, aluminium, scandium, yttrium, lanthanum, and ytterbium, have been produced by "direct" evolution, and in this case "indirect evolution" has also taken place with the production of quadrivalent carbon. Carbon gives rise directly to silicon and indirectly to nitrogen, oxygen, and fluorine. Silicon, by similar indirect processes, in which hereditary influence plays an important part, is supposed to have given rise to all the elements lying between titanium (atomic weight, 48.1) and arsenic (75). With the exception of manganese, these in turn appear to have given rise to direct evolution products of the same valency. A new form of the periodic table in which these ideas find expression is put forward; this table contains the elements arranged in seventeen vertical groups. For details respecting the relationships expressed by the evolutionary grouping of the elements, the original must be consulted. Mention may here be made of the fact that the incomplete table of elements given by Cuthbertson and Metcalfe (*Phil. Trans.*, 1907, A, 207, 135) from observations on the refractivities of the elements agrees closely with that of the authors.

With regard to the processes of condensation, which result in the formation of assemblages of corpuscles or "rings" around the original

proton aggregates, it is supposed that all the principal chemical properties of each element are determined by the structure of the ring, that "direct" evolution along vertical groups corresponds with the addition of similar rings, and "indirect" evolution along horizontal series with the addition of dissimilar or "distorted" rings. Each "ring" is supposed to consist of assemblages of corpuscles in sets of eight, but a certain number of corpuscles (for distinction termed "electrons") are attached in a different manner to the ring system. The number of such differentiated corpuscles determines the valency of an element, and chemical combination is due to the tendency of the electrons to yield sets of eight electrons which in some way constitute electrically neutral systems.

The last two sections of the paper deal with the existence of quantitative relationships between the atomic weights and the possibility of explaining the degradation of the radioactive elements by devolution processes governed by influences similar to those which regulate the evolution of the elements. An outcome of this idea is the view that the α -particles emitted by the various radioactive substances are identical with one or other of the four protons. The values obtained for the masses of the α -particles are not inconsistent with this view.

H. M. D.

Significance of the Atomic Hypothesis. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1181—1216, 1216—1218).—A theoretical discussion of the validity of atomic hypotheses. The relation between the atomicity of the elements and their electrical and heat conductivities and other properties are discussed at length. It is most probable that the metals are all monatomic, whilst most of the other elements are diatomic, and with the exception of sulphur are never more than tetra-atomic; highly complex association only occurring by the union of unlike individuals. Tables are given showing that K/K_1 is a constant approximately for the metals of each group in the periodic system (where K =atomic electrical conductivity at m. p. in absolute temperature, and K_1 =electrical conductivity at $1/2$, $1/3$, $1/4$ this temperature. Thus, for Zn at 692° , $K=50.0$, at $692/2=273=73^\circ$, $K_1=125$, $K/K_1=2.50$). These constants, as well as similar constants for thermal conductivity and other properties of the metals, also show the usual periodicity in reviewing them from right to left of the periodic table. For the metals, the temperature playing an analogous, but not identical, part with that played by the critical temperature for liquids will probably be the m. p. of the metal at zero pressure, but for practical purposes the m. p. at the ordinary pressure can be taken. A table is given showing that at the temperature $1/3$ m. p. (calculated as above), the atomic heat of the elements with but very few exceptions $= 6 \pm 0.5$.

Z. K.

Certain Relations between the Atomic Weights of the Elements. DELAUNEY (*Compt. rend.*, 1907, 145, 1279—1280).—The atomic weights of the elements can be represented with considerable accuracy by ratios of the type A^2/n , where A and n are whole numbers; thus, helium, $2^2/1$; potassium, $14^2/5$; bromine, $39^2/19$, &c. Moreover,

for closely related elements, the divisors (n) are in some instances approximately the same or in regular progression. Thus cadmium, mercury, and zinc have the values $15^2/2$, $20^2/2$, and $14^2/3$, whilst lithium, rubidium, and caesium have $13^2/24$, $47^2/26$, and $61^2/28$ respectively. In other cases, however, related elements have widely different divisors, whilst unrelated elements have similar ones. These anomalies can, however, be eliminated if the more general ratio $(Aa)^2/na^2$, where a is a whole number, be employed. Thus the value for potassium ($14^2/5$) can be made comparable with that of sodium ($22^2/21$) by taking $a=2$, when the former value becomes $28^2/20$. The divisors for a family of elements often fall into a regular series; thus for boron, scandium, yttrium, lanthanum, and aluminium the atomic weights are represented by $11^2/11$, $23^2/12$, $34^2/13$, $50^2/18$, and $25^2/23$.

E. H.

The so-called Physico-chemical Atomic Weights and the Calculation of the Weight of a Normal Litre of Gases. GUSTAV D. HINRICHS (*Chem. Zentr.*, 1907, ii, 1290; from *Mon. sci.*, 1907, [iv], 21, II, 581—583. Compare Abstr., 1893, ii, 316, 317; 1906, ii, 197).—The author denies the possibility of obtaining accurate atomic weights by weighing gases, because the so-called physico-chemical methods only confirm the gravimetric methods which he has shown to be false, and depend on gas theories, in particular, that of van der Waals.

The weight of a normal litre can be calculated by multiplying the absolute atomic weight by 44.655 mg. The discrepancy in the cases of hydrogen and carbon dioxide between the calculated values and those found experimentally by Leduc and by Rayleigh indicates that the molecular volumes of these gases are only 0.9936 of those of oxygen, nitrogen, and carbon monoxide.

C. S.

Are the Stoichiometric Laws Intelligible without the Atomic Hypothesis? OTTO KUHN (*Chem. Zeit.*, 1908, 32, 55—56. Compare Abstr., 1907, ii, 678).—A further adverse criticism of Wald's attempt to establish the stoichiometric laws without the aid of the atomic hypothesis (*Chem. Zeit.*, 1906, 30, 963, 978; Abstr., 1907, ii, 755).

G. Y.

The Metallic Form of Metalloids. EDUARD JORDIS (*Zeitsch. angew. Chem.*, 1907, 20, 2241—2245).—In the periodic system, the metals lie to the left and foot, the metalloids to the right and top, of the table. Between these are certain intermediate elements, such as arsenic and antimony, which may be obtained in both the metallic and the non-metallic states. Others besides the typical intermediate elements might be expected under favourable conditions to change their state. Of the nine non-metals, nitrogen and phosphorus occur as metals in alloys, whilst oxygen, sulphur, and probably iodine exhibit metallic properties in certain oxides, sulphides, and iodides, especially in regard to their optical, thermal, and electrical behaviour; hydrogen unites directly with metals, and forms the cation H^+ .

The metallic state is therefore a more common property of the

elements than is generally supposed, and it may be expected that under suitable conditions this state will be assumed by the remaining non-metals, chlorine, bromine, and fluorine, with greatest difficulty probably in the case of the last. The converse change, that of the metals into the metalloid state, is considered to take place less frequently, or in other manners. The passivity of the metals, the cathodic and anodic phenomena, and the properties of minerals and compounds of metals with metalloids are discussed from this point of view. G. Y.

Modification of Kundt's Method of Producing Dust-Figures by Stationary Waves, and a New Determination of C_p/C_v for Helium. ULRICH BEHN and H. GEIGER (*Ber. deut. physikal. Ges.*, 1907, 5, 657—666).—The time of vibration of a closed tube can be altered very simply by loading the ends of the tube; this is effected by cementing discs of metal symmetrically on to the two ends by means of sealing-wax. By taking the requisite number of such discs, the pitch of the vibrating tube may be made to correspond with an exact multiple of half wave-lengths in the enclosed gas, and stationary waves are then set up, giving rise to corresponding dust-figures.

The wave-lengths in helium and air have been compared by this method, and from the results the value of C_p/C_v for helium is found to be 1.63, indicating that the gas is monatomic. H. M. D.

A New Vacuum Regulator. K. W. HOLTERMAN (*Chem. Zeit.*, 1908, 32, 8).—The author describes and figures a vacuum regulator consisting of nine glass manometer tubes connected in series between the vacuum distillation apparatus and a bottle communicating with the outer air by a tube drawn to a fine point. The manometer tubes are charged with an amount of water such that air is drawn through the regulator when the pressure in the distillation apparatus falls below that desired. Variations in the atmospheric pressure are compensated by means of a tenth manometer tube arranged to rotate on its horizontal axis. G. Y.

Porous Materials as Substitutes for Stopcocks in the Manipulation of Gases. ALFRED STOCK (*Ber.*, 1907, 40, 4956—4959. Compare Prytz, *Ann. Physik*, 1905, [iv], 18, 617).—Prytz's porous material is replaced by a material made by burning a mixture of earthenware, water glass, and gum. Plates of considerable homogeneity are thus produced, they are not affected by dilute acids or boiling water, and can readily be fused into glass vessels. Their porosity is indicated by the following numbers: a plate of 8 mm. diameter and 2—3 mm. thickness allows 600—800 c.c. of air to pass per minute with a difference in pressure of 60 cm. of mercury. The plates do not admit of the passage of mercury, even with a difference in pressure of 1 atmosphere. The plates can be fused into the ends or middle of tubes, and used in much the same manner as suggested by Prytz. A more complex apparatus is described containing two porous plates and an ordinary cock surrounded by mercury. J. J. S.

Inorganic Chemistry.

Atomic Weight of Hydrogen. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1907, 29, 1718—1739).—In earlier papers (Abstr., 1889, 672; 1890, 1370), determinations of the composition of water have been recorded which indicated that the atomic weight of oxygen is probably slightly less than 15.896. At the close of each of these experiments, a small amount of gas was obtained which was assumed to be nitrogen; the weight of this gas, calculated as nitrogen, was subtracted from the weight of hydrogen, giving a correction of about 1 part per 1000. Later, after the appearance of Morley's papers (Abstr., 1895, ii, 261; 1896, ii, 640), it was considered likely that this gas came from the copper oxide and that its weight should be deducted from the weight of the oxygen instead of from that of the hydrogen. On applying this correction, the value 15.879 (or $H = 1.00765$) was obtained, which coincides with Morley's result. Further experiments are now described which have been carried out with the object of testing this explanation of the earlier results.

The apparatus employed was similar to that used in the previous work, and special precautions were taken to ensure the purity of the hydrogen and to avoid leakage. The weight of the hydrogen was determined by the increase in weight of a piece of apparatus containing copper oxide, and in which the water formed by the oxidation of the hydrogen was condensed.

The first experiments were vitiated by the retention of water by the copper oxide, and were therefore rejected. In subsequent experiments, efforts were made to reduce this source of error as far as possible.

In the second series, the hydrogen was obtained by the electrolysis of dilute sulphuric acid, and was weighed first in palladium, and again after being transferred to the copper oxide tube. The mean result of seven determinations gave $H = 1.00788 \pm 0.00002$.

In the third series, the hydrogen, obtained by the electrolysis of dilute sulphuric acid, was led directly into the copper oxide tube and converted into water. The mean of five experiments gave $H = 1.00771 \pm 0.00004$.

In the fourth series, the use of copper oxide was avoided by absorbing the hydrogen in palladium and converting it into water by means of oxygen, both gases being obtained by the electrolysis of dilute sulphuric acid. The mean of eight determinations gave $H = 1.00812 \pm 0.00003$.

In the fifth series, hydrogen and oxygen, obtained by the electrolysis of barium hydroxide solution, were combined by means of palladium. The mean of five experiments gave $H = 1.00787 \pm 0.00002$.

The most probable value for the atomic weight of hydrogen which can be calculated from these results is 1.00787. For certain reasons, however, it is considered that a more trustworthy value is a mean between this and Morley's value (1.00762 ± 0.00002), namely, 1.00775,

During the course of the work, evidence was sought with regard to the question as to whether change of weight occurs in a chemical reaction in which a large amount of energy is dissipated. Conclusive evidence was not obtained, but it was found that if any change of weight takes place, it must be very small. E. G.

Formation of Ozone by the Action of the Electric Discharge at Low Temperatures. E. BRINER and E. DURAND (*Compt. rend.*, 1907, 145, 1272—1274. Compare Abstr., 1907, ii, 759; Hautefeuille and Chappuis, Abstr., 1880, 847; Olszewski, Abstr., 1887, 634; Beill, Abstr., 1893, ii, 317; Troost, Abstr., 1898, ii, 569; Ladenburg, Abstr., 1899, ii, 18; Goldstein, Abstr., 1903, ii, 723).—By means of the apparatus described previously (Abstr., 1907, ii, 342), in which the sparking-bulb is replaced by the ordinary double-walled ozoniser, the authors have studied the action of the silent discharge on oxygen at low temperatures. When the ozoniser is cooled in a mixture of solid carbon dioxide and ether (-78°), a limiting concentration of 11% of ozone is obtained, which is the same as that observed by Beill, and is characteristic of this temperature. At -78° , 12 grams of ozone are formed per kilowatt-hour. By immersing the ozoniser in liquid air (-194°), the vapour tension of ozone is reduced nearly to zero, and it becomes possible to change oxygen almost completely (99%) into ozone. As the mean pressure is reduced from 203 mm. to 27 mm., the yield of ozone per kilowatt-hour rises to a maximum of 55 grams at 98 mm. and then falls. The ozone as it is formed condenses to a deep blue, viscous liquid. The optimum pressure of about 100 mm. is the same as that observed in sparking mixtures of nitrogen with oxygen and hydrogen, and in the formation of oxides of nitrogen by the electric arc (Haber and Koenig, this vol., ii, 34). The action of the electric spark on oxygen cooled to -194° produces ozone to the extent of only 0.79%, and this is probably due to the silent discharge accompanying the spark. E. H.

Acid Properties of Ozone. WILHELM MANCHOT and W. KAMP-SCHULTE (*Ber.*, 1907, 40, 4984—4990).—When ozone is passed into liquid ammonia which is strongly cooled, a deep orange-red colour is obtained; this vanishes, whilst the ammonia is still liquid when the temperature is raised. When the coloured liquid is introduced into cooled titanium sulphuric acid, hydrogen peroxide can be detected, and this is also the case with the colourless liquid.

Ozone forms a thick fog with ammonia at the ordinary temperature, whereby nitrite is not formed. A similar fog is given by other organic bases, and is the more intense the stronger the base. The ozone compounds of the alkali metals described by Baeyer and Villiger (Abstr., 1902, ii, 650), obtained by the action of ozone on their hydroxides, when orange-brown or yellow substances are formed, give intense colorations when introduced into strongly cooled titanium sulphuric acid, except in the case of sodium hydroxide. Cæsium gives the most, lithium the least, stable ozone compound. When heated in a stream of 8—9% ozone, the sodium compound is decolorised at about 90° ,

the potassium at about 110° , and the rubidium at about 140° ; the colour given by caesium hydroxide remains to above 160° . Lithium hydroxide gives no coloration with ozone, and must decompose below the ordinary temperature. The hydroxides of magnesium, calcium, strontium and barium decompose ozone very rapidly at the ordinary temperature; at lower temperatures, barium oxide shows a distinct coloration, that of calcium oxide is less marked, and magnesium oxide gives no colour. These metals behave therefore analogously to the alkali metals.

The oxygen-carrying power of the alkaline earths previously observed in the case of the action of ozone on metallic silver (Abstr., 1907, ii, 616) may, in view of the above, be explained as due to calcium hydroxide combining with ozone and giving up oxygen to the silver.

The formation of these compounds is attended by a considerable development of heat. They are decomposed by water, and ozone may be passed through 50% sodium hydroxide almost without decomposition until a temperature of 70° is reached. Additional proof of the acid properties of ozone is afforded by the following observations. Strong ozone above 6%, fumes in moist air; blue litmus paper is rendered faintly red, and other indicators show an unmistakable acid reaction. Ozone passed into water increases the conductivity; this appears to be due, in part, to a decomposition product, since the water remains a conductor when ozone is no longer to be detected.

E. F. A.

Persulphides of Hydrogen. GIUSEPPE BRUNI and ALESSANDRO BORGIO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 745—754).—The authors have prepared a number of persulphides of hydrogen, and find that the proportion of sulphur added to the alkali sulphide or the composition of the alkali polysulphide employed has no influence on the composition of the hydrogen persulphide obtained. Cryoscopic examination of the various products dissolved in bromoform indicates the probable existence in solution of compounds varying from H_2S_5 to H_2S_9 .

T. H. P.

Acid Energy of Thiosulphuric Acid and the Decomposition of this Acid. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1155—1158. Compare Berthelot, Abstr., 1889, 824).—Measurements of the amounts of heat absorbed when (a) 1 gram-molecule of hydrochloric acid and (b) 2 gram-molecules of hydrochloric acid are added to 1 gram-molecule of sodium thiosulphate, show that the absorption of heat, due to the formation of $NaHS_2O_3$ in the first reaction, approximates to that due to the formation of $Na_2S_2O_3$, from $NaHS_2O_3$ first formed, in the second, when the reactions are conducted at such dilutions that the changes due to secondary reactions become negligible. Consequently, the "acid energies" of the two hydrogen atoms in thiosulphuric acid are approximately equal.

As illustrating the instability of thiosulphuric acid, it is mentioned that on the addition at 12° of a gram-molecule of hydrochloric acid, dissolved in 16 litres of water, to a gram-molecule of sodium thiosulphate, dissolved in a similar quantity of water, sulphur begins to

be deposited after 1.5 minutes, and the reaction continues until one atom of the sulphur is liberated. When 2 gram-molecules of hydrochloric acid are employed in the place of 1 gram-molecule in such an experiment, the precipitation of the sulphur is never complete, indicating that, whilst the sodium hydrogen thiosulphate formed in the first case decomposes completely into sodium hydrogen sulphite and sulphur, the thiosulphuric acid liberated in the second case is only partially decomposed, yielding sulphurous acid and sulphur.

T. A. H.

Effect of Heating Yellow Phosphorus in Ammonia Gas. WILLIAM G. LLEWELLYN (*Chem. News*, 1907, 96, 296—297).—Neither yellow nor red phosphorus reacts with ammonia gas between 10° and 100°; white phosphorus is obtained by distilling yellow phosphorus in an atmosphere of ammonia.

W. H. G.

Carbon Suboxide. III. OTTO DIELS and PAUL BLUMBERG (*Ber.*, 1908, 41, 82—86. Compare Abstr., 1906, ii, 227; 1907, ii, 180).—An attempt to solve the problem of the constitution of carbon suboxide has been made by an examination of its molecular refraction and dispersion. The actual values obtained, mol. ref. 16.6 and mol. dis. 0.736, 0.739, and 0.862, are more in harmony with Diel's formula $\text{CO}:\text{C}:\text{CO}$, calculated values $M_D = 15.49$ and $\gamma - \alpha = 0.749$, than with Michael's (Abstr., 1906, ii, 442), for which the values $M_D = 13.57$ and $\gamma - \alpha = 0.435$ have been calculated.

The fact that the values actually obtained are somewhat higher than those calculated for Diel's formula points to an "exaltation" due to the numerous double bonds in the system $\text{O}:\text{C}:\text{O}:\text{C}:\text{O}$.

According to Brühl (*Trans.*, 1907, 91, 115), contiguous double bonds produce a measurable exaltation of the molecular refraction and dispersion, whereas compounds with "cumulative" double bonds are optically normal.

J. J. S.

Silicates. VII. EDUARD JORDIS (*Zeitsch. anorg. Chem.*, 1907, 56, 296—319. Compare Abstr., 1903, ii, 475, 542, 595; 1905, ii, 88, 248).—The preparation of crystalline sodium metasilicate is described, and some of the properties of aqueous solutions of alkali silicates are discussed.

In aqueous solution, sodium hydroxide retains silica in the proportion $2.5-2.7\text{SiO}_2 : 1\text{Na}_2\text{O}$. Fused sodium hydroxide dissolves more silicic acid than does the aqueous solution, so that the fused mass is partially decomposed by water. Concentrated solutions of sodium silicate gelatinise on cooling and become liquid again on warming.

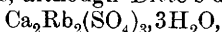
Crystallised sodium metasilicate, Na_2SiO_3 , with 6 and 10 H_2O , has been obtained by crystallisation from a solution containing 3 mols. of sodium hydroxide to 1 mol. of silica. It is purified by recrystallisation from *N*-sodium hydroxide, and washing with 50% alcohol. The metasilicate dissolves in water, forming a solution of definite and reproducible properties.

Attempts to prepare sodium orthosilicate, sodium hydrogen meta-

silicate, or potassium metasilicate in crystalline form in the wet way have so far proved unsuccessful.

Solutions of pure sodium silicate are not precipitated by ammonia or by electrolytes, but solutions of "water glass" yield precipitates under these conditions. The precipitate which separates from solutions of alkali silicates after a time consists mainly of impurities (aluminium and iron).
G. S.

Rubidium Calcium Sulphates. JOH. D'ANS and W. ZEH (*Ber.*, 1907, 40, 4912—4914. Compare Abstr., 1907, ii, 168).—A study of the double sulphates of rubidium and calcium has resulted in the isolation of two new salts, although Ditte's double salt,



could not be prepared (Abstr., 1877, i, 440).

Rubidium syngenite, $\text{CaRb}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, prepared by leaving finely-divided gypsum in contact with a 30% solution of rubidium sulphate, crystallises in strongly refracting needles, probably isomorphous with the potassium and ammonium syngenites. On boiling calcium sulphate with 30% aqueous rubidium sulphate, *rubidium dicalcium sulphate*, $\text{Ca}_2\text{Rb}_2(\text{SO}_4)_3$, is formed; its crystalline form is similar to that of the corresponding ammonium salt. The rubidium syngenite is converted into the dicalcium salt in contact with aqueous rubidium sulphate at 40°. Attempts to prepare the pentasulphate have, so far, been unsuccessful.

In the series potassium, ammonium, rubidium, the stability of the dicalcium salt increases, whilst that of the pentasulphate decreases.

W. R.

Action of Ammonium Persulphate on Metals. J. W. TURRENTINE (*J. Physical Chem.*, 1907, 11, 623—631).—When a strip of copper is immersed in ammonium persulphate solution, it loses in weight, and the loss in weight is very nearly the equivalent of the reduced persulphate. Copper, immersed in ammonium persulphate, behaves therefore like a copper anode in the electrolysis of sulphates. This analogy between chemical corrosion in ammonium persulphate and electrolytic corrosion in ammonium sulphate is borne out also by the behaviour of nickel, cadmium, and aluminium. In the case of nickel, the loss of weight is about 13% less than the equivalent of the reduced persulphate. Cadmium dissolves readily in ammonium persulphate without evolution of gas, but there is considerable discrepancy between the observed and calculated values for the loss of weight. Only slight corrosion of aluminium occurs in ammonium persulphate solution. Ammonium persulphate dissolves iron, forming ferrous sulphate, some of which is oxidised by the excess of the persulphate. It appears that the free acid formed by the hydrolysis of ferric sulphate acts as a catalytic agent in the reaction between iron and water. J. C. P.

Action of Silver Nitrate and of Mercuric Nitrate on some Inorganic Hydroxides. WILHELM BILTZ and FRIEDRICH ZIMMERMANN (*Ber.*, 1907, 40, 4979—4984).—When freshly-precipitated magnesium hydroxide is moistened with a solution of silver nitrate,

the hydrogel is coloured yellowish-brown, owing to the separation of silver oxide. The authors have studied the behaviour of other inorganic hydroxides towards both silver nitrate and mercuric nitrate. The various hydroxides were precipitated by ammonia from the hot solutions of their salts, washed until free from ammonia, and then saturated with *N*/10 silver nitrate. Glucinum, aluminium, indium, zirconium, stannic, antimony, and bismuth hydroxides respectively gave no reaction, zinc hydroxide was coloured faintly brown, cadmium hydroxide strongly brownish-yellow, and lead hydroxide somewhat violet-brown. With mercuric nitrate, the hydroxides of indium, zirconium, antimony, and bismuth gave no reaction, glucinum hydroxide was coloured yellowish-red, magnesium hydroxide strongly yellowish-red, zinc hydroxide faintly yellow, cadmium hydroxide strongly yellowish-red, aluminium hydroxide faintly yellow, lead hydroxide yellowish-red, and bismuth hydroxide brightly yellow. The behaviour of a number of hydroxides of rare elements was studied from the same standpoint.

A. McK.

Solubility of Calcium Carbonate in Aqueous Solutions of Potassium Chloride and Potassium Sulphate at 25°. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1907, 11, 577—580. Compare Abstr., 1902, ii, 320).—Calcium carbonate is much more soluble in aqueous solutions of potassium sulphate than in aqueous solutions of potassium chloride. The solubility curve for calcium carbonate in the chloride solutions passes through a maximum. When calcium carbonate is kept in contact with potassium sulphate solutions containing more than 2.98% K_2SO_4 , syngenite is formed.

J. C. P.

Soluble Basic Sulphates of Glucinum. CHARLES L. PARSONS, WILLIAM O. ROBINSON, and C. T. FULLER (*J. Physical Chem.*, 1907, 11, 651—658).—A solution of glucinum sulphate dissolves fairly large quantities of glucinum hydroxide, and the solutions obtained in this way have been examined by the authors. It is shown that the addition of glucinum hydroxide to a solution of glucinum sulphate raises the freezing point of the latter and lowers its conductivity. The solutions obtained are not true colloids, as shown by dialysis experiments, nor does the glucinum enter into a complex anion. It is suggested that the dissolved glucinum salt acts as a solvent for the hydroxide, just as acetic acid dissolved in water will dissolve camphor, which is itself insoluble in water.

J. C. P.

Alloys of Zinc and Nickel. VICTOR TAFEL (*Metallurgie*, 1907, 4, 781—785).—Alloys containing up to 50% of nickel were prepared by adding nickel to molten zinc covered with a layer of borax. The freezing-point curve has a eutectic point very close to the zinc end, the eutectic temperature being only 0.5° below the melting point of zinc. Eight different crystalline constituents were observed. I is pure zinc; the series of mixed crystals II contain from 12.2% to 23% of nickel; III is the compound $NiZn_3$, indicated by a maximum on the

freezing-point curve; the mixed crystals IV contain from 39.7% to 45.8% of nickel, and break up on cooling to 640° into the crystals V and VI. Crystals VII separate from the molten mass, but then react with it at 1025—1037° to form IV. The mixed crystals VIII are formed when alloys containing more than 45.8% of nickel are cooled to 780°. The exact nature of the crystals, with the exception of the compound NiZn_3 , could not be determined.

The brittleness of zinc is greatly increased by the addition of nickel; NiZn_3 is extremely brittle, and gives a characteristic blue coloration with dilute nitric acid. Photo-micrographs of the alloys are given.

C. H. D.

New Kind of Dioxides. I. LUIGI MARINO (*Zeitsch. anorg. Chem.*, 1907, 56, 233—245).—It is shown that the dioxides of manganese, lead, and barium react quite differently towards sulphur dioxide, and it is therefore suggested that the constitution of the three dioxides must be different.

Pure manganese dioxide was suspended in water, and sulphur dioxide passed in at 10—12° until a clear solution was obtained. Analysis showed that the solution thus obtained contained manganese dithionate and a little sulphate; the main reaction is therefore represented by the equation $\text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_6$. At the same time, the "induced" reaction $\text{MnS}_2\text{O}_6 + \text{MnO}_2 = 2\text{MnSO}_4$ takes place to a slight extent.

By the action of sulphur dioxide on lead peroxide, on the other hand, a heavy, white powder consisting of a mixture of lead sulphate and sulphite was obtained, and not a trace of dithionate was formed. Evidence is adduced to show that the successive stages of the reaction are as follows: $\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_3 + \text{O}$; $\text{SO}_2 + \text{O} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$; $\text{PbSO}_3 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + \text{H}_2\text{SO}_3$.

When barium peroxide is used, the first stage of the reaction is represented by the equation $\text{BaO}_2 + \text{H}_2\text{SO}_3 = \text{BaSO}_3 + \text{H}_2\text{O}_2$, the hydrogen peroxide then oxidising the sulphur dioxide and barium sulphite to sulphuric acid and barium sulphate respectively.

Selenious acid also behaves differently towards the peroxides of lead and manganese; the results of the investigation will be communicated later.

The difference in behaviour of the dioxides in question is ascribed to a difference of constitution, which for those of manganese and lead may be represented by the constitutional formulæ $\text{Mn} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ and

$\text{Pb} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$. As the sesquioxides of iron and cobalt give, like manganese dioxide, additive compounds with sulphur dioxide (Seubert and Elten, Abstr., 1893, ii, 278), they may also contain a group of the type $\text{M} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$;

the formula for ferric oxide would therefore be $\text{O}:\text{Fe}:\text{Fe} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$.

The constitutional formula of dithionic acid is also discussed.

G. S.

Action of Oxygen on Copper, Tin, Zinc, and the Alloys of Tin and Zinc with Copper. EDUARD JORDIS [with W. ROSENHAUPT] (*Chem. Zeit.*, 1908, 32, 19—21. Compare Jordis, this vol., ii, 98).—The rate of absorption of dry, and of moist, oxygen by copper, tin, zinc, and alloys of tin and zinc with copper has been determined at various temperatures and the results expressed in curves. The reaction commences with copper at about 80° , with tin above 100° , and with zinc at 150° ; at temperatures below 200° , the dry oxygen is absorbed slightly the more rapidly by copper and tin, the moist oxygen by zinc, but above 200° , whilst the relation between the rates of absorption by tin remains approximately unchanged, the moist oxygen is absorbed much more rapidly than the dry gas by copper and zinc. An alloy containing 70% of copper and 30% of tin acts as a mixture of the compound Cu_3Sn with an excess of copper, and the alloys of copper and zinc as mixtures of Cu_2Zn with an excess of copper or of zinc. The absorption curves of the alloys resemble to some extent those of the metal present in excess. The discussion of the results leads to the conclusion that the oxidation of these metals and alloys is not a simple process, but consists of several simultaneous reactions, one of which must be a diffusion of the oxygen in the metallic state through the metal or alloy. G. Y.

Action of Lime in Excess on Copper Sulphate Solutions. JAMES M. BELL and WALTER C. TABER (*J. Physical Chem.*, 1907, 11, 632—636).—The authors have determined the composition of the solution and of the precipitates obtained when lime and copper sulphate solutions are mixed in different proportions and concentrations. The results are summarised in the following table:

Gram per litre.		Solid phases.
CaO.	SO ₃ .	
1.206	0.0	$\text{Ca}(\text{OH})_2$, blue copper hydroxide.
1.780	0.872	$\text{Ca}(\text{OH})_2$, blue copper hydroxide.
1.908	1.060	$\text{Ca}(\text{OH})_2, \text{CaSO}_4, 2\text{H}_2\text{O}$, blue copper hydroxide.
1.888	1.052	$\text{CaSO}_4, 2\text{H}_2\text{O}$, blue copper hydroxide.
1.358	1.112	$\text{CaSO}_4, 2\text{H}_2\text{O}$, blue copper hydroxide.
1.120	1.144	$\text{CaSO}_4, 2\text{H}_2\text{O}$, green copper hydroxide.
0.880	1.280	$\text{CaSO}_4, 2\text{H}_2\text{O}$, green copper hydroxide.

In the preparation of Bordeaux mixture, a very large excess of lime is added, and the precipitate will consist of the three solids, lime, gypsum, and the blue copper hydroxide. J. C. P.

Solubility of Gypsum in Copper Sulphate Solutions. JAMES M. BELL and WALTER C. TABER (*J. Physical Chem.*, 1907, 11, 637—638).—The solubility of gypsum at first diminishes as the concentration of copper sulphate increases, until at a copper sulphate concentration of 30 grams per litre the solubility of gypsum reaches a minimum of 1.7 grams CaSO_4 per litre. Further increase in the copper sulphate concentration causes a rise in the solubility

(at first rapid and then slow), and a solution which is saturated with copper sulphate dissolves gypsum to the extent of 2.08 grams per litre.

J. C. P.

The Nature of the Phosphorescent Elements and Meta-elements of Sir W. Crookes. GEORGES URBAIN (*Compt. rend.*, 1907, 145, 1335—1337).—The phosphorescent spectra afforded by mixtures in varying proportions of the anhydrous sulphates of pure gadolinium and terbium contain the bands which were attributed by Sir W. Crookes to the elements or meta-elements G_a , G_z , G_b , ionium, and incognitum (Abstr., 1887, 334; 1906, ii, 62). The intensity of the bands varies with the composition of the mixture, and the mixtures containing less than 0.5% or more than 10% of terbium are very slightly phosphorescent. The author concludes that in these mixtures the terbium, which is the active phosphorescent substance, is not a mixture of several elements.

M. A. W.

Bayer's Bauxium. G. GRINER and GEORGES URBAIN (*Bull. Soc. chim.*, 1907, [iv], 1, 1158—1163).—In manufacturing alumina from the red bauxite of Var, the sodium aluminate obtained by roasting the mineral with sodium carbonate is decomposed by a current of carbon dioxide, and the sodium carbonate is recovered from the filtrate by evaporation. The mother liquors from the last process contain chromic, vanadic, molybdic, tungstic, phosphoric, arsenic, and silicic acids with small quantities of alumina, magnesia, lime, &c., and after the removal of these various constituents Bayer obtained (Abstr., 1895, ii, 313) a violet-coloured solution, which on exposure to air became yellow and gave other reactions which led him to suppose that it contained a new element "bauxium."

This material has now been examined spectrographically by the authors, and they find that it consists essentially of a mixture of vanadium and tungsten containing a trace of molybdenum and minute traces of copper, bismuth, lead, calcium, and sodium, and that a dilute solution of ammonium vanadate containing a small quantity of ammonium tungstate gives all the reactions which Bayer thought to be characteristic of bauxium.

Bayer's misapprehension of the nature of the solution he obtained appears to have been due to his supposition that vanadium can be completely removed from solution as ammonium vanadate and tungsten as tungstic acid, which it appears now is not the case.

A detailed description of the spectrographic method employed by the authors is given in the original.

T. A. H.

Gases Occluded in Steels. G. BELLOC (*Compt. rend.*, 1907, 145, 1280—1283. Compare Abstr., 1903, ii, 484).—The work described refers to (1) the nature of the gases; (2) the form of the curves in t and dv/dt relatively to the total volume and to the volume of each gas; (3) the relative proportions of each gas at different temperatures; (4) the relations of these curves to the critical points; (5) variation of the gases according to the thickness of the section of metal from which they are derived, and (6) their alteration with different steels. Two bars of a very soft steel containing 0.12% of carbon, 0.03% of silicon, 0.02% of

sulphur, 0.018% of phosphorus, and 0.35% of molybdenum, chosen so that its critical points are well separated, were examined. Their critical points were carefully determined by Roberts-Austen's differential method. The evolution of gases is in intimate relation with the critical points of the iron, and may be divided into three stages. (1) The evolution begins at a variable and ill-defined temperature (150° — 400°); the dv/dt curve has a small minimum at 200° and a small maximum at 300° , but the evolution is small below the point A_0 . (2) Between 500° and 600° the dv/dt curve exhibits a large maximum at the point A_1 , and then falls rapidly to a minimum (approaching zero) at the end of A_2 . The point A_1 has no well-defined influence in the steel considered. (3) The evolution increases again at the beginning of A_3 , then diminishes slowly, and seems to increase afresh with the temperature. Adopting Osmond's definition of the point A_0 , these stages can be interpreted thus: (1) In the region of the α -iron, the evolution of gas is very small, and apart from small irregularities tends to increase with the temperature. (2) The commencement of the conversion of α -iron into β -iron is characterised by an abundant evolution which diminishes as the conversion progresses. The transformation of the cementation carbon into "temper" carbon to the extent of 0.12% has no marked influence. (3) The evolution recommences with the transformation of the β -iron into γ -iron, and after passing through a maximum seems to increase with the temperature in the region of the γ -iron.

The gases evolved consist of carbon monoxide and dioxide, hydrogen and nitrogen. The first produced is carbon dioxide, which at the beginning forms almost the total volume. It disappears at about 550° (A_0). Nitrogen begins to appear at about 550° , and persists at all higher temperatures, but the amount is small, not rising above a mean value of 10%. Above 400° , hydrogen and carbon monoxide alone are evolved, but their proportions are subject to sudden alteration with the temperature. A larger volume of gas was evolved, and the evolution commenced sooner from the first bar than from the second, probably owing to initial loss of gas from the latter by its finer subdivision. The gases are very irregularly distributed in the steel, the proportion in the intermediate layers being much greater than in the superficial and central portions. As regards the state of the gas in the metal, observations made are not in favour of the existence of a dissociation-tension.

E. H.

Extraction of Gases Contained in Metals. OCTAVE BOUDOUARD (*Compt. rend.*, 1907, 145, 1283—1284).—The author has heated in a vacuum, commercial iron in the form of bars 1 square cm. in cross-section, sheet 1 mm. thick, wire 2 mm., 1 mm., and 0.5 mm. in diameter, and of filings. Wire 1 mm. thick when heated at the temperature of boiling sulphur (445°) does not evolve gas, but under the same conditions 31.5 grams of filings evolve 6.45 c.c. of gas, chiefly carbon monoxide and hydrogen. The results of heating the iron in its various forms at 1100° in a vacuum three times, allowing fifteen days' exposure to the air between the consecutive ignitions, are given in tabular form. They show that it is extremely difficult to extract the

gases contained in iron and steel. The metal after a third ignition at 1100° retains an appreciable volume of gas, varying according to its state of division (from 0.5% of total volume extracted in the case of filings to 20% with sheet- or bar-iron). A table is given containing the total percentage volumes and weights of carbon monoxide, hydrogen, carbon dioxide, and nitrogen expelled by three ignitions at 1100° of wire 0.5 and 1 mm. thick, sheet 1 mm. thick, and filings. The total percentage weights of gas evolved are 0.0957%, 0.1029%, 0.099%, and 0.2207% respectively, these quantities being of the same order as the amounts of sulphur and phosphorus ordinarily present.

The values obtained for nitrogen are of the same order as those observed by Braune (Abstr., 1905, ii, 638; *Rev. de Métallurgie*, 1907, 2, 834). In a vacuum, iron begins to volatilise at 900° , and does so very appreciably at 1100° .
E. H.

Solubility of Graphite in Iron. GEORGES CHARPY (*Compt. rend.*, 1907, 145, 1277—1279. Compare Abstr., 1902, ii, 209).—The determination of the solubility of graphite in iron is rendered very difficult by the exceeding slowness of the dissolution of graphite, or the conversion of the combined carbon into graphite, which necessitates prolonged heating, involving either carburisation or decarburisation of the surface according to the conditions.

An ingot of grey cast-iron, containing 3.75% total carbon (3.34% graphite), about 0.1% silicon and manganese, and traces of sulphur and phosphorus, was obtained by melting in a crucible some Swedish iron cemented with excess of wood-charcoal, and allowing it to cool slowly. Cubes of this iron (4 cm. edge) were heated for three to seven hours at temperatures varying from 750 — 1150° , quenched in water, and then annealed at 500° . After planing off a thickness of 2 mm. from the faces, the combined carbon was determined in the remaining cubes. It is found to increase from 0.31% at 750° to 2.47% at 1150° .

A white cast-iron containing 2.82% total carbon (all combined), obtained by running the fused metal into a metallic mould, when heated at 1150° , cooled slowly to 1000° , and then quenched in cold water gives an ingot of which the central portion contains 2.74% total carbon, 1.82% graphite, and 0.92% combined carbon.

When the crucible, prepared as above, containing the liquid iron is placed in a furnace, maintained at 1000° for three hours, and then plunged in cold water, an ingot is formed containing 3.10% total carbon, 2.15% graphite, and 0.95% dissolved carbon.

By the cementation of iron at 1000° (compare Abstr., 1903, ii, 430) with wood-charcoal, two irons were obtained containing (1) 2.50% carbon, of which 1.40% was graphite, and 1.10% dissolved carbon; (2) 3.10% carbon, 2.21% graphite, and 0.89% dissolved carbon.

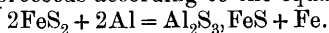
The conclusion is drawn that the solubility of graphite in iron diminishes with the temperature, and amounts to about 1% at 1000° .

E. H.

Chemical Behaviour of High Percentage Ferro-silicon. JOHANNES HAAS (*Chem. Zeit.*, 1908, 32, 8).—A 50% ferro-silicon dissolves in a concentrated solution of copper ammonium fluoride,

metallic copper separating as a flocculent, spongy precipitate. The reaction, which takes place spontaneously, is accompanied by a violent evolution of gas, hydrogen silicofluoride probably being formed. Silicic acid is not formed, and the evolution of hydrocarbons has not been observed. The copper ammonium fluoride solution is almost without action on 80% ferro-manganese. G. Y.

Decomposition of Iron Sulphides by Aluminium, and the Probable Existence of a Double Sulphide of Iron and Aluminium. HUGO DITZ (*Metallurgie*, 1907, 4, 786—792).—Sulphides are less energetically reduced by ignition with aluminium powder than oxides. A mixture of iron pyrites and aluminium in the proportion $3\text{FeS}_2:4\text{Al}$ yields less than one-half of its iron in the metallic form. In presence of an excess of aluminium, one-half of the iron is obtained. The copper present in the pyrites is only reduced when an excess of aluminium is employed. The slag appears to contain a double sulphide, $\text{Al}_2\text{S}_3\cdot\text{FeS}$, which has also been obtained by Houdard (Abstr., 1907, ii, 468) from ferrous sulphide and aluminium. The reduction thus proceeds according to the equation



When ferrous sulphide is reduced, the same double sulphide is formed, according to the equation $4\text{FeS} + 2\text{Al} = \text{Al}_2\text{S}_3\cdot\text{FeS} + 3\text{Fe}$.

C. H. D.

Roussin's Salts. V. ITALO BELLUCCI and P. DE CESARIS (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 740—745. Compare Abstr., 1907, ii, 29, 472).—On oxidation of potassium ferronitrosulphide with permanganate, each molecule of the former absorbs 26 atoms of oxygen, this being the amount necessary theoretically for the oxidation of all the elements to the highest grade. This result excludes all possibility of the presence of hydrogen in the molecule of Roussin's salts. Further, taken along with the complete resistance of these salts to the action of the most energetic reducing agents, this oxidisability indicates that most, if not all, of the iron atoms in the molecule are present in the ferrous condition. Comparison of the behaviour towards hydrochloric acid of potassium ferronitrosulphide with that of the complex sulphides, $\text{Fe}_2\text{S}_3\cdot\text{K}_2\text{S}$ and $2\text{FeS}\cdot\text{K}_2\text{S}$, shows that the three sulphur atoms in the molecule of Roussin's salts exist in the form of sulphide and are probably combined with the iron.

T. H. P.

Hydrolysis of Ferric Chloride. II. Action of Hydrochloric Acid. G. MALFITANO and LEOPOLD MICHEL (*Compt. rend.*, 1907, 145, 1275—1277. Compare Abstr., 1907, ii, 692).—The authors have compared the rates of change of the conductivity of ferric chloride solutions with that of the conductivity of solutions containing the same quantities of ferric chloride and varying quantities of hydrogen chloride. The results obtained are illustrated by curves. The latter show that the duration of the period of constant conductivity increases with the amount of hydrogen chloride added, and, other things being equal, the quantity of hydrogen chloride required to render the solution

stable increases considerably with the temperature and varies slightly with the concentration of the ferric chloride. The remarkable phenomenon is observed, that during the hydrolysis of a ferric chloride solution, a considerably larger quantity of hydrogen chloride can be formed than would have rendered the solution stable if added at first, the conductivity of hydrolysed solutions rising to values greater than those of solutions initially treated with hydrochloric acid. Moreover, small additions of acid only retard hydrolysis at the beginning, afterwards appearing to accelerate it. Measurements of the conductivities of $M/10$ solutions of ferric chloride alone and with varying quantities of hydrogen chloride ($M/30$ to $M/10$) (1) immediately after dissolution, (2) after thirty minutes' heating at 100° , and then (3) forty-six hours later show that the increase in conductivity on heating and its decrease subsequently, diminish as the quantity of acid added increases. The conclusion is drawn that the products of hydrolysis are not constant in composition, only those first formed being easily reconverted into FeCl_3 by the hydrochloric acid present, the action of the acid becoming more and more difficult as the hydrolysis progresses, and, further, that the products of hydrolysis are rendered more resistant by the presence of hydrogen chloride. To justify these conclusions, curves are given showing that the amount of hydrochloric acid which, added at the beginning, renders the solution stable, when added during hydrolysis, not only does not restore the solution to its original condition, but does not stop the hydrolysis.

These phenomena appear to be best explained by the hypothesis that the colloid formed from the products of hydrolysis is composed of complex ions.
E. H.

Ferric Chlorides. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1907, 11, 690—694).—The investigation deals with the cases in which there is relatively more ferric oxide than acid. It appears that at 25° no definite basic chloride is formed, the stable solid phase being one of a series of solid solutions containing ferric oxide, hydrochloric acid, and water.
J. C. P.

Ferric Sulphates. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1907, 11, 641—650).—Ferric sulphate solutions of varying concentration were shaken with freshly-precipitated ferric hydroxide at 25° for four months. At the end of this time, the clear solutions were separated and analysed. It is shown that no definite basic ferric sulphates are formed. In contact with solutions containing less than 25% SO_3 , the stable solid is one of a series of solid solutions, containing ferric oxide, sulphuric acid, and probably water. In contact with solutions containing from 25% to 28% SO_3 , the stable solid is a hydrated normal sulphate of the composition $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 10\text{H}_2\text{O}$. In contact with solutions containing more than 28% SO_3 , the stable solid is a hydrated acid sulphate of the composition $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 10\text{H}_2\text{O}$.
J. C. P.

A New Chromium Sulphate. PAUL NICOLARDOT (*Compt. rend.*, 1907, 145, 1338—1340).—When the green solution obtained by

boiling a solution of violet chromium sulphate is heated with barium carbonate, part of the sulphuric acid is precipitated, and on complete spontaneous evaporation of the filtrate a new *chromium sulphate*, $\text{Cr}_2\text{O}_3 \cdot 2 \cdot 5\text{SO}_3 \cdot 7 \cdot 5\text{H}_2\text{O}$, is obtained as a non-crystalline solid, readily soluble in water to form a green solution, but insoluble in alcohol or acetone, and precipitated from aqueous solution by these liquids. Solutions of the salt do not yield precipitates with barium chloride or with sodium phosphate; it differs in this respect from the sulphate of sulphochromyl hydroxide described, but not isolated, by Recoura (Abstr., 1896, ii, 27), and resembles the sulphate, $(\text{Cr}_2\text{O}_3(\text{SO}_3)_3 \cdot 8\text{H}_2\text{O})$, obtained by Recoura by dehydrating the solid violet chromium sulphate.

M. A. W.

Chromates. SAMUEL H. C. BRIGGS (*Zeitsch. anorg. Chem.*, 1907, 56, 246—260. Compare Trans., 1903, 83, 391; 1904, 85, 677).—The preparation and properties of certain chromates, dichromates, and double chromates are described.

Nickel dichromate, $2\text{NiCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, obtained by heating together nickel carbonate and chromic acid in aqueous solution at a high temperature, occurs in reddish-brown, transparent prisms, which are deliquescent. The corresponding *cobalt* salt, $\text{CoCr}_2\text{O}_7 \cdot \text{H}_2\text{O}$, prepared by an analogous method, forms black, lustrous, deliquescent crystals.

Ammonium cobalt chromate, $(\text{NH}_4)_2\text{Co}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, obtained by interaction of ammonium chromate and cobalt acetate in aqueous solution below -5° , occurs in well-formed, brownish-yellow prisms. The corresponding *cæsium* compound, prepared by an analogous method, was not obtained quite free from basic salt; it forms small, lustrous crystals.

The normal chromates of copper, zinc, and cadmium have already been isolated from aqueous solution and described by Schulze (Abstr., 1896, ii, 24); exact methods for preparing them are now given. Attempts to obtain normal chromates of these metals, analogous in behaviour to the corresponding sulphates, by interaction in non-aqueous solvents were unsuccessful.

A large number of compounds of pyridine with dichromates have been prepared; in most cases by interaction in aqueous pyridine solution of chromic acid or potassium dichromate and a salt of the particular metal. The compounds in question are fairly stable, nearly insoluble in water, and insoluble in the ordinary organic solvents. The majority of them are of the type $\text{M}''\text{Cr}_2\text{O}_7 \cdot 4\text{Py}$. The *copper* compound, $\text{CuCr}_2\text{O}_7 \cdot 4\text{Py}$, occurs in small, light green crystals or in well-formed, dark green prisms; the *zinc* compound in lustrous, orange prisms; the *cadmium* compound in orange crystals, and the *cobalt* compound as a dark brown powder. Corresponding *nickel* and *manganese* compounds were also prepared.

A *silver* compound, $\text{Ag}_2\text{Cr}_2\text{O}_7 \cdot 6\text{Py}$, was obtained in lustrous, orange crystals. On dissolving this compound in water containing a little pyridine, and cooling, a second silver compound, $\text{Ag}_2\text{Cr}_2\text{O}_7 \cdot 4\text{Py}$, separated in orange prisms.

Two *mercury* salts of the same composition, $\text{HgCr}_2\text{O}_7 \cdot 2\text{Py}$, are described. One, obtained from solutions containing little pyridine.

forms orange crystals, the other, which crystallises from excess of pyridine, occurs in lustrous, golden-yellow leaflets.

A *uranium* compound, $2\text{UO}_3 \cdot 3\text{CrO}_3 \cdot 2\text{Py}$, also forms lustrous, orange-coloured crystals. The pyridine double salts of zinc, cadmium, and mercury darken on exposure to light. G. S.

Potassium Ammonio-stannate. F. F. FITZGERALD (*J. Amer. Chem. Soc.*, 1907, 29, 1693—1698).—In an earlier paper (Abstr., 1907, ii, 545), an account was given of the preparation of potassium ammonio-zincate by the action of zinc on a solution of potassamide in liquid ammonia. Attempts have been made to prepare other salts of this class.

When excess of a solution of potassamide in liquid ammonia is added to a solution of stannic iodide in the same solvent, a crystalline precipitate of *potassium ammonio-stannate*, $\text{Sn}(\text{NK})_2 \cdot 4\text{NH}_3$, is produced, which, when heated at 145° , loses 3 mols. of ammonia. On further heating in a vacuum at 316° , a brick-red powder is obtained, which still contains some ammonia and is decomposed violently by water with evolution of gas and deposition of tin. E. G.

Columbium Sulphide. I. HEINRICH BILTZ and LUDWIG GONDER (*Ber.*, 1907, 40, 4963—4972).—For the preparation of columbium pentoxide, a by-product from the manufacture of tantalum compounds was used, containing 46 per cent. of columbium pentoxide, 36 per cent. of sodium oxide, 10 per cent. of iron oxide, traces of tungstic acid, a little tantalum oxide, and several per cent. of water. In order to remove iron, sodium, and tungsten, the product was fused with potassium hydrogen sulphate, water added, the columbic acid filtered off, and then boiled with a little concentrated hydrochloric acid and washed with dilute hydrochloric acid; the fusion was then repeated in order to remove the last traces of iron. The columbic acid was then separated from traces of tantalum according to Marignac's method; it was dissolved in pure hydrogen fluoride, potassium carbonate added, diluted with water, and allowed to crystallise, when a little potassium tantalum fluoride separated; on further concentration, potassium columbium hydroxyfluoride separated. The latter was then heated with concentrated sulphuric acid, fused with potassium hydrogen sulphate, boiled with water, and washed by decantation with dilute hydrochloric acid. The columbic acid, obtained in this manner, was still contaminated with a little sulphuric acid, retained by adsorption. The product was accordingly heated for several hours in a combustion tube, first in a current of ammonia, and finally in a current of oxygen.

The pure columbium oxide was then heated to redness for several hours in a current of a mixture of hydrogen sulphide and carbon disulphide, the product extracted with carbon disulphide, and finally dried over sulphuric acid. It is likely that columbium sulphide has not yet been obtained pure. The authors conclude that their preparations are mixtures of a columbium sulphide, CbS_2 or Cb_2S_5 , either with columbium or with a lower sulphide. A. McK.

Mineralogical Chemistry.

Oil from the Roof of the Cockshead Coal Seam, North Staffordshire. ARCHIBALD A. HALL (*J. Soc. Chem. Ind.*, 1907, 26, 1223—1224).—The dark brown oil, which deposits crystals at 18° and is solid at 15°, was found on investigation to be a mixture of the higher paraffins with some olefines and possibly some naphthenes and phenolic substances.

W. H. G.

Optical Investigation of the Bibieibat Naphtha. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1343—1358. Compare Abstr., 1907, ii, 883).—Of forty-seven naphthas examined, those from the uppermost layers are of maximum transparency, and, with but a few exceptions, of lowest sp. gr. The curve expressing the relation between the depth at which the naphtha is obtained and the corresponding coefficients of optical opacity approximates to a straight line; there is thus a genetic connexion between the various naphthas, and they are all filtration products of one original naphtha, but, since this process could not have occurred everywhere at the same speed, the naphthas obtained from various parts of the globe are not identical in properties. The relation between the pressure within the earth and that of the outer layers, as well as of the duration of filtration and the nature of the naphtha produced, is discussed. When the outer pressure exceeds the inner, no filtration can occur, but the naphtha becomes compressed, forming condensed products, such as asphalt (compare Marcussen, Abstr., 1907, i, 466). All the Bibieibat naphthas are normal, are not decomposed, and do not undergo racemisation when distilled at 250°/20 mm.

Z. K.

Paraffin Wax from the Ladysmith Pit, Whitehaven Collieries. PETER P. BEDSON (*J. Soc. Chem. Ind.*, 1907, 26, 1224—1225).—An investigation of a substance which was discovered as an exudation in a drift of the Ladysmith Pit of the Whitehaven Collieries. It is a dark brown material, having the consistency of vaseline, and consists of a mixture of paraffin hydrocarbons, containing a considerable proportion of the solid members of this series, with some olefines.

W. H. G.

American Pyrites Crystals. EDWARD H. KRAUS and I. D. SCOTT (*Zeitsch. Kryst. Min.*, 1907, 44, 144—153).—The following analyses are given of pyrites crystals from: I, Central City Mine, Gilpin Co., Colorado; II, a limestone quarry at Franklin Furnace, New Jersey; III, an unknown locality in Colorado:

	S.	Fe.	Co.	Ca.	Insol.	Total.
I.*	53·26	46·51	—	—	0·59	100·37
II.	53·30	45·20	1·25	trace	0·03	99·78
III.	53·08	46·35	—	—	0·53	99·96

* Ni, Co, As, Sb, and Au are absent.

Detailed crystallographic descriptions are given.

L. J. S.

Artificial Hæmatite Crystals. CHARLES E. MUNROE (*Amer. J. Sci.*, 1907, [iv], 24, 485—486).—Brilliant crystals of hæmatite were found attached to the inside surfaces of iron pipes which for seven years had conducted alternately hydrogen chloride and air in a plant for the manufacture of chlorine by the Deacon process. The well-developed crystals are grouped in rosettes, like the "iron-roses" of the Alps. In a six-inch pipe, the crystals measured 1 cm. across, and in a twenty-inch pipe they were 3 cm. across. L. J. S.

Olivine in Serpentine from Chester, Massachusetts. CHARLES PALACHE (*Amer. J. Sci.*, 1907, [iv], 24, 491—495).—A narrow vein, two inches or less in width, of olivine occurs in serpentine at Chester, in Massachusetts. The olivine has the form of grains or of rough crystals, and is associated with picrolite, chrysotile, brucite, and magnetite. The following analysis by W. T. Schaller shows that the material, although apparently pure, must be intermixed with magnesite, brucite, and serpentine :

SiO ₂ .	FeO.	MgO.	MnO.	CaO.	F.	H ₂ O at 100°.	H ₂ O >100°.	CO ₂ .	Total.
39.43	7.83	49.26	0.12	nil		1.20	1.49	0.77	100.10

The vein of olivine is very sharply defined from the surrounding serpentine, and is evidently a younger formation, representing a regeneration of olivine in the rock-mass. The serpentine pseudomorphs after olivine from this locality have been called "hampshireite," and recently the opinion has been expressed, but without sufficient grounds, that the original mineral was humite. L. J. S.

Albite from Greenland. C. DREYER and VICTOR GOLDSCHMIDT (*Meddelelser om Grønland*, 1907, 34, 1—60).—Measurements of well-developed, water-clear crystals of albite from South Greenland give the following crystallographic constants: $a:b:c = 0.6373:1:0.5599$; $\alpha = 94^\circ 18'$; $\beta = 116^\circ 41'$; $\gamma = 87^\circ 37'$. As shown by the following analyses by C. Winther, the material is pure albite: I, of material from Kangerdluarsuk; II, from Narsarsuk :

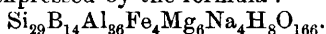
	SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Total.
I.	68.80	19.43	nil	nil	11.86	100.09
II.	68.80	19.40	0.20	,,	11.68	100.08

L. J. S.

Tourmaline from Asinara (Sardinia). AURELIO SERRA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 702—704).—Large, uniformly tinted, black crystals of tourmaline, D 3.08, found in pegmatitic rock at Asinara, gave on analysis :

SiO ₂ .	B ₂ O ₃ .	Al ₂ O ₃ .	FeO.	TiO ₂ .	P ₂ O ₅ .	MnO.	CaO.	MgO.
35.43	9.72	37.29	5.65	0.56	trace	0.89	1.10	4.60
Na ₂ O.	K ₂ O.	H ₂ O at 100°.	H ₂ O at red heat.	F.	Total.			
2.27	0.64	--	1.50	0.12	99.77			

The numbers are expressed by the formula :



T. H. P.

Physiological Chemistry.

Effect of Hirudin on Blood-Gases. JOSEPH BARCROFT and G. R. MINES (*J. Physiol.*, 1907, 36, 275—282).—In work on blood-gases, the principle of leech extract, called hirudin, is a valuable preparation. It may either be injected, or the blood may be received into a suitable syringe containing a small quantity of hirudin solution. If the injection is made slowly, no untoward results follow, and no disturbance of the normal blood-gases is produced. W. D. H.

Sugar in Blood. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1908, 7, 329—337).—The removal of protein by the adsorptive action of kaolin renders the estimation of sugar in the filtrate quite accurate in artificial mixtures containing serum to which a known amount of sugar is added. Colloidal iron hydroxide, although in distinction from kaolin an electropositive colloid, acts similarly. The free sugar of the blood-serum or plasma can therefore be estimated, and the figures obtained by the kaolin method from plasma show the presence of from 92 to 172 mg. of sugar per 100 c.c. Glycogen is also adsorbed and removed by kaolin. In fresh plasma, the yield of sugar after treatment with iron hydroxide is always less than after treatment with kaolin; it is therefore suggested that some of the sugar in the blood is combined with an electronegative colloid. W. D. H.

Proteoses in Blood. ERNST FREUND (*Biochem. Zeitsch.*, 1908, 7, 361—368).—Abderhalden has stated that even during the height of digestion the blood is free from proteoses. The present paper is largely polemical, and re-affirms the author's previous position on the presence of these substances in the blood. Abderhalden's method is criticised. W. D. H.

Proteins of Horse-Serum. JOHN MELLANBY. (*J. Physiol.*, 1907, 36, 288—333. Compare Abstr., 1907, ii, 631).—The usual methods of salt precipitation are not regarded as trustworthy for the separation of classes of proteins in serum. Alcohol shows a definite critical temperature for the precipitation of these proteins. The main conclusion drawn is that there are three main proteins present: globulin about 3% of the total, albumin- α about 85%, and albumin- β about 12%; the last named is the crystallisable albumin. W. D. H.

Leucoprotease and Anti-Leucoprotease of Mammals and Birds. EUGENE L. OPIE and BERTHA L. BARKER (*J. Exper. Med.*, 1907, 9, 207—221).—The inhibiting action of the blood-serum on the enzyme of the polynuclear leucocytes (leucoprotease) is exerted by the albumin fraction of the serum; the albumin fraction contains no proteolytic enzymes. The globulin fraction contains no anti-enzyme for leucoprotease; it contains, on the contrary, an enzyme which digests

proteins in a neutral or alkaline medium. This, which resembles leucoprotease, is held in check by its anti-enzyme which is present in great excess. The anti-enzymotic activity of the serum of different animals varies considerably, that of the rabbit, for instance, being stronger than dog's serum when tested either with dog's or with rabbit's leucoprotease. The serum of birds (pigeon and hen) almost completely fails to inhibit mammalian leucoprotease. The absence of the anti-enzyme is associated with an absence of leucoprotease in polynuclear leucocytes, bone-marrow, and spleen.

W. D. H.

Electrical Charge of Native Proteins and Agglutinins. CYRUS W. FIELD and OSCAR TEAGUE (*J. Exper. Med.*, 1907, 9, 222—225).—Tetanolysin and anti-tetanolysin travel towards the cathode under the influence of an electric current; the specific agglutinins are also electropositive; the protein matter of serum is not amphoteric, but travels towards the cathode whether the reaction is acid, neutral, or alkaline. Hardy's contrary results are attributed to the fact that he worked with "denaturalised" protein. The bacteria-agglutinin combination may be dissociated by means of the electric current.

W. D. H.

Oxygen Supply and Saliva. ANTON J. CARLSON and F. C. McLEAN (*Amer. J. Physiol.*, 1908, 20, 457—469. Compare Abstr., 1907, ii, 891).—Further experiments confirming previous results are given. Stimulation of the cervical sympathetic does not increase the percentage of organic solids in the subsequent saliva obtained by stimulation of cranial secretory nerves or by the injection of pilocarpine. Heidenhain's statement to the contrary was due to imperfect technique. This is considered to dispose finally of Heidenhain's theory of trophic secretory nerves.

W. D. H.

Causes of Rise in Electrical Conductivity under the Influence of Trypsin. WILLIAM M. BAYLLIS (*J. Physiol.*, 1907, 36, 221—252).—Fall of viscosity and liberation of adsorbed electrolytes from proteins will explain only a small fraction of the increase of electrical conductivity produced by tryptic action. The main cause is the production of "peptones" and amino-acids, and especially of dicarboxylic acids and hexone bases. Amino-acids are more soluble in solutions of other amino-acids than in water, but no evidence of salt formation was obtained. The formation of free carbaminoglycine and carbaminoalanine (Siegfried) is confirmed; carbaminoleucine is also present.

W. D. H.

The Relationship of Dysoxidisable Carbon and Nitrogen on Different Diets. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1908, 11, 144—145).—On a protein diet, the carbon nitrogen (C:N) ratio of the urine falls, because of the increase of urea, in which the C:N ratio is the lowest among urinary constituents. The carbon and nitrogen of the urine which are not in the form of urea or ammonia are spoken of as dysoxidisable; the relationship of this form of carbon and nitrogen is on a flesh diet, 1:5; on a carbohydrate diet, 1:2.4; on a fat diet, 1:3; and in inanition, 1:2.38.

W. D. H.

The Importance of So-called Plant-amides in Animal Metabolism. VALDEMAR HENRIQUES and C. HANSEN (*Zeitsch. physiol. Chem.*, 1907, 54, 169—187).—Experiments on rats show that if asparagine is the only nitrogenous substance in the diet, it is unable to maintain equilibrium or to act as a protein-sparer. The same is true for amides separated from eight-day old germinating seedlings (*Vicia faba*, *Phaseolus vulgaris*) or from potatoes and other vegetables.
W. D. H.

Nuclein Metabolism in a Dog with an Eck's Fistula. J. E. SWEET and PHOEBUS A. LEVENE (*J. Exper. Med.*, 1907, 9, 229—239).—In a dog with an Eck's fistula and on a purine-free diet, the output of uric acid was much higher than in normal animals. Feeding with nucleo-protein only slightly raised the amount. Feeding with adenine had a similar effect, but the experiment was only done once; indeed, the whole series of observations are admittedly too scanty. Nucleic acid caused diuresis and a marked rise in the uric acid output, some of which is attributed to the diuresis. If thymine is injected, part of it is eliminated by the kidneys, but how much is absorbed and how much is decomposed in the intestinal tract was not ascertained. On a low protein diet, the uric acid elimination suffered a marked fall.
W. D. H.

The Importance of Allantoin in Uric Acid Metabolism. WILHELM WIECHOWSKI (*Beitr. chem. Physiol. Path.*, 1908, 11, 109—131).—On administration of uric acid to animals (dogs and rabbits), it is, in part, excreted as such, but is mainly eliminated as allantoin, which is therefore regarded as an end product of uric acid metabolism.
W. D. H.

Secretory Activity of the Pancreas Under the Influence of Hydrochloric Acid and Intestinal Extract. L. POPIELSKI (*Pflüger's Archiv*, 1907, 120, 451—491).—The work of Bayliss and Starling on secretin is criticised, and the opinion advanced (and supported by experiments) that the injection of hydrochloric acid into the duodenum produces pancreatic secretion as the result of a nervous reflex. It is stated that extracts of all parts of the gastro-intestinal tract produce the same effect as the so-called secretin.
W. D. H.

The Nucleic Acid of the Pancreas. OTTO VON FÜRTH and ERNST JERUSALEM (*Beitr. chem. Physiol. Path.*, 1908, 11, 146—150. Compare Abstr., 1907, i, 993).—The pancreas contains as its principal nucleo-protein one which yields a nucleic acid differing in no essential points from that prepared from the thymus. The pancreas yields also another acid which is distinguished by its solubility in hot water (Hammarsten's nucleo-protein, Bang's β -guanylic acid), and is of simpler structure, its cleavage products being only guanine, phosphoric acid, and pentose. It is to this substance that the name guanylic acid should be restricted.
W. D. H.

The Superficial Layer of Cells and its Relation to their Permeability and to the Staining of Tissues by Dyes. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1908, 4, 1—34).—From experiments on the solubility of dyes in the presence of lipoids (ethyl acetate, butyrate, triacetin, &c.), the conclusion is drawn that the theory of an oily layer on the surface of cells is untenable, and that cell membranes are probably protein in nature; proteins combine chemically with certain dyes. In many cases, however, a discontinuous lipid layer may underlie the protein membrane. W. D. H.

The Biological Importance of Lecithin. W. GLIKIN (*Biochem. Zeitsch.*, 1907, 7, 286—298. Compare Abstr., 1907, ii, 566).—A high percentage of lecithin in the bone-marrow is associated in newly-born animals with those species (both in birds and mammals) in which there is a helpless, immature condition at the time of birth. W. D. H.

Action of Certain Metallic Ions on the Frog's Heart. JEAN GAUTRELET (*Compt. rend.*, 1907, 145, 1308—1309).—The following metals were dissociated electrically from their chlorides while introduced into the organism of the frog: potassium, copper, and mercury were found to be toxic to the muscular tissue of the heart; magnesium poisons the heart by acting on its nerves. In the case of iron dissociated from ferric chloride, both tissues are affected. Iron dissociated from ferrous chloride, and calcium act tonically on the myocardium; sodium and silver are inert. W. D. H.

Consumption of Dextrose by Mammalian Cardiac Muscle. FRANK S. LOCKE and OTTO ROSENHEIM (*J. Physiol.*, 1907, 36, 205—220).—A new perfusion method is described by which a solution of dextrose in oxygenated Ringer's solution can be repeatedly circulated through an excised rabbit's heart. Five to ten centigrams of the sugar disappear in eight to nine hours. This is not due to a minor metabolic or fermentative by-process, but is associated with the main chemical change which underlies cardiac activity. If the activity of the heart is reduced by the omission of calcium (or, better, of both calcium and potassium) from the fluid, the amount of sugar used up is lessened. No evidence was found of the formation of disaccharide in the fluid, or of the storage of glycogen in the heart. The amount of carbon dioxide formed runs parallel with the disappearance of sugar. Lactic acid is absent, and nitrogenous waste is very small. W. D. H.

Contraction of Muscle and Receptive Substances. I. JOHN N. LANGLEY (*J. Physiol.*, 1907, 36, 347—384).—The influence of nicotine on frog's muscles varies in degrees in different muscles. The local application of the drug produces two main kinds of results, namely, local twitchings and prolonged tonic contractions. The former are rarely, if ever, produced, except in the region of the nerve endings. The general bearing of the results recorded is deferred until a future paper, but the theory is suggested that the normal tone of

muscles is maintained by an action on the special receptive substance which causes prolonged contraction when stimulated by nicotine, that in some cases this may be restricted to the neural region of the muscle fibre, and that the tone is produced by a constant and not by an interrupted electric current (or stimulus) passing down the nerves.

W. D. H.

Physical Chemistry of Excitation (of Muscle) and of Narcosis. RUDOLF HÖBER (*Pflüger's Archiv*, 1907, 120, 492—516).—Isotonic solutions of normal salts of the alkali metals produce currents of rest of varying intensity and direction when applied locally to the non-injured sartorius muscle of the frog. When arranged according to their power of producing this current, the various anions and cations form two series, which coincide with those which have been deduced from their action on the solubility of egg-white and of lecithin (compare Höber, this vol., ii, 28; also, as regards lecithin, Porges and Neubauer, this vol., ii, 90). This coincidence is one of the reasons for the author's conclusion that excitation and the electrical reaction accompanying it are closely connected with the consistency of the muscle colloids.

Narcotics inhibit the change in the colloids (of the axis cylinder), which change accompanies the normal current of action, and in accordance with the current theory of narcosis, due to Hans Meyer and Overton, this colloidal change is supposed to occur in the lecithin. Narcosis would therefore consist, firstly, in the accumulation of the lipoid-soluble narcotic in the lipoid substance (lecithin), and, secondly, in the inhibition of the colloidal changes which excitation normally produces in this substance.

G. B.

Influence of Inorganic Colloids on Autolysis. Part III. Action of Poisons. M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1907, 7, 142—151. Compare Abstr., 1907, ii, 897).—The effects of various "poisons" on the catalytic acceleration of the autolysis of liver substance have been studied. They agree qualitatively, and to some extent quantitatively, with the effects on the decomposition of hydrogen peroxide by colloidal platinum (Bredig) and by blood catalase (Senter), which effects consist in a retardation of the action of the (inorganic or organic) ferment. A further analogy is especially seen in the case of hydrocyanic acid, namely, that the effect of traces of the poison on colloidal silver is not permanent. After forty-eight hours, the silver recovers its activity, so that it once more accelerates the autolysis.

G. B.

Behaviour of Human Milk to Rennet and Acids. BIANCA BIENENFELD (*Biochem. Zeitsch.*, 1907, 7, 262—281).—Rennet does not curdle human milk; after slight acidification and warming, caseinogen is precipitated by rennet, but this is the effect of the acid, not of the rennet. Lactic acid also precipitates caseinogen, and the precipitate contains only 16.2% of the total nitrogen. The remaining portions are precipitated by three-quarters saturation with ammonium sulphate. Human caseinogen appears to contain a carbohydrate complex.

W. D. H.

Gases Produced in the Alimentary Canal of Goats. ARTHUR E. BOYCOTT and G. C. C. DAMANT (*J. Physiol.*, 1907, **36**, 283—287).—Goats produce a large quantity of carbon dioxide (about 9 litres per day in a goat weighing 20 kilos). The amount of combustible gas (hydrogen and methane) varies from 3.5% to 6.6% of this; the proportion between the two gases averaging 1:2. Ten % of the total carbon dioxide at least is not the result of tissue metabolism, but leaves the alimentary canal, and is produced there by fermentation.

W. D. H.

The Action of Various Chemical Substances on Sugar Excretion and Acidosis. II. JULIUS BAER and LÉON BLUM (*Beitr. chem. Physiol. Path.*, 1908, **11**, 101—108. Compare Abstr., 1907, ii, 640).—A previous research has dealt with the action of glutaric acid in lessening the sugar excretion and acidosis in phloridzinised dogs. Several other acids of the same series were investigated; adipic acid (C=6) and pimelic acid (C=7) act in the same way, but less powerfully; suberic acid (C=8) is still less powerful, and azelaic acid (C=9) and sebacic acid (C=10) have no action at all. The higher acids are less easily burnt in the body, more passing unchanged into the urine, but this appears to be only one factor concerned. Benzoic acid does not act like glutaric acid.

W. D. H.

Detection of Glyoxylic Acid and its Occurrence in Human Urine. F. GRANSTRÖM (*Beitr. chem. Physiol. Path.*, 1908, **11**, 132—142).—The different colour reactions which indole, scatole, and tryptophan give with glyoxylic acid, formaldehyde, and other aldehydes are described. Eppinger's test for glyoxylic acid in urine is criticised. Although it is sometimes possible to detect indole and scatole, it is very doubtful whether glyoxylic acid ever occurs in human urine, normal or pathological.

W. D. H.

Uric Acid of the Urine. DETERMEYER and WAGNER (*Biochem. Zeitsch.*, 1908, **7**, 369—395).—Various factors playing a part in the condition of solution or precipitation of uric acid in the urine are considered. The most important are: (1) solution owing to salt formation with inorganic bases; (2) precipitation of free uric acid by organic acids, and (3) inhibition of this precipitation by certain organic substances, such as urochrome.

W. D. H.

Doubly-Refracting Substances from Pathological Organs. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1907, **54**, 239—254).—The crystalline doubly-refracting substance separated from diseased kidneys and previously called protagon is really an oleic acid ester of cholesterol. Further details of its preparation and properties, as obtained from kidneys and other diseased structures, are given, and the question of the meaning of cholesterol in the body discussed.

W. D. H.

Lactic Acid in Eclampsia. A. TEN DOESSCHATE (*Zeitsch. physiol. Chem.*, 1907, **54**, 153—168).—Sarco-lactic acid is undoubtedly present

in the blood and the urine of the mother, and in the umbilical blood of the foetus in cases of eclampsia. This substance, however, is not the cause of the convulsions, as has been supposed, but the result either of the convulsions or of the kidney disorder which underlies them. Hopkin's new test for lactic acid was used, and quantitative results in numerous cases given.

W. D. H.

Protein Metabolism in Poisoning by Bromobenzene. W. MCKIM MARRIOTT and CHARLES G. L. WOLF (*Biochem. Zeitsch.*, 1907, 7, 213—261).—In animals, bromobenzene increases the output of nitrogen; the relation between the different forms of excreted nitrogen is not markedly altered. The sulphur excretion runs parallel to this, the "neutral sulphur" and ethereal sulphates being especially increased. During inanition these effects are still more marked, but there is no acidosis. The drug produces no change in the excretion of amino-acids or in the respiratory quotient. After death, the liver and kidney cells are found to have undergone necrotic changes.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Chlorine in the Tubercle Bacillus. MOUSSU and GOUPIL (*Compt. rend.*, 1907, 145, 1231—1232).—The resistance to acids of the various constituents of the tubercle bacillus is one of its characteristic properties, and this is not destroyed by various reagents which destroy the bacilli (alcohol, ether, chloroform, light petroleum, potassium hydroxide, &c.). Exposure to chlorine, however, breaks up the bacilli, and they lose then their acid-resisting property.

W. D. H.

Phosphorus in the Fat of Micro-Organisms. E. ALILAIRE (*Compt. rend.*, 1907, 145, 1215—1217).—The fatty matter of numerous micro-organisms contains phosphorus. The only exception found was *Chlorella vulgaris*, in which the total amount of fat is small and chlorophyll is abundant. On the supposition that lecithin is present, the iodine test for choline after saponification was tried, but with negative results.

W. D. H.

Influence of Organic Matter on Nitrification in Impure Cultures. ADAM KARPIŃSKI and BR. NIKLEWSKI (*Bul. Acad. Sci. Cracow*, 1907, 596—615).—The presence of small amounts of some organic substances is favourable to nitrification in mixed cultures; soil extracts, humates, and acetates were found to be favourable, and even peptone and sugar, in small quantities, quickened nitrification in the first generations. The strength of solutions does not seem to be of much importance, favourable effects being produced, especially in the case of humates, by extremely small amounts.

N. H. J. M.

Microbiochemical Formation of Ammonia in Soil. RENATO PEROTTI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 704–709. Compare Abstr., 1906, ii, 304).—Calcium cyanamide undergoes a biochemical change in soil, its nitrogen being converted into ammonia, whilst dicyanodiamide does not undergo this change, but is utilised directly by various organisms. The explanation of this difference in behaviour seems to lie in the fact that calcium cyanamide is poisonous in nature, whilst dicyanodiamide in moderate concentrations is not. When the dicyanodiamide is increased in concentration to such an extent as to render it poisonous, the soil bacteria attack it, converting its nitrogen into ammonia. T. H. P.

Favourable Influence of Small Quantities of Zinc in the Growth of *Sterigmatocystis nigra*. MAURICE JAVILLIER (*Compt. rend.*, 1907, 145, 1212–1215).—Raulin, in 1870, described the favouring influence of small quantities of zinc on the mould mentioned above, known also as *Aspergillus niger*. Coupin attributed this to the antiseptic action of the zinc preventing the growth of other micro-organisms. The present research confirms Raulin's view that zinc is of real nutritive importance. W. D. H.

The Organic Compounds of Nitrogen, Phosphorus, and Sulphur in Vegetables. ALBERT STUTZER (*Biochem. Zeitsch.*, 190, 7, 471–487).—A method for the estimation of phosphorus and sulphur in organic union (as lecithin, &c.) in vegetable tissues is described. Schulze's observations on the value of organic phosphorus compounds in plants, and especially in seeds, are confirmed. After gastric digestion of vegetables, the insoluble residue contains nitrogen, phosphorus, and sulphur in organic combination, but the proportion of the three elements varies. The same is true for the fæces of sheep fed on various vegetables. The nature of the organic sulphur compounds is not known. W. D. H.

Occurrence of Quercitol. EDMUND O. VON LIPPMANN (*Ber.*, 1907, 40, 4936–4937).—An appreciable amount of crystallised quercitol was found between the wood and the bark of a recently felled oak. J. J. S.

Occurrence of Salts of Anhydroxymethylenediphosphoric Acid or Phytin in Plants. UMETARO SUZUKI and K. YOSHIMURA (*Bull. Coll. Agri. Tōkyō*, 1907, 7, 495–502).—The amount of organic phosphorus soluble in 0.2% hydrochloric acid represents approximately the amount of phytin present in plants. The following results (per cent. in dry matter) were obtained:

	Total.	as lecithin.	Phosphorus Soluble in 0.2% HCl.	
			Organic.	Inorganic.
Rice bran	2.27	0.02	1.68	0.13
Wheat bran.....	1.114	0.010	0.579	0.050
Seeds of <i>Sesamum indicum</i> ...	0.772	0.030	0.125	trace
Seeds of <i>Ricinus communis</i> ..	0.261	0.013	0.109	trace
Oil cake (<i>Brassica napus</i>).....	1.195	0.034	0.532	trace
Barley bran.....	0.541	0.010	0.238	0.089
Bran from <i>Panicum frument.</i>	0.765	0.026	0.344	trace

Preparations from rice bran, which amounted to 7—8% of the dry matter, gave the following results: loss on ignition, 27·31; P 23·48, Mg 17·48, and Ca 5·18%.
N. H. J. M.

Pectins from the Fruits of *Lonicera Xylosteum*, *Symphoricarpos Racemosa*, and *Tamus Communis*. MARC BRIDEL (*J. Pharm. Chim.*, 1907, [vi], 26, 536—543).—The pectins obtained from *Lonicera*, *Symphoricarpos*, and *Tamus* by Bourquelot and Hérissé's method (*ibid.*, 1898, [vi], 7, 473) gave α_D +183·36°, +190·9°, and +111·42° (200 mm.) respectively. All three yield mucic acid when treated with nitric acid, are coagulated by barium and calcium hydroxides and by pectase, and are rendered incoagulable by malt pectase. The pectin from *Lonicera Xylosteum* yielded arabinose when hydrolysed with sulphuric acid.
N. H. J. M.

Composition of Tea Leaves at Various Stages of Development. SHIN SAWAMURA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 145—146. Compare Kellner, *Abstr.*, 1887, 73).—The relative weights of the first, second, third, and fourth leaves and the twigs were 100, 203, 412, 577, and 717, and they contained respectively 72·48, 71·98, 73·28, 74·54, and 83·91% of water. The composition of the dry matter was as follows:

	Ether extract.	N-free extract.	Crude fibre.	Theine.	Tannin.	N.	Pure ash.
1.	6·91	18·40	10·87	3·578	13·97	7·545	4·969
2.	7·90	13·65	10·90	3·559	16·96	6·727	4·988
3.	11·35	18·50	12·25	3·232	15·78	6·294	4·867
4.	11·43	20·73	14·75	2·570	15·44	5·504	4·935
5.	8·03	26·96	17·08	2·146	11·14	5·112	6·249

N. H. J. M.

Carbohydrate Metabolism of the Sugar Beet (*Beta vulgaris*). SIEGFRIED STRAKOSCH (*Zeitsch. Ver. deut. Zuckerind.*, 1907, 623, 1057—1068).—The author's results are briefly as follows. Dextrose is formed in the mesophyll of the whole surface of the leaves of *Beta vulgaris*, and is the only sugar found in the mesophyll. The migration of dextrose into the leaf veins is followed by the appearance of levulose therein, and later by the formation of sucrose. The formation of starch in the chlorophyll granules occurs subsequently to the production of sucrose from its components, and only after the carbohydrates have accumulated to some extent in the mesophyll. Evidence is obtained in support of the view that the sucrose in the leaves of the beet must be regarded as the final product, and that it migrates to the root as such. The conversion of the monosaccharides of the leaf into sucrose is connected with the action of light, and ceases when the leaf is placed in the dark. The amount of the monosaccharides in the leaf is not appreciably altered by the migration of the sucrose into the root. This amount is not perceptibly diminished when the leaves remain in the dark for a long time, neither does prolonged exposure of the leaves to the action of light cause it to increase beyond a certain maximum attained in a short time.
T. H. P.

Darkening of Beet Juice. MAX GONNERMANN (*Zeitsch. Ver. deut. Zuckerind.*, 1907, 623, 1068—1087. Compare Abstr., 1899, ii, 790).—Sugar beet juice contains organic ferrous salts, tyrosinase, and catechol, the last named being probably formed by the action of tyrosinase on tyrosine. These substances produce no colouring matter in absence of air, but access of the latter to the liquid causes rapid darkening, especially if a trace of ammonia is present. The author has isolated catechol from the juice. T. H. P.

The Most Favourable Ratio of Lime to Magnesia for the Mulberry Tree. M. NAKAMURA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 129—133).—The best ratio for mulberry trees was found, in accordance with previous observations by Aso, to be $\text{CaO/MgO} = 3/1$. N. H. J. M.

Influence of Stimulating Compounds on Crops under Different Conditions. S. UCHIYAMA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 37—79).—A large number of plot experiments are described, in which various plants were grown without and with manganese sulphate. The soil was a diluvial loam rich in organic matter, and contained 0.076% Mn_2O_3 soluble in 1% citric acid, and 0.413% soluble in hot 10% hydrogen chloride. In the case of wheat and barley, very little effect was produced by manganese sulphate, whilst grasses, buckwheat, radishes, carrots, *Brassica campestris*, and tea plants were considerably benefited. Ferrous sulphate was also found to be beneficial in some cases, but less so than manganese. In some cases, a mixture of the two sulphates gave the best results. The amounts of manganese sulphate varied from 10 to 37.5 kilos. per hectare (reckoned as Mn_2O_3). Better results were obtained when it was applied as a top dressing than with the other manures.

Further experiments, in which plants grown in bottomless cylinders received varying amounts of manganese sulphate, showed in each case a more or less stimulating action. In the case of barley, the grain and total yield were increased 18% and 24% respectively by 25 kilos. of Mn_2O_3 per hectare, both smaller and larger applications producing less effect. The effect of manganese depends to some extent on the nature of the soil, being greater on loam than on sandy soil; the effect is diminished by alkaline manures.

Potassium iodide increased the yield of *Panicum miliaceum* (28%) and of barley (34%), the most suitable amounts being 376 and 500 grams per hectare respectively. Sodium fluoride has a powerfully stimulating action on *Panicum*, and also increased the yield of barley; the amounts of fluoride applied were 940 and 5000 grams per hectare. N. H. J. M.

Distribution of Solute Between Water and Soil. FRANK K. CAMERON and HARRISON E. PATTEN (*J. Physical Chem.*, 1907, 11, 581—593).—The authors have studied the distribution of various solutes (gentian-violet, sodium eosin, manure extract) between water and various soils. The distribution of solute between solvent and absorbent presents the same general characteristics with soils as with

other absorbents. For any series of soils or other absorbents, the order of the absorptive capacities for one solute may be quite different from the order for another solute. The distribution of a solute between solvent and absorbent may generally be represented by the formula $C^n/C_1 = K$, where n may be less than, equal to, or greater than unity. When soils, however, are the absorbents, the flocculation introduces a modifying factor, and the form of the distribution equation may become more complex.

J. C. P.

Humus Formation. SHIGEHIRO SUZUKI (*Bull. Coll. Agric. Tokio*, 1907, 7, 513—529. Compare *ibid.*, 419, and Abstr., 1906, ii, 889).—The nitrogen of humus is mainly in the form of a kind of protein, only traces of amino-acids being present. Udránszky's artificial nitrogenous humic acid, obtained by boiling dextrose and urea with hydrochloric acid (*Zeitsch. physiol. Chem.*, 1888, 12, 42), cannot therefore resemble natural humus.

The following substances were obtained by treating humic acid (500 grams) with hot concentrated hydrochloric acid: alanine, 2.39; leucine, 2.16; aminovaleric acid, 0.57; impure aspartic acid, 2.16; copper salts of active and inactive proline, 0.67 and 0.50; copper salts of unknown acids, 30.30, and ammonia, 1.90 grams. Glutamic acid, tyrosine, and histidine were also present.

N. H. J. M.

Sodium Nitrate Compared with Ammonium Sulphate. PAUL BÄSSLER (*Bied. Zentr.*, 1907, 36, 857; from *Jahresber. Agrik. chem. Versuchs. u. Samenkontrollstat. Köslin*, 1905—1906, 14).—The greatest effect with potatoes was produced when the manures were applied in two portions, before planting and before the second hoeing. The two manures gave practically the same result. The worst results were obtained by applying the whole amount of the manures before planting; ammonium sulphate produced considerably less effect than sodium nitrate.

N. H. J. M.

Behaviour of Nitrate in Paddy Soils. G. DAIKUHARA and T. IMASEKI (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 7—36. Compare Nagaoka, Abstr., 1905, ii, 837).—Results of determinations of dextrose and sucrose in paddy rice and in dry land rice at three or four periods of growth showed that the amount of sugar is practically the same, and, further, that manuring with ammonium sulphate and sodium nitrate respectively has no effect on the sugar content. The low yields of rice obtained when nitrate is employed cannot therefore be due, as suggested by Nagaoka, to deficiency of sugar in paddy plants.

The unsuitability of nitrate for paddy soils is due to loss of nitrogen by denitrification, to the greater production of poisonous nitrites on paddy soils as compared with dry land, and to loss of nitrates by the system of irrigation. Even in the case of dry land there may be some loss by denitrification in the subsoil; in rainy seasons, when organic manures have been applied along with nitrate, denitrification may be energetic in the subsoil and may also take place in the surface soil.

When nitrates are applied to paddy soils, it is best to avoid the use of organic manures unless in a well-rotted condition.

N. H. J. M.

Manurial Effect of Calcium Cyanamide under Different Conditions. S. UCHIYAMA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 93—103).—Pot experiments with barley and *Brassica campestris* in loamy and sandy soils. Calcium cyanamide acts best under conditions approaching neutrality. Under favourable conditions, it is equal to ammonium sulphate; the results were less favourable on sandy soil than on loam.

Ammonium sulphate gave better results in conjunction with sodium phosphate than with superphosphate.

N. H. J. M.

Manuring with Bone Dust. S. UCHIYAMA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 105—120).—The results of sand-culture experiments with barley showed that the availability of bone dust is diminished by magnesite, and that it is less in conjunction with sodium nitrate than with ammonium sulphate. In the case of sandy soil, it was found that potassium sulphate and carbonate in presence of bone dust and sodium nitrate gave similar results. Wood ash and bone dust may therefore be used together.

Bone dust (25 grams) kept in contact with water (2.5 litres) for four and a-half months showed an increase of 70% soluble P_2O_5 over the amount dissolved in the same time in presence of chloroform. The presence of potassium carbonate had a far greater effect than bacteria.

N. H. J. M.

Behaviour of Bone and Mineral Phosphates in Soil. CARLO MONTANARI (*Bied. Zentr.*, 1907, 36, 797—801; from *Staz. sper. agrar. ital.*, 1906, 39, 323).—The absorptive power of soils for soluble phosphates depends on the amounts of alkaline earth carbonates, of iron and aluminium oxides, and especially of humus substances.

The continued employment of phosphates diminishes the amount of alkaline earth carbonates in the soil, di- and tri-phosphates being produced. There is also a diminution of alumina and iron oxide, a withdrawal of the alkali of clay producing substances and, consequently, a diminution of the absorptive power of the soil and production of free silicic acid.

N. H. J. M.

Are Soils containing less than 0.02% SO_3 Benefited by Special Manuring with Sulphates? G. DAIKUHARA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 135—143).—Results of pot experiments in which barley was grown in three soils, containing respectively 0.016, 0.013, and 0.010% of sulphuric acid (as SO_3), showed that these amounts sufficed to meet the needs of barley.

N. H. J. M.

Influence of Solubility on Availability. G. DAIKUHARA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 87—91. Compare Abstr., 1906, ii, 388).—When calcium is present as

carbonate, the necessary amount of magnesium (as crystallised sulphate) for barley in sand culture is very small, the best ratio of lime to magnesia being 60:1. In water cultures containing calcium and magnesium nitrates, the best ratio is between 1:1 and 2:1. This holds good for sandy soils, whilst in clay soils the ratio $\text{CaCO}_3:\text{MgSO}_4$ will vary (compare Nakamura, *Abstr.*, 1906, ii, 389). In the case of barley, the agronomic equivalents of crystallised magnesium sulphate and magnesite are as 4.9:100; with rice the equivalent is 9.8.

N. H. J. M.

Manuring with Magnesium Sulphate. G. DAIKUHARA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, 1, 81—86).—Magnesium sulphate is the most effective magnesium compound to employ for regulating the lime factor, and it is best to apply it annually as a top dressing in small quantities. On a loamy humus soil, 10 parts of the salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) are agronomically equivalent to 100 parts of the finest-ground magnesite.

N. H. J. M.

Analytical Chemistry.

Gas-generating Apparatus for Analytical Purposes. EUGEN MÜLLER (*Chem. Zeit.*, 1907, 31, 1257).—A modification of J. M. Sanders's apparatus (*ibid.*, 1184). As now constructed, it consists of a U-tube with two, or only one, ground stoppers and a gas-delivery tube. The advantages gained are: saving of material, obtainment of a pure (washed or dried) gas, and proper regulation of the gas-current.
L. DE K.

Estimation of Organically-combined Iodine and Chlorine in "Erythrosine." FERDINAND JEAN (*Ann. Chim. anal.*, 1908, 13, 12—14 *).—Two portions of 0.5 gram each are burnt to ash, one with addition of 0.5 gram of sodium carbonate, 0.5 gram of potassium carbonate, and 5 grams of magnesium oxide. The ashes are treated with water, the solutions are carefully neutralised with acetic acid, made up to 100 c.c., and the iodine and chlorine are estimated. The difference between the results of the two ashes is then due to organically-combined iodine or chlorine.

The estimation of the halogen is carried out as follows: 50 c.c. of each solution are titrated for iodine only by Pisani's method (*N/10* silver in presence of iodide of starch). The other 50 c.c. are then titrated with *N/10* silver for joint iodine and chlorine, using potassium chromate as indicator.
L. DE K.

Estimation of Total Sulphur in Urine. HUGO SCHULZ (*Pflüger's Archiv*, 1907, 121, 114—116).—Ten c.c. of urine are heated in a round-bottomed flask with 10 c.c. of fuming nitric acid; the

* And *Bull. Soc. chim. Belg.*, 1908, 22, 45—46.

heating is continued for about fifteen minutes, that is, until all violent action has ceased, and the contents of the flask are then cooled. Water and hydrochloric acid are now added, the solution is transferred to a beaker, and the sulphuric acid is precipitated in the usual way as barium sulphate.

W. P. S.

Assay of Highly Concentrated Sulphuric Acid. ERNST BUCHWALD (*Chem. Zeit.*, 1907, 31, 1256).—About 5 grams of the sample are weighed accurately in a small weighing bottle and then made up to a litre. The solution is placed in a burette, and run into a flask containing 50 c.c. of accurately prepared *N*/10 sodium hydroxide, free from carbon dioxide, and coloured with phenolphthalein, until the liquid is decolorised.

Good results are also obtained by Kjeldahl's iodometric process (liberation of iodine from a mixture of potassium iodide and iodate).

L. DE K.

Titration of Sodium Thiosulphate. THADDEUS MILOBENDSKI (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1404—1411).—The three methods of titrating sodium thiosulphate, namely, those of Zulkowsky and of Volhard, and direct titration with iodine, have been found to be equally good; but in cases where the iodine is only very slowly liberated, the thiosulphate should be titrated by Zulkowsky's method without, however, allowing, as usual, half an hour for the completion of the reaction.

Z. K.

Modification of Kjeldahl's Process for Estimating Nitrogen in Foods. REMO CORRADI (*Boll. chim. farm.*, 1907, 46, 861—864).—2.5 Grams or, if the amount of the nitrogen is less than 3%, 5 grams of the food are weighed, dried in a steam-oven, and heated for five to six hours in a Kjeldahl flask with 30 c.c. of fuming sulphuric acid. The colourless, or pale yellow liquid, is introduced into a 250 c.c. flask containing about 40 c.c. of water, the cooled solution being then rendered faintly acid by means of 20% sodium hydroxide solution, and finally made up to volume. Twenty-five c.c. of the liquid are then treated with 25 c.c. of sodium hypobromite solution, prepared by mixing 25 c.c. of bromine, 350 c.c. of 30% sodium hydroxide solution, and 275 c.c. of water. The nitrogen evolved is measured in a slightly modified Dupré's azotometer (compare *Abstr.*, 1906, ii, 505), the volume being increased by 1.7%. This method gives numbers differing insensibly from those obtained by the ordinary Kjeldahl process.

T. H. P.

Employment of Nitron for Determining Nitrates in Soils and Plants. JAKOB LITZENDORFF (*Zeitsch. angew. Chem.*, 1907, 11, 2209—2231).—Correct results are obtained with soils containing 20—30 parts per million of nitric nitrogen. When, however, smaller amounts are present, the extracts have to be evaporated down, and in this process substances are produced which hinder the separation of the nitrate. This difficulty can be overcome by repeatedly adding hydrogen peroxide to the extract during evaporation, and by heating

the sufficiently concentrated extract with hydrogen peroxide in a flask in boiling water for several hours until decolorised. N. H. J. M.

Estimation of Phosphorus in Calcium Carbides. F. WILLY HINRICHSSEN (*Chem. Zentr.* 1907, ii, 1356—1357; from *Mitt. K. Materialprüfs.-Amt. Gross. Lichterfelde West*, 25, 110—112).—On passing impure acetylene through a solution of sodium hypochlorite, explosions occur now and then, and the phosphorus is not completely absorbed, as it occurs, in part, as an organic phosphorus compound.

The process recommended by Lidholm (*Abstr.*, 1904, ii, 776) gives satisfactory results. L. DE K.

A New Modification of Petermann's Method for Estimating Citrate-Soluble Phosphoric Acid in Precipitated Calcium Phosphate (Futterkalk). GUSTAV FINGERLING and ADOLF GROMBACH (*Zeitsch. anal. Chem.*, 1907, 46, 756—761).—One gram of the sample is put into a 200 c.c. flask and moistened with 5 c.c. of alcohol, 100 c.c. of Petermann's alkaline citrate solution are added, and the whole is rotated for half an hour. The liquid is then heated at 40° for another hour with constant shaking, and, when cold, diluted with water to 200 c.c. and filtered. One hundred c.c. of the filtrate are mixed with 20 c.c. of strong nitric acid, evaporated to half the bulk, and, when cold, neutralised with ammonia and mixed with 50 c.c. of Hallenser's solution. To the cold solution are then added, drop by drop, 20 c.c. of magnesium mixture, and, after shaking for half an hour, the precipitate may be collected. L. DE K.

Detection of Arsenic by Means of the Marsh Apparatus. HEINRICH STRUVE (*Zeitsch. anal. Chem.*, 1907, 46, 761—764).—The author recommends the use of sheet zinc, which almost invariably he finds to be free from arsenic. Addition of activating agents are superfluous. L. DE K.

Estimation of Commercial Silicon ; Separation of Silica and Silicon. FRITZ LIMMER (*Chem. Zeit.*, 1908, 32, 42).—0.25—0.50 Gram of the finely-powdered sample is heated in a slow current of dry chlorine, care being taken not to apply heat until every trace of air has been expelled from the apparatus. The silicon (also aluminium, iron, &c.) is volatilised, whilst the silica remains in the residue, which is then tested in the usual way by fusion with alkali carbonate, &c. The silica is deducted from the amount of total silica obtained from a separate portion of the sample and the difference calculated into silicon. L. DE K.

Estimation of Carbon in Pig-Iron and Steel. MAX ORTHEY (*Chem. Zeit.*, 1908, 32, 31—33).—A criticism of some of the methods used for the estimation of carbon in iron or steel. Särnstrom's modified chromic acid process and the copper ammonium chloride method are quite satisfactory for the ordinary kinds of iron. The method of burning in a current of oxygen in presence of bismuth oxide gives good results with all kinds of iron. In the case of samples

oxidised with great difficulty, the chlorine process may be used as a check. Some other recognised methods were tried, but with less satisfactory results.

L. DE K.

The Use of Silver in the Combustion of Nitrogenous Substances. F. EPSTEIN and RICHARD DOHT (*Zeitsch. anal. Chem.*, 1907, 46, 771—773).—A silver spiral, 10 cm. long, heated to intense redness is again recommended instead of metallic copper in order to decompose the nitrogen oxides formed in the combustion of nitrogenous organic substances (C and H estimation). Silver also effectually retains halogens.

L. DE K.

Dennstedt's Method of Elementary Analysis Applied to the Hæmoglobin Derivatives. JEAN ZALESKI (*Bull. Acad. Sci. Cracow*, 1907, ii, 646—651).—The elementary analysis of substances such as acetonehæmin or iodohæmin (Merunowicz and Zaleski, *ibid.*, 633) is attended with great difficulty when ordinary methods are employed, but is rendered simple by the use of Dennstedt's method (compare Abstr., 1906, ii, 51).

G. B.

Estimation of Carbon Dioxide in Electrolytic Chlorine. PETER PHILOSOPHOFF (*Chem. Zeit.*, 1907, 31, 1256—1257).—The author (Abstr., 1907, ii, 908) now dispenses with the use of brine in order to facilitate the readings, and reads off the volume of the gas before and after absorption by means of a graduated levelling tube attached to the Bunte burette and filled with mercury.

L. DE K.

Quantitative Estimation of Metals in Organic Substances. J. ROTHE (*Chem. Zentr.*, 1907, ii, 1362—1364; from *Mitt. K. Materialprüfs.-Amt. Gross. Lichterfelde West*, 25, 105—106).—The dried substance is heated in a round-bottomed flask with 15 c.c. of fuming nitric acid and 2 c.c. of sulphuric acid for every gram taken, at first gently, afterwards more strongly, on a sand-bath. Substances which are readily inflammable are first moistened with four times the weight of nitric acid, D 1.4. When sulphuric fumes begin to appear, the contents are allowed to cool and another portion of nitric acid is added, and this operation may be repeated if necessary. Finally, the bulk of the sulphuric acid is driven off, and any metal will be found in the residual mass.

L. DE K.

Analysis of Sodium Peroxide. R. NIEMEYER (*Chem. Zeit.*, 1907, 31, 1257).—With care, the permanganate method gives trustworthy results. 0.15—0.2 Gram of the peroxide is weighed out in a little dish placed in a weighing tube. This is then seized with a pair of tongs, and quickly immersed in a beaker containing 500 c.c. of water; care should be taken that none of the peroxide floats on the surface, as otherwise the experiment fails. A sufficiency of dilute sulphuric acid is now added, and the liquid titrated at once with *N*/10 permanganate.

L. DE K.

Quantitative Separation of Barium from Strontium. ZELDA KAHAN (*Analyst*, 1908, **33**, 12—14).—The method proposed depends on the precipitation of the barium as chromate in ammonium acetate solution. The solution containing the barium and strontium salts is treated with ammonium dichromate solution until precipitation is nearly complete; the dichromate solution is added drop by drop with constant stirring. Ammonium acetate solution is then added until the solution becomes colourless, a few more drops of the dichromate solution are added so that the solution remains pale yellow, and next, a little more ammonium acetate solution. After the lapse of about three hours, the precipitate of barium chromate is collected in a Gooch crucible, washed with ammonium acetate solution until the filtrate gives only a slight coloration with silver nitrate solution, and is then dried at a temperature of 180° and weighed. W. P. S.

Estimation of Mercuric Chloride in Pastilles. UMBERTO SAPORETTI (*Boll. chim. farm.*, 1907, **46**, 865—867).—The amount of mercuric chloride contained in pastilles used for antiseptic purposes may be readily estimated as follows. Five of the pastilles are dissolved in water in a porcelain basin or crystallising dish with tall sides, and to the solution, decolorised with chlorine water or dilute hydrochloric acid, sodium hypophosphite is added gradually as long as any action takes place. The finely-divided mercury is then caused to collect into a globule by gently boiling the solution, and is washed with dilute hydrochloric acid. The amount of mercury is estimated by weighing or measuring. For the latter estimation, the author has devised a narrow burette or “hydrargyrometer,” by means of which the weight of mercuric chloride per five pastilles can be read off directly. T. H. P.

Estimation of Manganese in Potable Water. EDMUND ERNYEI (*Chem. Zeit.*, 1908, **32**, 41—42).—The sample is acidified with sulphuric acid and any iron removed by shaking with a slight excess of zinc oxide. One hundred c.c. of the filtrate are mixed with 5 c.c. of 30% sulphuric acid, the chlorine is removed with slight excess of silver sulphate, and the whole is boiled for twenty minutes after adding 1—2 grams of potassium persulphate. When cold, the liquid is made up to the original volume; the permanganate formed is estimated by adding potassium iodide and titrating with $N/100$ thiosulphate with starch as indicator. The process may be used also for the estimation of manganese in ferruginous water deposits. L. DE K.

Detection of Nickel as Double Nickel Ammonium Molybdate. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, **13**, 16. Compare Abstr., 1907, ii, 818).—A modification of the author's previous test for nickel. The neutral or slightly acid solution is mixed with a small quantity of saturated solution of ammonium molybdate and then with a large excess of saturated solution of ammonium chloride. The mixture is heated gently, when, should nickel be present, it becomes turbid in a few minutes. L. DE K.

Volumetric Estimation of Tin by Means of Potassium Dichromate. H. REYNOLDS (*Chem. News*, 1908, 97, 13—15).—The process is based on the fact that sulphonated azobenzene is bleached by stannous chloride, and that the red colour is restored by potassium dichromate.

The metal is dissolved in hydrochloric acid in a current of carbon dioxide free from oxygen, a definite amount of potassium dichromate (1 c.c. = 0.01 gram of tin), very nearly sufficient to complete the oxidation, is added, and then sufficient of the indicator to fully mask the green colour of the reduced chromate. More dichromate is now added until the colour changes to red.

The process may be used for the assay of ferro-tin and Britannia metal. L. DE K.

New Method for Separating Titanium and Zirconium. MAX DITTRICH and S. FREUND (*Zeitsch. anorg. Chem.*, 1907, 56, 344—345).—The method depends on the fact that a neutral solution of titanium nitrate gives in the cold with ammonium salicylate a precipitate (titanium salicylate) easily soluble in hot water, whilst the corresponding precipitate with zirconium nitrate is insoluble in excess of the reagent.

A solution of the mixed nitrates, neutralised with sodium carbonate, is added drop by drop to a boiling concentrated solution of ammonium salicylate (1 salt to 5 water). The solution is then boiled for some time, concentrated, filtered, the precipitate washed with a boiling solution of ammonium salicylate until free from titanium, and the zirconium then estimated as dioxide.

The titanium is precipitated from the boiling filtrate with excess of ammonia, and also estimated as the dioxide. G. S.

Separation of Titanium and Thorium by Means of Ammonium Salicylate. MAX DITTRICH and S. FREUND (*Zeitsch. anorg. Chem.*, 1907, 56, 346—347).—The separation is effected exactly as described in the preceding abstract; thorium, like zirconium, being completely precipitated from a neutralised solution of the nitrate when the latter is slowly added to a boiling concentrated solution of ammonium salicylate. G. S.

Simultaneous Precipitation of Titanium and Zirconium in the Presence of Iron. MAX DITTRICH and S. FREUND (*Zeitsch. anorg. Chem.*, 1907, 56, 337—343. Compare Abstr., 1905, ii, 287).—Four methods for the simultaneous precipitation of titanium and zirconium salts from a mixture also containing iron are given.

A complete separation in the presence of sodium acetate is possible when the iron is in the ferrous state. The mass obtained by fusing a mixture of the three salts with acid potassium sulphate is dissolved in water, saturated with hydrogen sulphide, filtered, nearly neutralised with sodium carbonate, and the hydrogen sulphide removed by passing a stream of carbon dioxide through the hot solution. Then, whilst the solution is protected from oxidation by means of carbon dioxide, excess

of sodium acetate is added, the solution heated for one hour, and the mixed precipitate of titanium and zirconium removed by filtration.

According to another method, which has some advantages, ammonium sulphate is used instead of acetate, otherwise the procedure is the same as above. The titanium and zirconium are obtained as oxides.

The separation in question may also be effected by means of sulphurous acid or sodium thiosulphate; full details are given in the paper.

The titanium in the mixed precipitate is estimated colorimetrically with sulphuric acid and hydrogen peroxide, and the zirconium by difference. G. S.

Separation of Thorium, Titanium, and Zirconium from Iron.

MAX DITTRICH and S. FREUND (*Zeitsch. anorg. Chem.*, 1907, 56, 348—352. Compare preceding abstracts).—It is shown that the complete separation from iron of (a) titanium and thorium, (b) thorium and zirconium, (c) titanium, zirconium, and thorium can be effected by the sodium acetate method described in the preceding abstract. In order to separate the individual oxides from the mixture of the three oxides obtained in (c), they are converted into nitrates, the zirconium and thorium are precipitated with ammonium salicylate as described above, and are then separated by the ammonium oxalate method due to Jannasch. G. S.

The Action of Methyl Sulphate on Oils of the Aromatic and Aliphatic Series. THOMAS WEATHERILL HARRISON and F. MOLLWO PERKIN (*Analyst*, 1908, 33, 2—9).—The authors find that Valenta's method (*Abstr.*, 1906, ii, 310) is untrustworthy for the estimation of tar oils in mixtures of the same with mineral oils. Whilst tar oils are soluble in all proportions in methyl sulphate, mineral oils are not insoluble. The method is, however, of use qualitatively; methyl sulphate removes most of the tar oil together with only a small quantity of mineral oil when shaken with mixtures of these oils. If the methyl sulphate layer is then saponified with potassium hydroxide and the solution diluted and extracted with ether, the tar oil, mixed with only a small portion of mineral oil, is recovered. It can then be tested to prove that it is a tar or aromatic oil. The fact that methyl sulphate dissolves a portion of an oil is no proof that the dissolved portion is an aromatic hydrocarbon. W. P. S.

Estimation of Naphthalene in Coal Gas and in Spent Oxide of Iron. C. J. DICKENSON GAIR (*J. Soc. Chem. Ind.*, 1907, 26, 1263—1264).—The method described previously (*Abstr.*, 1906, ii, 201) has been modified as follows, so as to be available either gravimetrically or volumetrically. The naphthalene picrate obtained is collected on a filter and washed with about 400 c.c. of dilute picric acid solution to remove the acetic acid, and is then washed into a beaker with a little cold water; 180 c.c. of water are added together with 25 c.c. of *N*/10 sodium hydroxide solution and the mixture is boiled for ten minutes, with the result that the naphth-

alene is liberated. If on testing with lacmoid indicator the solution does not give a green coloration, a further quantity of sodium hydroxide is added and the boiling continued. *N*/20 picric acid solution is now added in excess, as is shown by the indicator becoming yellowish-brown, and the solution is titrated with *N*/10 sodium hydroxide solution until the green coloration is permanent. The quantity of sodium hydroxide solution required to decompose the naphthalene picrate is thus found; 1 c.c. of *N*/10 sodium hydroxide solution corresponds with 0.0128 gram, or 0.197 grain, of naphthalene.

For the estimation of naphthalene in spent oxide of iron, 10 grams of the undried oxide are placed in a closed flask and extracted with 100 c.c. of 80% alcohol. At the end of three hours, the solution is poured through a filter, the residue is washed with dilute alcohol, and to the filtrate are added 300 c.c. of concentrated picric acid solution. After a short time, the naphthalene picrate is collected on a filter, and the naphthalene is then estimated volumetrically as described above, except that there is no necessity to wash the picrate before decomposing it with sodium hydroxide solution.

W. P. S.

Estimation of Alcohol in Wine. MARCEL DUBOUX and PAUL DUTOIT (*Ann. Chim. anal.*, 1908, 13, 4—9).—Five volumes of redistilled aniline are mixed with 3 volumes of alcohol (95° French). A mixture of 1 volume of nitrobenzene and 9 volumes of alcohol may be used also. Fifteen c.c. of the mixture are placed in a test-tube, 3.5 cm. in width and 15 cm. long, fitted with a doubly-perforated cork through which pass a delicate thermometer and a glass stirrer bent upwards at the lower end. Ten c.c. of the alcoholic solution (wine-distillate) are added, and the whole is heated with constant stirring until a clear solution is obtained. The temperature at which this occurs is noted and reference made to a table constructed from similar experiments made with alcoholic mixtures of known composition.

L. DE K.

Formation of Methylacetol (Acetylmethylcarbinol) in the Acid Fermentation of Wines. J. PASTUREAU (*J. Pharm. Chim.*, 1908, [vi], 27, 10—12).—The author states that acetylmethylcarbinol is a normal constituent of wine-vinegars, and that it is formed during the acetic fermentation of the wine. Its presence may be ascertained and its amount determined by subjecting the neutralised vinegar to distillation under reduced pressure or by passing a current of steam. The ketone is then estimated in the distillate either by Fehling's solution or by means of ammoniacal silver nitrate containing sodium hydroxide. 2.85 Grams of copper reduced = 1 gram of methylacetol; 4 atoms of silver = 1 mol. of methylacetol.

Methylacetol is also characterised by yielding with phenylhydrazine acetate an osazone melting at 243°, of which the corresponding osotetrazone melts at 151°. With semicarbazide, a semicarbazone is obtained melting at 200°.

L. DE K.

General and Physical Chemistry.

Chemistry in Space. GIACOMO L. CIAMICIAN (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 3—4).—A reply to Paternò (this vol., ii, 77).
T. H. P.

Stereoisomerism and the Law of Entropy. ARTHUR MICHAEL (*Amer. Chem. J.*, 1908, 39, 1—16).—A theoretical paper, in which attention is drawn to the intimate connexion between the energy relations of stereoisomeric compounds and their chemical behaviour.
E. G.

State in Solution of the Camphorcarboxylates of Aliphatic and Aromatic Amines as revealed by the Rotatory Power. JULES MINGUIN (*Compt. rend.*, 1908, 146, 287—290. Compare Abstr., 1905, ii, 130).—The author has measured the rotatory power of $M/100$ solutions of camphorcarboxylic acid (1) alone; (2) containing equivalent quantities of propyl-, butyl-, diethyl-, and triethyl-amine, and (3) containing excess of the same amines, and finds that the deviations of the rotatory power of solutions (3) from that of solutions (1) are practically the same as those of the rotatory power of solutions (2) from that of solutions (1), showing that the aliphatic amine camphorcarboxylates are undissociated, or only very slightly dissociated, in solution. Moreover, the results verify the law (Haller and Minguin, Abstr., 1903, i, 267) that in the same optically active homologous series the same fraction of the molecular weight under the same conditions produces the same deviation. The aliphatic amines in their capacity as solvents have no influence on the rotatory power. *Propylamine camphorcarboxylate* forms crystals, m. p. 110° (decomp.); the *diethylamine* salt has m. p. 124° , and the *butylamine* salt, m. p. 155° .

Measurement of the rotatory power of $M/300$ solutions of camphorcarboxylic acid in alcohol, ether, benzene, toluene, xylene, and acetone, and of the same solutions containing an equal molecular quantity of aniline, shows that the optical activity of the acid is largely influenced by the solvent, and that the addition of aniline has practically no effect. The conclusion is drawn that *aniline camphorcarboxylate* (solid, m. p. 65° decomp.) is completely dissociated in solution. Excess of aniline lowers the rotatory power from $\alpha^{12} = 3^{\circ}$ (in 2-dm. tube) with an equivalent amount of aniline to $\alpha^{12} = 1^{\circ}26'$ with all aniline. This change is probably due both to the formation of an aniline salt of a lower rotatory power than that of the acid (since α reaches a constant value with the concentration $70M/300$ of aniline), and to the influence of the aniline as a solvent.

Addition of a large excess of aniline to a $M/100$ solution of camphorcarboxylic acid and triethylamine very considerably reduces its rotatory power, and that this is not due to the displacement of the amine from triethylamine camphorcarboxylate by aniline is shown by

the fact that a similar, although smaller, reduction is produced when equivalent quantities of both amines (both largely in excess of the acid) are added to a *M*/100 solution of the acid. A similar phenomenon is observed with butylamine camphorcarboxylate.

The camphorcarboxylates of methylaniline, dimethylaniline, ethylaniline, *o*- and *m*-toluidine, and α - and β -naphthylamine are likewise completely dissociated in solution, and these amines act similarly to aniline towards the aliphatic amine salts. E. H.

Resolution of the Spectral Lines of Barium, Yttrium, Zirconium, and Osmium in a Magnetic Field. BURTON E. MOORE (*Ann. Physik*, 1908, [iv], 25, 309—345).—An attempt has been made to discover series in the spectral lines of certain metals by grouping together those lines which show a similar behaviour in the magnetic field. In the spectra of the metals examined, the types discovered are very complicated, and very few regularities, applicable to more than a small number of lines, could be observed. Yttrium and zirconium are particularly rich in new types of resolution. Runge's rule, that the distances of the components from the middle are aliquot parts of the "normal distance," is confirmed.

C. H. D.

Spectrum of Strontium in the Orange and Red. PETER JECHEL (*Chem. Zentr.*, 1907, ii, 1588—1589; from *Zeitsch. wiss. Photochemie*, 1907, 5, 322—339).—The spectrum of strontium has been photographed with the aid of a large Rowland concave grating, the source of light being an electric arc between carbon poles; the positive carbon is drilled and filled from time to time with strontium chloride. The strontium spectrum in the orange and red consists of five groups of lines and bands, which are described in detail. The results agree satisfactorily with Deslandres's formula. G. Y.

Energetics and Chemistry of Banded Spectra. JOHANNES STARK (*Physikal. Zeitsch.*, 1908, 9, 85—94).—A theoretical paper dealing with the structure of the atom considered as an aggregation of electrons. Two types of electrons are distinguished: the one type, arranged in the form of a ring, represents the positive electricity of the atom, and the second type consists of negative electrons which neutralise the positive charge of the ring and are separated from the atom when ionisation takes place, these being termed valency electrons. Banded spectra are supposed to be determined by the valency electrons, the energy radiated when the valency electrons enter into combination with the positively charged atomic groups representing the potential energy corresponding with the separation of the valency electrons from the atomic aggregates. Three kinds of valency electrons are also distinguished, and the characteristics of banded spectra are discussed in terms of these three types. H. M. D.

Anomalous Modifications of the Band Spectra of Different Compounds in the Magnetic Field. A. DUFOUR (*Compt. rend.*, 1908, 146, 229—231).—The band spectra of strontium and barium

fluoride, and of calcium, strontium, and barium chlorides, obtained by volatilising the salts in a flame placed in the centre of a Weiss electromagnet, exhibit similar anomalous modifications to those observed in the case of calcium fluoride (*ibid.*, 118).
M. A. W.

Spectra of Non-dissociated Compounds. HENRI BECQUEREL (*Compt. rend.*, 1908, 146, 257—259. Compare *ibid.*, 153).—Polemical against Dufour (preceding abstract) (compare also Jean Pecquerel, *Abstr.*, 1906, ii, 317; this vol., ii, 3; Wood, this vol., ii, 150; Henri Becquerel, *Abstr.*, 1889, 553).
E. H.

Spectrum of the Ruby. A. MIETHE (*Ber. Deut. physikal. Ges.*, 1907, 5, 715—717).—In addition to the absorption band noticed by Vogel, the spectrum of the ruby is characterised also by a number of absorption lines, particularly two very close together in the red. These two lines, which with a pocket spectroscope are seen as one line, appear to be due to chromium. The author shows that there is a simple connexion between the position of the absorption lines and the fluorescence lines of the ruby.
J. C. P.

Absorption of Light in Solutions of Aniline Colours from the Standpoint of Optical Resonance. STANISLAW KALANDEK (*Physikal. Zeitsch.*, 1908, 9, 128—134).—According to Kossonogoff's theory (*Physikal. Zeitsch.*, 1903, 4, 208, 258), the absorption bands of a given coloured substance should be displaced towards the red end of the spectrum when the substance is dissolved in solvents with increasing refractive powers. The absorption bands of four colouring matters dissolved in aniline and ethyl alcohol, and of two others in aniline and water, have been compared. The requirements of the theory are satisfied qualitatively in five cases, but with corallin, in aniline and ethyl alcohol, the displacement of the bands is in the opposite direction from that indicated by the theory. An attempt is made to explain the quantitative deviations which are met with in all the cases examined.

The changes in the absorption spectra, which take place when the concentration and thickness of the absorbing column are varied, are also recorded for a number of substances dissolved in water and ethyl alcohol.
H. M. D.

Detection of Ultra-violet Rays. CARL SCHALL (*Chem. Zentr.*, 1907, ii, 1442; from *Phot. Woch.*, 1907, 33, 321—322).—Paper soaked in a solution of 1 gram of *p*-phenylenediamine in 4 c.c. of dilute nitric acid (2 c.c. acid, D 1.2, and 3 c.c. water) and dried rapidly over a bunsen flame is recommended as test paper for ultra-violet rays. On exposure to ultra-violet light, the paper becomes blue, less so on exposure to white light. The paper remains unchanged in daylight in a room, but becomes grey or greyish-blue in the open. The blue colour is produced instantaneously by the rays from a quartz lamp, more slowly by those from a uviol lamp. The rays from gas, Auer, electrical glow, and Nernst lamps do not affect the paper. The spectrum of the Heraeus lamp has a blue band extending into the ultra-violet.
G. Y.

Changes in the Colour of Calcium Sulphide under the Influence of Light. JOSÉ R. MOURELO (*Arch. Sci. phys. nat.*, 1908, [iv], 25, 15—25).—When calcium sulphide is prepared by heating calcium oxide, obtained from different forms of the carbonate, with sulphur or in a current of dry hydrogen sulphide, the white or greyish-white colour of the sulphide is found in many cases to change into a reddish-violet when the substance is exposed to light. Sulphides prepared from calcium sulphite, thiosulphate, or sulphate do not exhibit this colour change. The exact conditions for the production of the colour-sensitive sulphide could not be ascertained, for pure and impure calcium carbonates, natural and artificial, sometimes yield a colour-sensitive sulphide, and at other times, under the same conditions, a sulphide is obtained which is quite inert towards light. The colour-sensitiveness seems to be independent of the phosphorescent power, some samples with strongly, and others with very feebly, developed phosphorescent properties exhibiting the same sensitiveness towards light in regard to the colour change. Experiments are described which indicate that the change in colour is confined to the surface of the sulphide exposed to light. The observed effects are not attributable to oxidation, and are referred to chemical changes directly induced by light. H. M. D.

Pseudo-reversible Photochemical Processes. Photochemical Cyclic Action. ROBERT LUTHER and JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1908, 61, 513—544).—An example of pseudo-reversible photochemical action is furnished by the oxidation of oxalic acid by atmospheric oxygen in presence of light and iron salts. A solution of ferrous oxalate, when kept in the dark in contact with air, changes colour and is oxidised to ferric oxalate. If this solution containing ferric oxalate is exposed to bright light, reduction takes place, ferrous oxalate is regenerated, and carbon dioxide is liberated. This reaction is not a perfectly reversible one, because there is involved an irreversible change, namely, the oxidation of oxalic acid by atmospheric oxygen. It is a case of cyclic action ("Uebertragungskatalyse").

Another case of photochemical catalysis, studied quantitatively by the authors, is the oxidation of phosphorous acid by atmospheric oxygen in presence of light and iodine. The reactions here involved are: (1) $2\text{HI} + \text{O} = \text{I}_2 + \text{H}_2\text{O}$, a change which is slow in the dark, but rapid in light (see Plotnikoff, Abstr., 1907, ii, 212); (2) $\text{H}_3\text{PO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{H}_3\text{PO}_4 + 2\text{HI}$, a reaction which takes place rapidly, and on which light has no influence (see Federlin, Abstr., 1903, ii, 14). The authors show that in the absence of iodine the velocity of the irreversible change, $\text{H}_3\text{PO}_3 + \text{O} = \text{H}_3\text{PO}_4$, is negligibly small either in the dark or in light.

The kinetics of the separate reactions and of the total reaction are considered from the theoretical point of view, and formulæ are deduced for the course of the photochemical change. The results of the experimental work which the authors have carried out are in harmony with their formulæ. Thus the equilibrium concentration of the iodine is proportional to the intensity of the light, proportional to the

velocity of the photochemical reaction, and inversely proportional to the velocity of the opposing reaction (2). It is found, also in harmony with theory, that rise of temperature favours the opposing reaction. From the authors' work, the general conclusion may be drawn that the laws governing pseudo-reversible photochemical reactions resemble very closely those to which perfectly reversible reactions are subject.

The paper contains a description of an apparatus which provides for the constant saturation of a liquid with oxygen, and at the same time permits a determination (from the diminution in volume) of the rate at which the oxygen is reacting with the liquid. J. C. P.

The Atomic Weight of Radium. HENRY WILDE (*Mem. Manchester Phil. Soc.*, 1907, 52, No. 1, 1—3).—The author has previously expressed the view that the atomic weight of radium is 184 (*Abstr.*, 1907, ii, 149); this view is now confirmed by a calculation of its equivalent, which proves to be 92, from the ratio $\text{Ag} : \text{RaCl}_2$. P. H.

Decay of Radium-B and -C at High Temperatures. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1908, 9, 113—117. Compare Makower and Russ, *Abstr.*, 1907, ii, 421; Bronson, *Abstr.*, 1905, ii, 567).—The question as to whether radioactive change is influenced by high temperatures has been again examined experimentally. The method was similar to that adopted by Bronson (*loc. cit.*). The conclusion is drawn that the rate of decay of radium-C is independent of the temperature up to 1300°. This result does not agree with the observations of Makower and Russ (*loc. cit.*), who found that the rate of decay of radium-C was smaller at high temperatures than at room temperature. H. M. D.

Radio-Lead. BELÁ SZILARD (*Compt. rend.*, 1908, 146, 116—118).—The object of this work is to determine how the radiums *D*, *E*, and *F* are separated from the substance known as radio-lead by certain chemical reactions. Recrystallisation of the nitrate from a neutral solution gradually removes the radium-*F* (polonium), which remains in the mother liquor, but does not appreciably influence the amounts of radiums *D* and *E* in the crystals. The same separation can be effected in a strongly acid solution. Addition of sodium ethyl sulphate to a solution of a salt of the active lead, gives, after a time, a slight precipitate containing the greater part of the radiums *E* and *F*, but only a trace of radium-*D*.

Dissolution of radioactive lead carbonate in concentrated sulphuric acid, and evaporation of the filtrate to dryness, leaves a residue only slightly enriched in radium-*D*. Commercial carbamide, but not the pure substance, gives a rosy precipitate in active lead solutions, which contains a great part of the radiums *E* and *F*, but very little of radium-*D*. Ammonium carbonate gives a similar, but less active, precipitate. The latter seems to be a true chemical reaction, and the precipitate has almost the same activity immediately after formation as after several days. Hofmann and Zerban showed (*Abstr.*, 1902, ii, 211; 1903, ii, 732) that the double thiosulphate of sodium and active lead decomposes

spontaneously, giving a precipitate of which the first fractions are more active than those following. The author finds that this reaction is influenced both by light and by filtration, the formation of the precipitate being hastened by these agencies, whilst its composition is changed, its colour becoming red if produced in a strong light. The first fraction is the most active, and contains five to seven times more radium-*D* than the later fractions. The latter have all about the same activity, but contain very little radium-*D*, of which the greatest part remains in solution. If the first fraction is reconverted into nitrate, a second precipitation gives a better yield. In some cases, the separation of the active substances is influenced advantageously by light.

Removal of radium-*D* has not been effected, radium-*F* (polonium) can be removed by many chemical reactions, and radium-*E* also with a little more difficulty. Radiums *E* and *F* in some cases can be removed simply by addition of a substance in suspension. The time constant of radium-*E* corresponds in certain cases with that of radium-*E*₁ and, in others, with that of radium-*E*₂. E. H.

Penetrating Radiation. W. W. STRONG (*Physikal. Zeitsch.*, 1908, 9, 117—119).—Three lines of evidence are brought forward to show that the greater part of the ionisation observed in closed vessels is due to a penetrating form of radiation emitted by radioactive substances present in the atmosphere. In the first place, the radium content of the earth's surface is too small to account for the observed ionisation effects. Secondly, the ionisation is found to vary with changes in the atmospheric conditions; with normal atmospheric conditions, diurnal variation similar to that exhibited by temperature can be traced. Thirdly, constant ionisation values are observed in caves, there being no evidence of diurnal variation. H. M. D.

Have X-Rays an Action on Radioactive Substances? CHARLES E. GUYE, A. SCHIDLOF, and M. KERNBAUM (*Arch. Sci. phys. nat.*, 1908, [iv], 25, 26—35).—Experiments have been made to ascertain whether the rate of decay of the activity of radioactive substances is altered when they are subjected to the action of X-rays. The substances examined were polonium, the induced activity from radium, an impure radium compound, and radium emanation; the rate of decay of these when acted on by X-rays being directly compared with the rate when not subjected to this influence. In no case was any definite difference observable. H. M. D.

So-called Moser-Rays. ELISABETH LÉGRÁDY (*Zeitsch. Photochem.*, 1908, 6, 60—67).—The photochemical action exhibited by certain metals in the dark has been investigated. By means of a small, gas-tight chamber provided with inlet and outlet tubes, the influence of different gases and of moisture on the activity of the metals could be examined.

In the absence of metals, the photographic plates were not acted on when dry air, nitrogen, or hydrogen was passed through the chamber. A negative result was also obtained with dry air and nitrogen in the

presence of freshly-polished aluminium, cadmium, magnesium, and zinc, but the plates were acted on when the gases were not dried. Hydrogen was found to be active in the presence of the above metals whether dried or moist.

From these observations, the author draws the conclusion that the metals, *per se*, have no photochemical properties, and that the observed photochemical effects are dependent on the presence of hydrogen (or hydrogen compounds). The directly active agent is supposed to be ionised hydrogen, which is produced from molecular hydrogen (or from water) by the action of the metals.

Experiments are also described which show that the action cannot be attributed to the emission of active rays by the metals, or by the ionised hydrogen. Certain metals appear to exhibit two kinds of photochemical activity, but the second type, which gives rise to light pictures, has not been examined in detail.

H. M. D.

Radioactivity of the Kissingen Mineral Springs. FELIX JENTZSCH (*Physikal. Zeitsch.*, 1908, 9, 120. Compare this vol., ii, 9).—The author withdraws his criticism of the formula used by H. W. Schmidt (*Physikal. Zeitsch.*, 1906, 7, 209) for calculating the radioactivity of mineral waters from ionisation experiments. The difference between this formula and that employed by the author is due to a slight modification in the experimental method.

The numbers previously given for the water of the Rakoczy spring are recalculated on the assumption that the natural radiation in a closed electroscope is to be referred to causes other than the emanation present in the air. Data are given for the activity of samples of Rakoczy water which have been kept for periods reaching to three years. The activity decreases for about fifteen months and then increases, and it is suggested that this may be due to the gradual formation of an emanation-emitting substance.

H. M. D.

Radioactivity of the Waters of Lavey-les-Bains. ED. SARASIN, CHARLES E. GUYE, and JULES MICHELI (*Arch. Sci. phys. nat.*, 1908, [iv], 25, 36—44).—The radioactivity of the Lavey springs has been measured by the method of Elster and Geitel, and found to be 11 in terms of Mach's unit. With the exception of the Dissentis springs, this represents a radioactivity of much greater magnitude than that of any Swiss waters which have been examined. The activity is probably due to radium emanation, since it falls to the half value in four days.

H. M. D.

Radioactivity of the Waters of Plombières. ANDRÉ BROCHET (*Compt. rend.*, 1908, 146, 175—177).—The author has determined the radioactivity of minerals and other solids, of gases, and of waters collected in Plombières. That of the solids is either zero or approaches the limit of sensitiveness of the apparatus (a Curie electroscope having an aluminium leaf and micrometer, adapted to a condenser).

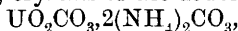
Three hours after collection, the gas from the Vauquelin spring had a radioactivity of 14.9; from the Thalweg gallery, 13.6, and that from the Savonneuses gallery, 6.1, expressed in milligramme-minutes

per 10 litres of gas. For the former two gases, Curie and Laborde found 5.7 and 3.2 respectively, but their experiments were made four days after collection.

The radioactivity of the gas extracted from the water from Vauquelin (temperature 69°) is 0.84 (Curie and Laborde found 0.22); of Roman Robinet (temperature 70°), 0.43; from the Capucins (temperature 46°), 2.03 (Curie and Laborde found 0.46), and from the Savonneuses gallery, No. 1 (temperature 22°), 0.75, No. 2 (temperature 28°), 1.29. The emanation extracted from the water from the Capucins loses half its activity in four days. The results establish the fact that there is no relation between the radioactivity of the waters and their temperature.

E. H.

Anomalous Behaviour in the Radioactivity of Certain Uranium Compounds. HERMAN SCHLUNDT and RICHARD B. MOORE (*Physikal. Zeitsch.*, 1908, 9, 81—85).—When excess of a hot 4-normal ammonium carbonate solution is added to a nearly saturated solution of uranyl nitrate, the uranium and uranium-*X* both dissolve completely. On cooling, crystals of the double carbonate,



separate, but the whole of the uranium-*X* remains dissolved.

The radioactivity of the double carbonate increases after a time, a maximum being attained at the end of about twelve days. A similar increase takes place when the substance is gently heated. In both cases, the increase in activity is accompanied by a slight deepening of the yellow colour of the crystals. The phenomenon appears to be due to the decomposition which the substance undergoes, the removal of ammonia, carbon dioxide, and water resulting in a diminution of the retardation of the particles which are emitted by the active element contained in the compound. The increase in the activity is proportional to the loss of weight, a similar effect being observed when thin layers of uranyl acetate and nitrate are gently heated. The experimental results are compared with the calculated increases in activity, assuming that the retarding power of the volatile products of decomposition is inversely proportional to the square root of the atomic weights of the elements contained in these products.

H. M. D.

Association of Helium and Thorium in Minerals. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1907, 80, A, 56—57).—Boltwood (*Abstr.*, 1907, ii, 220) has recently suggested that the helium in radioactive minerals always originates from the uranium-radium series of transformations. The author has now examined a mineral from Greenland yielding helium, which contains only traces of radium, much too small to account for the helium present, but yields abundant thorium emanation; he therefore considers that the helium in this case is a product of thorium radioactivity.

G. S.

Ionium. WILLY MARCKWALD and B. KEETMAN (*Ber.*, 1908, 41, 49—50).—The authors' investigations confirm the results obtained by Boltwood (*Abstr.*, 1907, ii, 836) and Hahn (*ibid.*, 921). Attempts to separate ionium and thorium have as yet been unsuccessful.

An investigation of autunite shows that 10 grams of this mineral does not contain so much as 0.1 mg. of lead; this is remarkable, since lead is generally supposed to be the final product of the transformation of uranium.

W. H. G.

Amalgam Concentration Cells, Chemical Cells, and Daniell Cells Constructed with Solid Electrolytes. M. KATAYAMA (*Zeitsch. physikal. Chem.*, 1908, 61, 566—587).—The *E.M.F.* of the cells referred to was measured by the usual compensation method, except that a quadrant electrometer was employed as zero instrument.

The first type of cell studied was Pb amalgam c_1 | solid PbBr_2 | Pb amalgam c_2 , and it is shown that the *E.M.F.* of such a cell may be calculated by the formula $E = RT/2F \cdot \log c_2/c_1$, where c_2 and c_1 are the concentrations of the lead in the two amalgams.

The chemical cells were of the type Metal | Metallic haloid | Halogen, and many precautions, detailed in the paper, must be observed if trustworthy values for the *E.M.F.* of such a cell are to be obtained. The cells actually examined were as follows: Ag | solid AgCl | Cl, for which $E = 1.130 + 0.0006 (20 - t)$ between 15° and 159° ; Pb | solid PbCl_2 | Cl, for which $E = 1.581 + 0.00065 (60 - t)$ between 60° and 155° ; Pb | solid PbBr_2 | Br, for which $E = 1.338 + 0.00065 (60 - t)$ between 60° and 162° .

Three cells of the type of the Daniell element were also constructed and studied, with the following results: Pb | solid PbCl_2 | solid AgCl | Ag, $E = 0.480 + 0.0001 (60 - t)$ between 23° and 151° ; Pb | solid PbBr_2 | solid AgBr | Ag, $E = 0.342 + 0.00025 (20 - t)$ between 20° and 145° ; Ag | solid AgCl | solid AgBr | Ag, $E = 0$, except for slight differences due to experimental errors.

J. C. P.

Concentration Cells. I. Cadmium Chloride Cells. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1506—1521).—Three kinds of concentration cells were investigated in various cadmium chloride solutions: (1) those in which there is no transport of an ion; (2) those in which the anion is transported; (3) those in which the cation is transported.

Curves are drawn showing the relation between the logs. of concentration of the solution and the corresponding *E.M.F.* for the three cases. The following concentration cells were studied: Cd | $m\text{CdCl}_2\text{aq}$ | $n\text{CdCl}_2\text{aq}$ | Cd; Cd | $\text{CdCl}_2\text{aq} \cdot \text{KCl}$ | $\text{HgCl} \cdot \text{Hg}$; $\text{Hg} \cdot \text{HgCl}$ | $m\text{CdCl}_2\text{aq}$ | $n\text{CdCl}_2\text{aq}$ | $\text{HgCl} \cdot \text{Hg}$; Ag. AgCl | $m\text{CdCl}_2\text{aq}$ | $n\text{CdCl}_2\text{aq}$ | AgCl. Ag; Cd | $m\text{CdCl}_2\text{aq}$ | AgCl. Ag. AgCl | $n\text{CdCl}_2$ | Cd (where m and n are the concentration of the solutions and $m > n$).

It is impossible to apply Moser's method here for the calculation of the transport numbers, but another method for effecting this is deduced. When, however, the numbers so obtained for chlorine in cadmium chloride are compared with those obtained by the customary Hittorf's method, they agree well for dilute, but not for concentrated, solutions; the conclusion is therefore drawn that, whereas Nernst's theory of diffusion for electrolytes is completely justified for dilute solutions, it is not applicable to concentrated solutions, and in all probability the laws governing the latter are of an essentially different character.

Z. K.

Alkali Electrode. PAUL T. MULLER and H. ALLEMANDET (*J. Chim. Phys.*, 1907, 5, 533—556).—The authors have prepared an alkali electrode consisting of mercury and yellow mercuric oxide in contact with solutions of different bases. The purification of the reagents and the arrangements employed for preventing contamination with carbon dioxide during the measurements are fully described. In order to increase the conductivity, the solution in the alkali compartment also contained potassium nitrate.

The electrode was connected with a calomel electrode, thus constituting a cell $\text{Hg} \mid \text{HgCl} + \text{KCl} \mid \text{KNO}_3 + \text{KOH} + \text{HgO} \mid \text{Hg}$, and the potential measurements carried out by the compensation method at 25°. Results are given for $N/10$ to $N/1000$ solutions of the hydroxides of potassium, sodium, lithium, thallium, barium, strontium, and calcium, and it is shown that with proper precautions the *E.F.M.*'s are reproducible to about a millivolt. In $N/100$ solution, the so-called "absolute" value of the single potential difference (calculated by means of Ostwald's value for the calomel electrode) varies only from 0.5042 to 0.5078 for the different bases, the mercury being positive, in satisfactory agreement with the view that the OH' ion concentration alone determines the potential. At higher concentrations, the alkaline earth bases give a slightly greater *E.M.F.* than the alkali bases, indicating a less complete electrolytic dissociation in the former case, but the difference in the degree of dissociation in corresponding solutions could not be calculated from the results, owing to the uncertainty introduced by the diffusion potential at the liquid junction.

Even in the most dilute solutions there is a slight difference of potential, not much greater than the experimental error, between the *E.M.F.* of the potassium and sodium electrodes; this is ascribed to the fact that in the former case the potassium nitrate added to increase the conductivity has an ion in common with the alkali surrounding the electrode.

G. S.

Nickel Peroxide Electrodes. FRITZ FOERSTER (*Zeitsch. Elektrochem.*, 1907, 13, 414—434).—Bellucci and Clavari (Abstr., 1905, ii, 823) have shown that, in the oxidation of nickelous hydroxide, the primary product is always NiO_2 . The author finds that the active mass of a nickel peroxide accumulator plate after complete discharge consists of $\text{Ni}(\text{OH})_2$ when it is dried over sulphuric acid. The active oxygen in a fully-charged electrode was estimated by treating a portion of it with acid hydrogen peroxide and measuring the oxygen evolved, or by boiling with hydrochloric acid and estimating the chlorine produced; in this way, it was found that the oxidised mass contains from 0.53 to 0.56 atom of active oxygen to 1 atom of nickel. After washing and drying as quickly as possible over sulphuric acid, the substance had the composition $\text{Ni}_2\text{O}_3 \cdot 1.1\text{—}1.3\text{H}_2\text{O}$. This is quite stable when dry, but decomposes slowly at the ordinary temperature when wet. The equilibrium potential of a charged electrode in 2.8*N*-potassium hydroxide solution diminishes, quickly at first, more slowly afterwards, to a constant value which is identical with that obtained with Ni_2O_3 . Oxygen gas is evolved during this change. The decreased concentration of the potassium hydroxide in

the pores of the electrode, due to the charging, would account for a higher potential at first, but it is found that a similar increase of potential at the iron electrode disappears in less than one hour, whereas twenty to thirty days are required for the peroxide electrode. The author therefore regards it as more probable that the fully-charged electrode consists of a solid solution of NiO_2 in Ni_2O_3 . The evolution of oxygen which takes place from a freshly-charged electrode is due to the decomposition of the NiO_2 .

The author does not agree with Zedner (Abstr., 1906, ii, 595) as to the meaning of the different portions of the discharge curve. The comparatively rapid fall of *E.M.F.* at the beginning of the discharge is regarded as due to the disappearance of the NiO_2 existing in solid solution in Ni_2O_3 . The first period of approximately constant *E.M.F.* corresponds with the reduction of Ni_2O_3 to $\text{Ni}(\text{OH})_2$, and the second period of constant *E.M.F.* (about 0.55 volt below the first) is due to an oxide lying between Ni_2O_3 and NiO . In charging the electrode, a higher *E.M.F.* is required than that observed during discharge, owing to the fact that NiO_2 is the primary product of oxidation, Ni_2O_3 being formed by its reaction with $\text{Ni}(\text{OH})_2$, the change is therefore not strictly reversible.

T. E.

[Nickel Oxide Electrode.] FRITZ FOERSTER (*Zeitsch. Elektrochem.*, 1908, 14, 17—19).—A reply to Zedner's criticism (this vol., ii, 12); the author maintains that the behaviour of a freshly-charged nickel oxide electrode is quite inexplicable on Zedner's assumption that it contains occluded oxygen, but is in complete harmony with the view that it contains NiO_2 . The actual degree of hydration of the oxides contained in the electrode in contact with the concentrated solution of potassium hydroxide cannot be determined by analysis of washed and dried samples.

T. E.

Wehnelt Cathode in High Vacua. A. WEHNELT (*Physikal. Zeitsch.*, 1908, 9, 134—135).—The author replies to Soddy (this vol., ii, 81), and maintains that he has never held the view attributed to him that the large currents attainable in spectrum tubes provided with a Wehnelt cathode are entirely due to electrons emitted by the strongly heated cathode. It is, however, claimed that currents may pass through highly exhausted tubes, in which the only carriers are the electrons emitted by the cathode, but the intensity of such currents is of a much smaller order of magnitude (10^{-2} amperes). The fact that maximum saturation currents are obtainable which are independent of the pressure, provided this is less than 0.1 mm., is evidence of such electron currents.

The part played by the electrons emitted by the hot cathode in the case of the larger ionisation currents, consists in the removal of the large fall of potential at the cathode, which results from the deficiency of electrons in consequence of the very different velocities of the positive ions and the electrons.

H. M. D.

Electrical Resistance and Expansion of the Metals. WITOLD BRONIEWSKI (*J. Chim. Phys.*, 1907, 5, 609—635. Compare Abstr., 1906, ii, 646; *J. Chim. Phys.*, 1907, 5, 57).—In previous

papers, the relation between the variation of the electrical resistance and the expansion of monatomic metals and of some polyatomic metals has been dealt with; in the present paper, the consideration of polyatomic metals is completed, and a résumé of the results is given.

The polyatomic metals are divided into two groups: (a) the iron group, "for which the space between the atoms is constant"; (b) the antimony, selenium, and gallium groups, "for which the space between the atoms is variable." The behaviour of the first group has already been considered (*loc. cit.*).

Unlike monatomic metals, the quotient of the atomic latent heat of fusion by the absolute temperature of fusion is not constant for polyatomic metals; it is 4.86 for bismuth, and 1.80 for thallium. For the second group of metals mentioned, it is shown from available data that the variation of the electric resistance with temperature is represented satisfactorily by the formula $\gamma_t = \text{const.} \times T(2F + T)$, where γ_t is the resistance at a definite temperature, T is the absolute temperature, and F is the absolute temperature of fusion, a formula which also holds for monatomic metals.

Matthiesson has shown (1863) that for a pure and impure form of the same metal the relation $\gamma R = \gamma' R'$ holds, where γ and γ' and R and R' are the temperature-coefficients and the specific resistances of the pure and impure metal respectively. The limiting specific resistances, R , for a number of pure metals are calculated from the known values of γ, γ' and R' , and the results are compared with the experimental values. It is considered probable that the observed diminution of the temperature-coefficient of the resistance of palladium and platinum with temperature is due to traces of impurities, and that the pure metals, like nearly all other metals, have a positive temperature-coefficient of conductivity. G. S.

Ionisation of Liquid Dielectric Media by Radium Rays. GEORGE JAFFÉ (*Ann. Physik*, 1908, [iv], 25, 257—284).—The electrical conductivity of light petroleum, carbon tetrachloride, carbon disulphide, and benzene is increased by exposure to radium rays. The relation between the current (i) thus produced and the *E.M.F.* (e) applied to the electrodes is: $i = f(e) + c.e$, where c is a constant. When the field strength is greater than a certain value between 500 volt/cm. and 1000 volt/cm., the term $f(e)$ is a constant, and the relation between current and potential is then a linear one. There is thus considerable analogy between the behaviour of liquid dielectric media exposed to the action of radium rays and the behaviour of ionised gases.

J. C. P.

A Relation Between Ionic Mobility and Temperature-coefficient. EWALD RASCH and F. WILLY HINRICHSSEN (*Zeitsch. Elektrochem.*, 1908, 14, 46—47).—Using the values calculated by Kohlrausch and Drucker, it is shown that the product $a_{18} \cdot \log l_{18}$ is a constant, l_{18} and a_{18} being the mobility of an ion and its temperature-coefficient at 18°. The values of the constant calculated lie between 0.0367 and 0.0404 for the univalent ions, and between 0.0407 and 0.0434 for the bivalent ions. T. E.

Abnormal Mobility of the Ions of some Rare Earths.

JULES ROUX (*Compt. rend.*, 1908, **146**, 174—175).—The mobility of the univalent ions, except hydrogen (318) and hydroxyl (174), approximates to the value 67 (Cl, 65; Rb, 68), that of the bivalent ions to 48 (Zn, 46; Ca, 51), and that of the negative trivalent ions to 85 ($\frac{1}{3}$ [Fe(CN)₆], 82; $\frac{1}{3}$ [Cr(CN)₆], 90). Hitherto, the mobilities of the positive trivalent ions have not been determined, owing to the hydrolysis of their salts. Some of the metals of the rare earths, however, form perfectly neutral solutions, and by measurement of the conductivity of solutions of lanthanum nitrate and of the bromides (prepared by Bourion's method, *Abstr.*, 1907, ii, 773) of lanthanum, yttrium, cerium, gadolinium, and samarium at concentrations 1/100th, 1/200th, and 1/10,000th normal, the author has determined the mobility of the ions of these metals. The following values were obtained at 18° with respect to mercury at 0°. Lanthanum (in nitrate), 111 at *N*/100, 112 at *N*/200; (in bromide) 111 at *N*/100, 112.5 at *N*/200, 116 at *N*/10,000; yttrium, 115 at *N*/100, 116.5 at *N*/200; cerium, gadolinium, and samarium, 112, 91, and 66 respectively at *N*/100. Thus these ions (except that of samarium) have a greater mobility than either univalent, bivalent, or negative trivalent ions. The low value for samarium suggests the possibility of separating this metal from the others by diffusion or by electrolysis. With a rise of temperature, the mobility of the lanthanum ion in *N*/100 solutions of the nitrate increases from 111 at 18° to 131 at 25°.

E. H.

A Relation Between Electrical Conductivity and Temperature. EWALD RASCH and F. WILLY HINRICHSSEN (*Zeitsch. Elektrochem.*, 1908, **14**, 41—46).—An equation of the same form as van't Hoff's equation ($d\log K/dT = -q/RT^2$) expresses the connexion between the conductivity of an electrolyte and the temperature. Putting α , the conductivity, in place of *K*, and assuming that *q* is a thermal constant, the exact physical meaning of which is undefined, there is obtained, after integration, $\log \alpha = -\gamma/T + C$, where γ and *C* are constants. This equation is shown to hold good for antimony trichloride (100—210°), three kinds of glass (200—350°), porcelain (50—210°), linseed oil (24—135°), water and ice (−17—50°), a mixture of zirconia and yttria (432—987°), and fused sodium chloride (800—950°). The numbers in brackets are the temperatures between which the relationship is tested.

T. E.

Electrolytic Conductivity of Bromine and Iodine in Nitrobenzene Solution. LUDWIK BRUNER (*Bull. Acad. Sci. Cracow*, 1907, 731—738. Compare Bruner and Dluska, this vol., i, 146).—The results obtained in the investigation of the action of bromine on toluene in nitrobenzene solution having suggested that halogens are electrolytically dissociated in this solvent, the author has commenced the study of the conductivity of bromine and iodine in organic solvents. The present paper contains an account of the preliminary experiments. It is found that bromine and iodine in nitrobenzene solution have a marked conductivity, which varies with the time.

The cause of this variation remains unknown, but cannot be a substitution in the nucleus of the solvent, since in that case the variation would increase with the concentration, whereas it is found to be greatest in dilute solution. The value of Δ increases rapidly in concentrated solutions, the resistance being almost independent of the concentration.

Bromine does not conduct in carbon tetrachloride, nor does iodine in toluene solution. G. Y.

Conductivity of Picric Acid Solutions and the Ionic Conductivity of Hydrogen. HERBERT GORKE (*Zeitsch. physikal. Chem.*, 1908, **61**, 495—502).—The conductivity of dilute solutions of picric acid has been determined with special precautions. Extrapolation of the observed values gives $\Lambda_{\infty} = 346.4$ at 18° and $\Lambda_{\infty} = 384.3$ at 25° . From these figures, it may be shown that picric acid does not obey Ostwald's dilution law (compare Rothmund and Drucker, *Abstr.*, 1904, ii, 231). The conductivity of solutions of sodium picrate has also been measured, and the conductivity of the picrate ion is found to be 26.0 and 30.7 at 18° and 25° respectively. Hence the ionic conductivity of hydrogen is 320 at 18° and 353 at 25° , and the temperature-coefficient is 0.0148 (compare Kohlrausch's value 0.0153). These values for the ionic conductivity of hydrogen are higher than those given by Kohlrausch and by Ostwald and Luther. The author himself regards them as possibly 1% too low; even allowing for this, they would still be lower than the values which are deduced from Noyes and Sammet's work (*Abstr.*, 1903, ii, 126). J. C. P.

The Existence of Positive Electrons in the Sodium Atom. ROBERT W. WOOD (*Phil. Mag.*, 1908, [vi], **15**, 274—279; *Physikal. Zeitsch.*, 1908, **9**, 124).—Plane polarised white light is passed through sodium vapour, unmixed with any other gas, and placed in a strong magnetic field parallel to the direction of the light. Before exciting the magnet, a Nicol prism is placed so as to extinguish the light which has passed the sodium vapour. When the magnet is excited, a large number of bright lines become visible when the light which now passes the second Nicol is examined spectroscopically. The author has succeeded in showing that in some of these lines the plane of polarisation has been rotated to the right, and in others to the left. Since the direction in which the plane of polarisation is rotated by the *D* lines indicates that they are due to the vibration of negative electrons, the opposite rotation observed in some of the lines would indicate the existence of positive electrons in the sodium atom.

T. E.

Difference of Potential in the Arc Produced by a Continuous Current between Metallic Electrodes. CHARLES E. GUYE and L. ZEBRIKOFF (*Arch. Sci. phys. nat.*, 1907, [iv], **24**, 549—574).—The formula deduced by Mrs. Ayrton for the relation between the length of the arc, the difference of potential, and the intensity of the current was verified by her when carbon poles were used. The authors find

that this formula is applicable also when the poles consist of gold, platinum, silver, palladium, copper, cobalt, nickel, or iron.

J. C. P.

Electric Discharge in Monatomic Gases. FREDERICK SODDY and THOMAS D. MACKENZIE (*Proc. Roy. Soc.*, 1908, 80, A, 92—109).—The high resistance offered to the electric discharge in spectrum tubes containing monatomic gases has been studied. For this purpose, the conditions of the discharge through helium, argon, neon, mercury, hydrogen, nitrogen, and carbon dioxide have been compared. Non-conductance equivalent to that represented by an inch gap in air at atmospheric pressure was attained at the following pressures: helium 0.35 mm., argon 0.04 mm., neon 0.07 mm., hydrogen 0.03 to 0.04 mm., nitrogen 0.035 mm., carbon dioxide 0.02 mm. of mercury. With a spark gap of 10 mm., mercury vapour was found to conduct with difficulty at a pressure of 0.1 mm., and thus resembles helium in regard to the high pressure at which it ceases to be conducting. The results obtained indicate that the difference between helium and other gases is one of degree only, and that the monatomic gases are relatively inert, electrically as well as chemically. To explain the observed facts, it is only necessary to assume that the helium molecule is at all pressures only about one-fifth to one-tenth as effective electrically as a molecule of hydrogen. This view has been confirmed by determining the relation of the potential to the pressure in helium, argon, and hydrogen at high pressures. Some observations relating to the Campbell Swinton effect indicate that the bubbles formed when the glass of a discharge tube is fused are due to chemical decomposition of the glass under the influence of the local heating, which takes place in the course of the bombardment of the glass by the enclosed gas particles.

H. M. D.

Certain Phenomena Exhibited by Small Particles on a Nernst Glower. C. E. MENDENHALL and L. R. INGERSOLL (*Phil. Mag.*, 1908, [vi], 15, 205—214).—Small globules (0.1 to 0.2 mm. diameter) of molten metals may be supercooled as much as 370° (rhodium and platinum). Gold, palladium, silicon, and iridium behave similarly. A flash, due to liberation of the latent heat, occurs at the moment of solidification. A reversible change in radiating power occurs in rhodium at 1050°. Small globules of molten metals slide or roll along a Nernst glower, and solid particles roll end over end. Boron, rhodium, palladium, silver, barium oxide, columbium oxide, iridium, platinum, and gold move with the current, and magnesium oxide, silicon, titanium, chromium, manganese, iron oxide, cobalt, nickel, copper, and ruthenium against it. The rate of motion varies widely with the nature of the particle, cobalt and copper giving the fastest motion; it also increases with the current flowing, and to a less extent with the temperature. Carbon dioxide, oxygen, or a vacuum do not affect the motion. It does not occur on metallic conductors. No satisfactory explanation of the motion has been found.

T. E.

Magnetic Behaviour of Air, Argon, and Helium in Relation to Oxygen. PAUL TÄNZLER (*Ann. Physik*, 1907, [iv], 24, 931—938).—Whilst air and oxygen are paramagnetic, argon and helium are diamagnetic. J. C. P.

Decomposition of Complex Chemical Compounds in a Variable Magnetic Field. J. ROSENTHAL (*Sitzungsber. k. Akad. Wiss. Berlin*, 1908, 20—26).—Evidence has been obtained that complex organic compounds are decomposed when subjected to the action of varying electromagnetic forces. The substances examined, dissolved or suspended in water, were brought into a solenoid, through the coils of which intermittent or alternating currents were passed. For the success of the experiment, the frequency of intermittence or alternation must have a definite value which depends on the nature of the substance examined. With the requisite frequency, the heat developed in the liquid is very much smaller than when other frequencies are employed, and the author supposes that, in the first case, the energy is chiefly used up in bringing about the decomposition of the complex molecules, whilst with unfavourable frequencies rise of temperature is the only result. For starch, the effective frequencies lie between 440 and 480 oscillations per second, and for proteins the number is 320—360, whilst other substances examined (glucosides, disaccharoses) require very much higher frequencies. The decomposition of starch takes place in stages, the succession of products being the same as those found in the action of diastatic enzymes. Proteins give rise to albumoses and peptones. The analogy between the action of the electromagnetic forces and that of enzymes is regarded as important from the standpoint of the general theory of enzyme action.

H. M. D.

Zeeman Phenomenon. W. LOHMANN (*Zeitsch. Photochem.*, 1908, 6, 1—24, 41—60).—By means of an echelon diffraction grating, the Zeeman phenomenon has been investigated for the chief spectral lines of sodium, mercury, helium, neon, and krypton. Observations were made parallel and at right angles to the magnetic lines of force, and the gradual resolution of the spectral lines with increasing intensity of the magnetic field was traced by observations in fields varying from about 2000 to 15,000 Gauss. Here it may be noted that the extent to which the component lines are separated is proportional to the strength of the magnetic field. The differences in the Zeeman effect, which are observable with the different spectral lines, indicate that these are to be ascribed to atoms of unlike structure.

H. M. D.

Expansion of Commercial Pentane and the Scale of the Pentane Thermometer. FRIEDRICH HOFFMANN and RUDOLF ROTHE (*Chem. Zentr.*, 1907, ii, 1369—1370; from *Zeitsch. Instrumentenkunde*, 1907, 27, 265—271).—The expansion of commercial pentane has been calculated previously from observations at three fixed points with the aid of a quadratic interpolation formula. The authors' determinations show that the error of pentane thermometers standardised in this

manner may amount to 2° . It is necessary to determine the expansion at least at four points. In the method employed, two dilatometers filled with pentane are compared with a platinum resistance thermometer. A thermostat, cooled by liquid air and electrically heated, for use at temperatures between -190° and -130° is described. The expansion at t° is represented by the expression: $A_t = 10^{-6}t(1506.97 + 3.453_5t + 0.0097_5t^2 - 0.00001t^3)$. The corrections to be applied to the old pentane thermometer at different temperatures are given in a table. The b. p. of oxygen as observed by Grunmach (Abstr., 1906, ii, 655), when corrected for the error of the pentane thermometer, for the pressure, and for the presence of 2% of nitrogen, is $-182.66^{\circ}/760$ mm., which is in agreement with the observations of other investigators. G. Y.

Measurement of the Velocity of Sound in Liquids and of the Ratio of the Two Specific Heats of Ether with the Help of Kundt's Dust Figures. KARL DÖRSING (*Ann. Physik*, 1908, [iv], 25, 227—251).—The liquids examined were water, alcohol, ether, strong ammonia solution, concentrated hydrochloric acid, sodium chloride solutions, chloroform, carbon disulphide, turpentine, and "benzin."

With rising temperature, the velocity of sound in water increases, whilst the velocity in other liquids diminishes. In liquids which contain either dissolved gases or salts, the velocity of sound increases with the amount of the dissolved gas or salt. The ratio of the two specific heats for ether at 15° is 1.376.

It should be noted that in order to obtain dust figures in liquids, the vibration of the liquid column must be in harmony with that of the containing tube. The dust employed by the author was powdered pumice stone. J. C. P.

A New Method of Determining the Melting Point of Metals. IWAN I. SHUKOFF and W. J. KURBATOFF (*J. Russ. Phys. Chim. Soc.*, 1907, 39, 1546—1548).—A similar apparatus has been described by Loebe (Abstr., 1907, ii, 735), but the authors claim priority. Z. K.

Internal Friction and Density of the Bunsen Flame. AUGUST BECKER (*Ann. Physik*, 1907, [iv], 24, 823—862).—Measurements have been made of the extent to which small solid spheres are buoyed up at various points in the interior of a bunsen flame, and in currents of different gases moving with known velocity. From these observations, it appears that the variation of the internal friction from point to point of the bunsen flame is similar to that detected by Bunsen for the thermal and chemical action, and by Lenard for the emissivity. From the variation of the internal friction, it is possible to make an estimate of the composition of the gaseous mixture at different points in the flame. J. C. P.

Curves of Instantaneous Heat Power determined from Chemical Reactions. ALDO MIELI (*Gazzetta*, 1907, 37, ii, 636—647).—The heat power of a constant source of heat is defined as the quantity of heat, either positive or negative, developed per unit

of time. With a variable heat source, the notion of an instantaneous heat power must be employed. The author deduces theoretically the time curves of instantaneous heat power for different chemical reactions.

For a simple isothermal reaction, this curve is homologous with that expressing the velocity of the reaction. The same is the case with reversible or lateral reactions, but with polygrade reactions the two curves are not homologous. Similar relations hold for these various types of reactions when the latter take place adiabatically.

The general case, in which a reacting system is exchanging heat with its surroundings, but is not at constant temperature, is also considered.

T. H. P.

Calorimetric Method Applied to the Study of Slow Reactions. JACQUES DUCLAUX (*Compt. rend.*, 1908, 146, 120—123).—The corrections, which must be applied to the numbers observed in the calorimetric study of a reaction, and become large and uncertain when the reaction is a slow one, can be reduced to very small quantities by using as a calorimeter a Dewar tube provided with a cork and immersed completely in the water of a thermostat, and by ensuring that initially the tube and liquids studied have the same temperature as the thermostat. For a tube containing 35 c.c. of liquid and having an excess temperature of 1° after one minute duration, the correction is only 0.002° , and the method has the very great advantage that this correction can be determined once for all with an approximation of at least 1 in 20. The volume of air above the liquid being small, no correction is necessary for evaporation, and the rise of temperature being slow, the lag of the thermometer causes an inappreciable error. The only difficulty, arising when it is required to measure absolute quantities of heat, consists of the determination of the water-equivalent of the calorimetric tube, which may amount to 20% of the whole heat value. It can be determined either from the dimensions of the tube, or by comparative experiments with substances developing a known quantity of heat.

Besides being used for thermochemical measurements, the method has a very important application in the study of diastatic reactions of all kinds. By its means, the course of a reaction can be followed, since, in the absence of any complication due to a secondary reaction, the quantity of matter transformed in dilute solutions is proportional to the rise of temperature, continued observations of which will therefore lead to the determination of the law of the transformation. The method has been successfully applied to the catalysis of hydrogen peroxide solutions by ferric hydroxide, the inversion of sucrose, and the saponification of ethyl and amyl acetates. The degree of accuracy obtained when using a thermometer reading to 0.02° is two to four times less than the ordinary titrimetric or polarimetric methods, but it could be increased at the expense of simplicity by using an electrical thermometer. The method has the advantage of being applicable to any liquid whatever at any temperature below 100° , the only condition essential being that an appreciable quantity of heat is developed.

E. H.

Determination of the Heat of Combustion of Organic Compounds by Use of the Platinum Resistance Thermometer. EMIL FISCHER and FRANZ WREDE (*Sitzungsber. k. Akad. Wiss. Berlin*, 1908, 129—146).—By substituting a platinum resistance thermometer for the mercury thermometer commonly used, the accuracy with which the heat capacity of the bomb, stirrer, &c., can be determined is considerably increased. The estimated maximum possible error in the calibration of the apparatus used by the authors is 0.05%.

For the purpose of obtaining standard values which may be used in the calibration of other calorimetric bombs, the heats of combustion of sucrose and benzoic acid have been carefully determined. The calculated heats of combustion for 1 gram of substance (weighed in vacuum) are for sucrose 16.545, for benzoic acid 26.475, kilowatt seconds. Assuming that 1 kilowatt second = 0.2390 Cal., the numbers are respectively 3.954 and 6.328 Cal.

H. M. D.

Heat of Formation of Anhydrous Barium and Strontium Oxides. ROBERT DE FORCRAND (*Compt. rend.*, 1908, 146, 217—220).—Pure anhydrous barium and strontium oxides can be obtained in the form of colourless powders by heating the corresponding hydroxide in a current of dry hydrogen at 800—850° (Abstr., 1907, ii, 683, 928). The heats of solution of these oxides, calculated from their heats of solution in dilute hydrochloric acid, are for 1 gram-molecule of SrO in 20 litres and 1 gram-molecule of BaO in 12 litres of water at 15°, 30.8 Cal. and 35.640 Cal. respectively. The discrepancies between these values and those obtained by Thomsen (29.34 Cal. and 34.52 Cal.) are probably due to the impurities which are always present in alkali-earth oxides obtained by ignition of the nitrates. The heat of formation of the oxide of calcium, lithium, strontium, or barium, calculated from the heat of solution of the oxide (Abstr., 1907, ii, 683, 928) and of the metal (Guntz, Abstr., 1903, ii, 410; 1905, ii, 300; 1906, ii, 229), is 151.90, 143.32, 137.60, or 125.86 Cal. respectively, and the corresponding values for the peroxides of the metals are 157.33, 152.65, 152.10, and 145.71 Cal. respectively. The author draws attention to the close approximation between the thermochemical constants of strontium and lithium (compare Wyrouboff, Abstr., 1897, ii, 173).

M. A. W.

Heats of Dissolution of the Alkali Metals, and the Heats of Formation of their Protoxides. ÉTIENNE RENGADÉ (*Compt. rend.*, 1908, 146, 129—131. Compare Abstr., 1907, ii, 737).—Owing to the explosive violence with which rubidium and caesium react with water, Joannis' apparatus (Abstr., 1888, 1238) cannot be used to determine their heats of solution. The author has employed, instead, a modification of Mahler's calorimetric bomb, of which a diagram and description are given. By means of this apparatus, the heats of dissolution of sodium, potassium, rubidium, caesium, and their protoxides were measured. The sodium used contained less than 0.1% of potassium, the potassium was re-distilled in a vacuum from the commercial metal, and the rubidium and caesium were prepared from the pure chlorides.

The following are the mean values obtained from a concordant series of experiments: (1) $(\text{Na}, \text{Aq}) = 44.1 \text{ Cal.}$, $(\text{K}, \text{Aq}) = 46.4 \text{ Cal.}$, $(\text{Rb}, \text{Aq}) = 47.25 \text{ Cal.}$, $(\text{Cs}, \text{Aq}) = 48.45 \text{ Cal.}$; (2) $(\text{Na}_2\text{O}, \text{Aq}) = 56.5 \text{ Cal.}$, $(\text{K}_2\text{O}, \text{Aq}) = 75.0 \text{ Cal.}$, $(\text{Rb}_2\text{O}, \text{Aq}) = 80.0 \text{ Cal.}$, $(\text{Cs}_2\text{O}, \text{Aq}) = 83.2 \text{ Cal.}$

The heats of dissolution of rubidium and caesium are lower than the values 48.2 and 51.6 given by Beketoff, whilst the values for sodium and potassium are slightly higher than those of Joannis. The numbers obtained for the heats of dissolution of rubidium and caesium oxides differ from those previously found by the author. The discrepancy in the case of the former oxide may be due to the fact that rubidium oxide gradually decomposes on exposure to light with liberation of the metal.

From the series (1) and (2), the following values are calculated: $(\text{Na}_2\text{O}) = 100.7 \text{ Cal.}$, $(\text{K}_2\text{O}) = 86.8 \text{ Cal.}$, $(\text{Rb}_2\text{O}) = 83.5 \text{ Cal.}$, $(\text{Cs}_2\text{O}) = 82.7 \text{ Cal.}$, for the heats of formation of the oxides. Both series of numbers indicate a perfectly regular variation in the thermal properties of the alkali metals with increasing atomic weight. The anomalous value for caesium obtained by using Beketoff's value for the heat of dissolution of the metal is no longer observed, and the alkali metals are now shown to follow the general rule of decreasing affinity for oxygen with increasing atomic weight. E. H.

Densities of Some Fused Salts and their Mixtures at Various Temperatures. RICHARD LORENZ, H. FREI, and A. JABS (*Zeitsch. physikal. Chem.*, 1908, **61**, 468—474).—The method employed was essentially that described by Brunner (*Abstr.*, 1904, ii, 244).

The results obtained for the densities of the pure fused salts may in all cases be represented by a formula of the type $\gamma = a + bt$, where γ is the weight of 1 c.c., t is the temperature on the centigrade scale, and a and b are constants. The formulæ for the various salts are as follows: potassium nitrate (m. p. 329°), $\gamma = 2.044 - 0.0006t$; sodium nitrate (m. p. 310°), $\gamma = 2.12 - 0.0007t$; lead chloride (m. p. 512°), $\gamma = 5.627 - 0.00144t$; lead bromide, $\gamma = 6.175 - 0.00145t$; cadmium chloride, $\gamma = 3.731 - 0.000685t$; potassium bromide, $\gamma = 2.626 - 0.00081t$. In the case of sodium chloride, potassium chloride, and sodium bromide, the authors' results are represented satisfactorily by Brunner's formulæ (*loc. cit.*).

Densities at various temperatures and various concentrations have also been determined for the following pairs of salts: lead and potassium chlorides; lead and barium chlorides; lead and potassium bromides; cadmium and potassium chlorides. The variation of density with temperature and concentration may be represented by the formula $\gamma = a - b.t + c.Nt + d.N$, where N is the molecular proportion of one constituent, $1 - N$ the molecular proportion of the other, and a , b , c , and d are constants. J. C. P.

A Simple Form of Release for Victor Meyer's Vapour-Density Apparatus. THOMAS S. PATTERSON (*Chem. News*, 1908, **98**, 73).—A device which enables the little tube containing the weighed quantity of substance to be introduced into the apparatus in a vertical position.

A cork diaphragm, with an eccentrically-bored hole, is fitted at the base of the wide part of the neck. The cork closing the apparatus has a hole bored in a slanting direction, through which a glass tube passes. The tube of substance is dropped into this, and by rotating the cork it is allowed to fall through the hole in the diaphragm.

P. H.

New Method Suggested for Determining Vapour Densities. II. PHILIP BLACKMAN (*Chem. News*, 1908, 97, 27. Compare Abstr., 1907, ii, 931).—The apparatus previously described has been simplified. In the new form, the manometer consists of a capillary U-tube, one end of which is sealed, and the other closed by a short thread of mercury. The U-tube is placed in the glass cylinder, the stopper at the lower end being made tight by pouring in a little mercury.

H. M. D.

An Apparent Exception to the Theory of Heterogeneous Dissociation Equilibria. RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1908, 61, 455—456).—Attention is directed to Baker's observations (*Trans.*, 1894, 65, 611; 1898, 73, 422), according to which perfectly dry ammonium chloride vaporises without dissociation. From these and other experiments, it appears in fact that ammonium chloride, when vaporised, exerts about 1 atmosphere pressure at 360°, whether it is dissociated or undissociated. In the first case, the partial pressure of the undissociated molecules is very small; in the second case, it is about 1 atmosphere. This result is inconsistent with the theory of heterogeneous equilibria, according to which the concentration of the undissociated vapour should, at a given temperature, be independent of the presence of other gases, including the dissociation products. With the view of finding whether this inconsistency is real or apparent, the subject has been treated experimentally by Johnson (see following abstract).

J. C. P.

Vapour Pressure of Dry Sal Ammoniac. FREDERICK M. G. JOHNSON (*Zeitsch. physikal. Chem.*, 1908, 61, 457—463. Compare Abegg, preceding abstract).—An apparatus is described, made entirely of glass, in which ammonium chloride could be dried perfectly and examined (1) as regards vapour pressure, and (2) as regards vapour density. The pressure was measured with the help of a flat, spiral glass tube, which acted as a manometer (see Ladenburg and Lehmann, *Verh. physikal. Ges.*, 1906, 8, 20).

The author confirms Baker's results, and finds that the density of perfectly dry ammonium chloride at 345° is that of the undissociated compound. The vapour pressures at various temperatures of this specially dried ammonium chloride and also of the ordinary ammonium chloride have been determined, and it is found that the vapour pressure of the undissociated salt in the one case is equal to the sum of the vapour pressures of the dissociation products in the other case. The result is not in harmony with the theory of heterogeneous dissociation equilibria, but no simple explanation of this can be suggested.

J. C. P.

Relationships between Compressibility, Surface Tension, and other Properties of Substances. THEODORE W. RICHARDS and J. HOWARD MATHEWS (*Zeitsch. physikal. Chem.*, 1908, **61**, 449—454. Compare Ritzel, *Abstr.*, 1907, ii, 740).—In this preliminary communication, the authors record values for the compressibility, boiling point, density, surface tension, vapour tension at 20°, and molecular latent heat of vaporisation for thirty-seven organic liquids. The compressibility (β) and the surface tension (γ) are found to be connected by the following equation: $\beta\gamma^{4/3} = \text{const.} = 2.5 \times 10^{-3}$, which is valid for all the liquids examined, except four halogen compounds. The fact that substances with a high surface tension are only slightly compressible is discussed from the point of view of the theory that the atoms are compressible. It is pointed out that compressibility must depend, not only on the volume changes resulting from the alteration of the molecular distances, but also on the internal changes of the molecules. J. C. P.

Surface Tension of Liquids Investigated by the Method of Jet Vibration. P. O. PEDERSEN (*Proc. Roy. Soc.*, 1907, **80**, A, 26—27).—Lord Rayleigh showed many years ago (*ibid.*, 1879, **29**, 71) that the surface tension of a liquid could be calculated from observations on a vibrating jet when the length of the standing waves, the velocity and cross-section of the jet, and the density of the liquid are known. The author has worked out methods for determining these magnitudes, and has obtained very consistent results for the surface tension.

The surface tension of water, toluene, and aniline are 74.30, 28.76, and 43.00 dynes/cm. at 15°. Some measurements have also been made with aqueous solutions. G. S.

Decolorising Action of Charcoal. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1907, **245**, 686—689).—A reply to certain criticisms made by Glassner and Suida (*Abstr.*, 1907, ii, 932) on a paper by Rosenthaler and Türk (*Abstr.*, 1907, ii, 12). The former authors did not observe that charcoal adsorbs relatively much more strongly from dilute than from concentrated solutions, because they used dyes. In the case of dyes, various chemical complications disturb the purely physical phenomena of adsorption. Rosenthaler and Türk, on the other hand, worked with caffeine and with dextrose, and were thus able to observe the great effect of the concentration of the solution. G. B.

Velocity of Absorption of Gaseous by Solid Substances. ARTHUR HANTZSCH and G. WIEGNER (*Zeitsch. physikal. Chem.*, 1908, **61**, 475—490).—Re-examination of the experimental basis of a previous paper (*Abstr.*, 1904, ii, 541) shows that the conclusions then reached must be modified. The absorption of ammonia by solid acids and of hydrogen chloride by solid bases does under certain conditions take place in approximate accord with the formula for a unimolecular reaction, but it is not possible to draw any trustworthy conclusions as to the magnitude of the affinity constant of the acid or base from the magnitude of the absorption constant. The absorption of ammonia or hydrogen chloride in a diluted condition takes place according to the

formula for a bimolecular reaction only in a limited number of cases. Difference in the rate of absorption cannot be employed as a means of distinguishing true acids from pseudo-acids, or true bases from pseudo-bases.

J. C. P.

Absorption of Gases by Rubber Tubing. RUDOLF DITMAR (*Chem. Zentr.*, 1907, ii, 1578—1579; from *The India Rubber Journal*, 34, 85—86, 197—198).—An arrangement is described for measuring the pressure of a gas in a rubber tube, jacketed with the same or with another gas. In experiments with a tube of red rubber of unknown composition, air is found to exert pressure when the tube is surrounded by air. Carbon dioxide, on the other hand, is absorbed by the rubber tube when the jacket is air, or to a smaller extent when the jacket is hydrogen, whilst hydrogen is absorbed, although to a smaller extent than carbon dioxide, when the tube is surrounded by air or carbon dioxide, but exerts pressure when the tube is jacketed with hydrogen. The absorption of carbon dioxide by a tube of Para rubber is found to be the same whether the atmosphere surrounding the tube is carbon dioxide or air.

G. Y.

[Diffusion of Metals in Mercury.] G. MCPHAIL SMITH (*Ann. Physik*, 1908, [iv], 25, 252—256).—The author criticises Wogau's view (*Abstr.*, 1907, ii, 606) that certain metals, when dissolved in mercury, are in the monatomic condition, and suggests that in many cases, at least, compounds of mercury and the dissolved metal are formed (compare Haber, *Abstr.*, 1902, ii, 638; Smith, *Abstr.*, 1906, ii, 673; 1907, ii, 463). It is pointed out that when Wogau's values for the diffusion constants of the metals are divided by the corresponding atomic weights, and the figures so obtained are plotted against the atomic weight, two curves result; on one of these lie the figures for Li, Na, K, Ca, Rb, Sr, Cs, Ba, and Tl, the metals which form compounds with mercury; on the other, lie the figures for Zn, Cd, Sn, and Pb, the metals which do not combine with mercury.

J. C. P.

Organic Solvent and Ionising Media. X. Solvent Power and Dielectric Constant. PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1908, 61, 633—639. Compare *Abstr.*, 1904, ii, 227; 1906, ii, 149, 335, 336, 527; 1907, ii, 231, 437, 519, 734).—The variation in the solubility of tetraethylammonium iodide in water and a number of organic liquids is recorded. For the purpose of this paper, the solubility (s) is expressed as molecular percentage of the salt in the saturated solution, that is, if the saturated solution contains n molecules of tetraethylammonium iodide for every N molecules of solvent, then $s = 100n/(n + N)$.

It is found that the solvent power for tetraethylammonium iodide falls off as the dielectric constant of the solvent diminishes; in fact, $s^{\frac{1}{2}}$ is very nearly proportional to the dielectric constant. An analogous result is obtained with tetrapropylammonium iodide as solute.

J. C. P.

Solutions in Mixtures of Alcohol and Water. ERNST CUNO (*Ber. Deut. physikal. Ges.*, 1907, 5, 735—738; *Ann. Physik*, 1908, [iv], 25, 346—376).—The author has determined the composition of the two layers which are formed when varying quantities of potassium carbonate or manganese sulphate are dissolved in mixtures of alcohol and water. In the case of both salts, alteration of temperature has only a very slight effect on the composition of the two layers. The expressions suggested by Bodländer (*Abstr.*, 1891, ii, 794) and by Herz and Knoch (*Abstr.*, 1905, ii, 709) are fairly constant for medium alcohol concentrations.

The conductivity of potassium carbonate and manganese sulphate in mixtures of alcohol and water has also been studied. For a given quantity of salt, the conductivity rapidly diminishes as the concentration of the alcohol increases. Increase in the proportion of alcohol leads also to a displacement of the maximum conductivity in the direction of solutions containing less salt. J. C. P.

Crystallisation from Aqueous Solutions. ROBERT MARC (*Zeitsch. physikal. Chem.*, 1908, 61, 385—398).—It is suggested that there is a rate of crystallisation from a supersaturated solution quite distinct from a diffusion velocity. This view is supported by experiments on the rate of crystallisation of potassium sulphate from supersaturated solutions at 0°. A quantity of fine crystals was introduced into a supersaturated solution, the solution was vigorously stirred, and the process of crystallisation was followed by taking out samples of the solution from time to time and analysing. The quantity of crystals introduced at the beginning of the experiment was three to five times the quantity which separated during the crystallisation. The surface of the crystals may be taken as proportional to $(W)^{\frac{2}{3}}$, where W is the weight of crystals present, and the rate of crystallisation is approximately proportional to the surface of the crystals calculated in this way.

It appears that the crystallisation proceeds according to the formula for a bimolecular reaction, and that the temperature-coefficient is about 1.6 for an interval of 10°. The theoretical interpretation of these results is postponed until more experimental material is available. J. C. P.

Action of Some Electrolytes on Colloidal Silver Solutions. The Process of Coagulation. H. W. WOODSTRA (*Zeitsch. physikal. Chem.*, 1908, 61, 607—632).—The various solutions of colloidal silver employed by the author were prepared by the methods of Muthmann, Carey Lea, and Bredig. The colloidal silver prepared by Muthmann's method resembles that prepared by the other methods, in being electro-negative and in promoting the decomposition of hydrogen peroxide.

The procedure adopted in studying the coagulative power of different salts was to find in each case which, of a number of solutions of gradually diminishing concentration, was just unable to produce turbidity on addition of a given quantity of colloidal silver solution. The concentration of this particular salt solution is described as the "limiting concentration" for that salt.

The coagulation is accompanied by peculiar colour effects, the nature of the colour depending apparently on the anion of the salt. Chlorides (except lead chloride) give a bluish-white opalescence, resembling silver chloride. Coagulation by lead chloride and by sulphates is accompanied by a red coloration.

The power of salts to coagulate colloidal silver solutions depends almost entirely on the cation, and increases with the valency of the cation (compare Whetham, *Abstr.*, 1900, ii, 62). For a given salt, the "limiting concentration" diminishes (1) with the age of the colloidal solution on which it is allowed to act, and (2) with increasing concentration of the colloidal solution.

The author discusses the various theories of coagulation which have recently been brought forward, and concludes that the formation of large aggregates from the fine colloidal particles is to be attributed to the electrical action of the ions. His experiments are in general harmony with Whetham's views (*loc. cit.*). J. C. P.

The Process of Gelatinisation. III. S. A. LEVITES (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 208—215. Compare *Abstr.*, 1902, ii, 312; 1903, ii, 641).—The transition from the colloidal to the gelatinised condition can be conveniently followed by measurement of the viscosity. With this object in view, the influence of concentration, of temperature, and of foreign substances on the viscosity of colloidal solutions has been examined.

For concentrated colloidal solutions, the viscosity η is approximately represented by the exponential formula $\eta = A^x$, where A is a constant, and x the concentration of the dissolved colloid. For dilute solutions, closer agreement with the experimental data is obtained by means of the linear expression $\eta = 1 + a.x$, in which a is a constant.

Lowering of temperature increases the viscosity, but for a given solution there exists a certain temperature minimum below which the viscosity gradually increases with time according to a linear equation.

Foreign substances (crystalloids), which increase the viscosity of water, increase the viscosity of colloidal solutions, and a similar relationship holds for crystalloids, which diminish the viscosity of water. This does not hold if two or more crystalloids are added to the colloidal solution, or if the crystalloid reacts chemically with the dissolved colloid. H. M. D.

Non-miscibility and the Mass Law. WILDER D. BANCROFT (*J. Physical Chem.*, 1908, 12, 30—35).—A theoretical discussion of the deviation of a reversible change $A + B \rightleftharpoons AB$ from the simple equilibrium equation $yz = Kx$, which may be expected when the two components A and B are not completely miscible in the pure condition. Such a system is exemplified in chloral + water \rightleftharpoons chloral hydrate. The author argues that the non-miscible components A and B will render each other less soluble in the compound AB , and hence increase one another's chemical potential (compare McIntosh, *Abstr.*, 1898, ii, 65). The result will be a forcing back of the actual percentage dissociation of AB . The degree to which the chemical potentials

of *A* and *B* would be affected is not known, but the author considers the effect on the equilibrium in several hypothetical cases.

R. J. C.

Equilibria in Ternary Systems; Additive Products of Aromatic Nitro-derivatives and Mercuric Chloride. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 29—39. Compare Abstr., 1907, i, 25).—The author has investigated the equilibria in the systems *p*-nitrotoluene and mercuric chloride, *p*-nitroanisole and mercuric chloride, and α -nitronaphthalene and mercuric chloride, using ethylurethane as third substance (compare this vol., ii, 94). The results are in complete accord with the theoretical deductions concerning equilibria in ternary systems (*loc. cit.*). The double salts which these aromatic nitro-derivatives form with mercuric chloride have the same composition as the corresponding double salts formed by iodoxy-derivatives with mercuric chloride, and it is probable that similar relations exist between the corresponding mercuric bromide double compounds.

T. H. P.

Attempt to Measure the Rate of Neutralisation at Low Temperatures. RICHARD ABEGG and J. NEUSTADT (*Zeitsch. Elektrochem.*, 1908, 14, 2—3).—Alcoholic solutions of hydrochloric acid and lithium hydroxide were mixed at -80° , but neutralisation was completed in the time required to mix the solutions. At -100° , the reaction did not appear to be quite complete thirty and forty seconds after mixing, but one minute later it was complete. The conductivity of the solutions was used to follow the progress of the change. Alcoholic solutions are too viscous at temperatures below -100° to permit of rapid mixing.

T. E.

Reaction Velocity in Gases which are in a State of Motion. MAX BODENSTEIN and KARL WOLGAST (*Zeitsch. physikal. Chem.*, 1908, 61, 422—436).—It is incorrect to assume always that when a mixture of reactive gases passes through a vessel kept at a constant temperature their concentration diminishes uniformly from the entrance to the exit of the tube. If the temperature is such that the gases react slowly, if the vessel is not very narrow in proportion to its width, and if the rate of passage of the gases is not too great, then thorough mixing will occur, the composition of the gaseous mixture will be the same throughout the tube, and the same as that of the issuing mixture. Formulæ applicable to these conditions are developed, and they differ from the formulæ usually employed. Thus, for a unimolecular reaction, *X*, the absolute amount of the product formed will be proportional to the duration *T* of the experiment, to the volume *v* of the reaction vessel, and to the concentration $\frac{A-X}{V}$ of the substance which is undergoing change: hence $k = 1/T \cdot V/v \cdot X/(A-X)$. The formula which is similarly deduced for a bimolecular reaction is $k = 1/T \cdot V^2/v \cdot X/(A-X)(B-X)$.

The validity of the latter formula was tested by experiments on the rate of combination of hydrogen and iodine. Mixtures of hydrogen

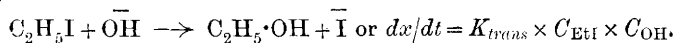
and iodine, with hydrogen in large excess, were passed through tubes heated to constant temperatures (406° , 430° , 440°), and the issuing mixtures were analysed. At these temperatures, the reaction between hydrogen and iodine is slow, so that, if the gases are not passed too rapidly, the conditions are fulfilled on which the foregoing formulæ are based. The results are in satisfactory accord with the formulæ, and values are obtained for the velocity constant of the reaction $H_2 + I_2 = 2HI$, which agree well with those deduced from the experiments made in closed vessels (Abstr., 1899, ii, 637).

Jellinek's experiments (Abstr., 1906, ii, 437) are considered from the authors' point of view, and the velocity coefficients calculated by their formula vary less than those calculated in the usual way.

J. C. P.

Urazoles. XII. Velocity Constants and Mechanism of the Reactions of Alkyl Halides with Urazoles and Urazole Salts. SALOMON F. ACREE and G. H. SHADINGER (*Amer. Chem. J.*, 1908, 39, 226—227. Compare this vol., i, 224).—An investigation is being carried out with the object of elucidating the mechanism of the reactions which take place between alkyl salts and other substances, such as hydroxides, carbonates, nitrates, and urazoles. The present paper deals with the velocity of the reactions of alkyl halides with 3-thio-1-phenylurazole and its metallic salts, sodium thioacetate, and potassium hydroxide. The rate of change of the urazole into its disulphide and the rate of hydrolysis of methyl iodide in 50% alcohol have also been determined. The reaction between sodium 3-thio-1-phenylurazole and ethyl iodide was followed by conductivity measurements, and evidence was obtained that ethyl iodide does not unite to an appreciable extent with the sodium or urazole ions.

The results of the work lead to the following conclusions. In the reactions of alkyl halides with urazoles, hydroxides, carbonates, and thioacetates, the alkyl halide reacts with the anion of the other compound, thus :



The hypothesis of Bruyn and Steger (Abstr., 1899, i, 849) that alkyl halides react with other substances by dissociation into alkyl and halogen ions and subsequent union of the alkyl ion with the anion, Nef's view that the reaction is due to the dissociation of the alkyl halide into the corresponding halogen acid and an unsaturated methylene complex which reacts with other substances, and Euler's hypothesis (Abstr., 1906, i, 789) that the reaction is due to the formation of a complex cation and its subsequent reaction with the anion are discussed and shown not to be in harmony with the evidence now obtained.

The alkyl halide molecules react with the anion of the substance which is being alkylated, probably forming an intermediate unstable complex anion, $C_2H_5I\cdot\bar{X}$, which immediately yields halogen ions and C_2H_5X .

Alkyl iodides react more readily with the urazoles than do alkyl

bromides, and the bromides more readily than the chlorides. Primary alkyl halides are more reactive than secondary alkyl halides towards urazoles, and the latter more so than the tertiary compounds. This may be partly due to the so-called space interference. E. G.

Hydrolysis of Salts. AUGUSTE ROSENSTIEHL (*Bull. Soc. chim.*, 1908, [iv], 3, 86—89).—The author has shown in a former paper (Abstr., 1907, ii, 610) that all salts of which the aqueous solutions obey Berthollet's laws are completely hydrolysed in solution, and the present paper is confined to a discussion of the cases in which both the bases and acid formed on hydrolysis are soluble in water and do not readily reveal themselves. The experimental evidence is that supplied by H. Rose (*Ann. Phys. Chem.*, 1853, 86, 101) in his work on the action of water on various salts, and includes such observations as the following: (1) a dilute aqueous solution of an alkali carbonate on ebullition loses some carbon dioxide; (2) a concentrated solution of sodium carbonate precipitates from a solution of lead nitrate the substance $6(\text{PbO}, \text{CO}_2), \text{Pb}(\text{H}_2\text{O}_2)$, whilst a dilute solution furnishes the product $3(\text{PbO}, \text{CO}_2), \text{Pb}(\text{H}_2\text{O}_2)$; (3) a concentrated solution of borax gives a reddish-violet colour with reddened litmus paper, whereas a dilute solution of borax gives a blue colour; (4) alkaline osmates are inodorous when dry, but on solution in water develop the odour of osmic acid, and, similarly, a dilute aqueous solution of an alkali salt of a fatty acid has always a slight odour of the fatty acid, although the dry salt may be inodorous. The action of water in these cases is (a) chemical (in effecting hydrolysis) and (b) physical (in maintaining by its mass the new condition set up by the hydrolysis).

T. A. H.

Hydrolysis of the Salts of Weak Acids and Weak Bases and its Variation with the Temperature. HARALD LUNDÉN (*J. Chim. Phys.*, 1907, 5, 574—608).—The dissociation constants, k_a and k_b , of certain weak acids and bases, of which the values of k_a and k_b respectively lie between 10^{-7} and 10^{-10} , have been determined by conductivity measurements as previously described (Abstr., 1907, ii, 443) at intervals of temperature between 10° and 50° (in the case of boric acid, only between 15° and 40°).

For boric acid, k_a for the dissociation $\text{H}_3\text{BO}_3 \rightleftharpoons \text{H}^+ + \text{H}_2\text{BO}_3^-$ is 5.48, 6.62, and 8.49×10^{-10} at 15° , 25° , and 40° respectively; when the acid is neutralised with ammonia, only the salt $\text{NH}_4\text{H}_2\text{BO}_3$ is formed in appreciable amount. For pyridine, k_b is 1.06, 4.25, and 8.6×10^{-9} at 10° , 40° , and 60° respectively; for *p*-nitrophenol, k_a is 4.5, 7.0, and 12.7×10^{-8} at 10° , 25° , and 50° respectively, and for 2:4:6-trimethylpyridine, k_b is 1.22, 2.05, and 3.75×10^{-7} at 10° , 25° , and 50° respectively. In connexion with the results for *p*-nitrophenol, it is pointed out that the colorimetric method for determining the dissociation constants of indicators employed by Friedenthal and Salm (Abstr., 1906, ii, 218) does not give trustworthy results.

The dissociation constant for water has been calculated from the constants for *p*-nitrophenol and 2:4:6-trimethylpyridine, and the degree of hydrolysis of the salt formed by these two compounds; the

values are 0.31, 1.05, and 5.17×10^{-14} at 10° , 25° , and 50° respectively, in excellent agreement with Kohlrausch's values from the conductivity of pure water.

From the variation of the dissociation (ionisation) and of the degree of hydrolysis of the salts with temperature, the heats of dissociation and of neutralisation respectively have been calculated for the compounds mentioned above. The values obtained agree satisfactorily with those obtained calorimetrically as far as comparison is possible. The heat of neutralisation of boric acid is $11,440 - 37.8t$ cal., and that of pyridine $6037 - 14.5t$ cal.; the heat of dissociation of ammonia is $-2608 + 58.05t$ cal.

The heat of dissociation increases with the temperature for all the electrolytes examined, but the temperature-coefficient for the heat of neutralisation may be positive or negative. G. S.

Theory of the Saponification of the Glycerides. RUDOLF WEGSCHEIDER (*Monatsh.*, 1908, 29, 83—133).—A discussion of the results of various authors who have studied the hydrolysis of the glycerides. The view that the hydrolysis takes place in three stages is supported by observations made in determining the velocity constants of the hydrolysis of other esters. The arguments are shown to apply to all the seven reactions which may occur within the three stages. The conditions are laid down under which the velocity coefficients of similar reactions, with substances differing in the number of their reactive groups, are proportional to the numbers of such groups.

The theory of the progressive hydrolysis of the glycerides is developed on the assumption that all the possible isomerides are formed. New conditions are discovered, under which the whole reaction may be bimolecular or, in presence of an excess of the hydrolysing agent, unimolecular, and a basis is provided for the theoretical treatment of observed deviations.

The following general conclusions are arrived at: the hydrolysis of the glycerides takes place in stages, in the course of which all the possible isomerides are formed. If the whole reaction, as measured by the amount of acid liberated, takes place with tri- or di-glycerides approximately according to the law of unimolecular reactions, and if the unimolecular constants for the hydrolysis of mono-, di-, and tri-glycerides are almost equal, the velocity constants for the various reactions must be related as follows: (1) the hydrolysis constants of the two monoglycerides must be equal. (2) The hydrolysis constant of the *s*-diglyceride must be double that of a monoglyceride and equal to the sum of the two hydrolysis constants of the *as*-diglyceride. (3) The sum of the two hydrolysis constants of the triglyceride is three times the constant for a monoglyceride. This is the case in the hydrolysis in acid solution, but has not yet been shown to apply to the alkaline hydrolysis.

If the hydrolysis of the triglyceride is unimolecular, but not that of the diglyceride, the various hydrolysis constants must be represented by the expressions: $k_1 = 3KB/C$, $k_2 = -3K/C$, $k_{11} = K$, $k_{21} + k_{22} = 2K$, $k_{10} = [K(2a - k_{21}) - a^2]/B - k_{21}$, $k_{20} = K$, in which K is the constant for the whole, apparently unimolecular, reaction, $a = k_{21} + k_{22}$,

$B = 2K - a$, and $C = K - a$, or by the expressions: $k_1 + k_2 = 3K$, $k_{11} = [12K - k_1 + k_{21}(3Kk_1)^2]/k_1(3K + k_1)$, $k_{21} = K$, $k_{22} = [6K(K - k_{21})]/3K + k_1$, $k_{10} = [12Kk_1 + k_{21}(3K - k_1)^2]/2k_1(3K + k_1)$, $k_{20} = K$.

The non-appearance of mono- and di-glycerides in recognisable amounts amongst the products of the hydrolysis of insoluble triglycerides in heterogeneous systems by means of aqueous solutions cannot be urged as an argument against the view that the hydrolysis takes place in stages, as, in general, if the transformation of an almost insoluble substance is accompanied by a process of solution, the appearance of an intermediate product in quantity is possible only if its velocity of transformation or its solubility is markedly smaller than that of the original substance. The various points are treated mathematically in an appendix which forms the second and larger part of the paper.

G. Y.

Catalytic Power of Silica and Alumina. JEAN B. SENDERENS (*Compt. rend.*, 1908, 146, 125—127. Compare Abstr., 1907, i, 577).—The silica precipitated from sodium silicate, washed free from acid, dried, and completely dehydrated by moderate calcination, is a catalyst of alcohols giving ethylenic hydrocarbons exclusively. Thus it dehydrates ethyl alcohol at 280°, giving 99.5% of ethylene. But the same silica, after being calcined in a platinum crucible at a bright red heat for an hour, does not act on ethyl alcohol below 340°, and then gives 5.3% of hydrogen and 94.7% of ethylene, whilst, if it is calcined for six hours at a white heat, the decomposition of ethyl alcohol requires a temperature of 390° and then gives 17.1% of hydrogen. Hyaline quartz, when finely powdered, does not begin to catalyse alcohol below 460°, giving ethylene and 52% of hydrogen, and, if this quartz is previously calcined for six hours at a white heat, the decomposition temperature of alcohol rises to 480° and the yield of hydrogen to 95.2%.

Similar behaviour is observed with alumina. The latter, prepared by precipitation from a salt, washed, dried, and slightly calcined, is exclusively a dehydrating catalyst towards alcohols, giving with ethyl alcohol 99.5% of ethylene at 275°, whilst, after calcination for six hours at a white heat, it does not decompose alcohol below 420° and then gives 12% of hydrogen.

The conclusion is drawn that silica and alumina, when gently calcined, are dehydrating catalysts, whilst prolonged calcination, besides diminishing their catalytic power, tends to make it more dehydrogenating in character. The author considers that this will explain the disagreement amongst chemists as to the action of silica and alumina on alcohols.

E. H.

Action of Alternating Currents of High Frequency on the Decomposition of Hydrogen Peroxide by Colloidal Platinum.

A. LEBEDEF (Bull. Soc. chim., 1908, [iv], 3, 56—75).—For these experiments a coil, giving a spark 40 cm. long, was employed with a primary current varying from 2.5 to 4.5 amperes. The platinum electrodes were each 2 sq. cm. in area, and each was enclosed in a small glass tube having a constricted aperture covered with parchment

paper and dipping in the reaction liquid, contained in a voltameter, which is figured in the original. The water employed as a solvent had a conductivity 2×10^{-6} , and the colloidal platinum was prepared by Bredig and von Berneck's method (Abstr. 1900, ii, 213). The whole apparatus was immersed in a thermostat at 25° .

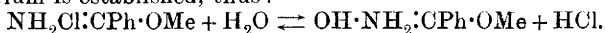
In the several series of experiments made, it was found that the normal rate of decomposition of the peroxide by the colloidal platinum (Bredig and von Berneck, *loc. cit.*) was diminished under the influence of alternating currents of high frequency, and the irregularity of the diminution is attributed to irregularity in the primary current employed. On the contrary, the rate of decomposition increased under the influence of the current when a small quantity of sodium hydroxide was added to the reaction liquid, thereby increasing its conductivity. When a direct current from a 70 volt battery was employed, no effect on the rate of decomposition of the peroxide was noticed, and this was also the case when a direct discontinuous current was taken from the coil, with an air-break of 0.75 cm. length.

The greater part of the paper is taken up with a discussion of the bearing of these preliminary results on theories of catalytic action, and it is shown that the results are readily explicable on the assumption that catalytic action is due to a change in state of the surface of the catalyst, and in this connexion attention is directed to Helmholtz's idea that between the two phases, solid and liquid, there exists a thin double layer, carrying an electric charge, which tends to diminish surface tension. The influence of an electric current on catalytic action can then be explained as due to the change in potential difference, and consequently in surface tension, that it induces, and the further effect due to the addition of an electrolyte, such as sodium hydroxide, to the reaction liquid would be explained as due to change in potential difference induced by the electrical charges on the ions. As to the mechanism of the reaction, the author dissents from Haber's view (Abstr., 1900, ii, 720) that the platinum is alternately oxidised and reduced, and suggests, instead, that the oxygen is merely stored temporarily in the colloidal platinum in the form of a solid solution.

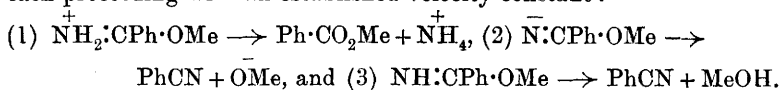
T. A. H.

Catalysis. I. Catalysis of Esters and of Imino-esters by Acids. JULIUS STIEGLITZ (*Amer. Chem. J.*, 1908, 39, 29—63).—This paper is based on the results of experiments which have not yet been described.

Methyl iminobenzoate is slowly decomposed by water with formation of methyl alcohol and benzonitrile, very small quantities of methyl benzoate and ammonia being also produced: (1) $\text{NH}:\text{CPh}\cdot\text{OMe} \rightarrow \text{C}_6\text{H}_5\cdot\text{CN} + \text{MeOH}$; (2) $\text{NH}:\text{CPh}\cdot\text{OMe} + \text{H}_2\text{O} \rightarrow \text{Ph}\cdot\text{CO}_2\text{Me} + \text{NH}_3$. Both reactions are practically non-reversible under the conditions of the experiment. In presence of hydrochloric acid, however, the velocity of the second reaction is greatly increased, whilst the first reaction may be entirely suppressed. The acid unites with the imino-ester, the hydrochloride is partially hydrolysed, and a condition of equilibrium is established, thus:



It has been proved that the reacting substance which gives ammonia and a benzoate is the hydrochloride, or rather its positive ion, and that the accelerating action of the acid is simply due to the formation of larger reacting masses of the active ion from the scarcely ionised weak base. Non-electrolytes do not affect the velocity of the reaction between imino-ester salts and water, but electrolytes have a decided "salt effect" (Euler, Abstr., 1900, ii, 269). The decomposition into nitrile and alcohol, according to reaction (1), is greatly accelerated by the addition of alkali hydroxides, owing to an increase in the concentration of the negative ions. In the decomposition of an imino-ester in aqueous solution, the non-ionised molecules of the ester also break down into nitrile and alcohol, but the velocity constant is very small in comparison with that of the negative ions. An imino-ester decomposes, therefore, in accordance with three simultaneous reactions, each proceeding with an established velocity constant:



A mathematical treatment of these reactions is given, and their theoretical significance and application to the catalysis of ordinary esters are discussed. The results of the work lead to the conclusion that none of the usual assumptions regarding catalytic action (compare Euler, Abstr., 1900, ii, 532; 1901, ii, 5; 1904, ii, 318) is absolutely true under any conditions, and that the only fundamental fact common to all catalytic actions is that of acceleration, due to an increase in the active mass or concentration of a reacting component. E. G.

Catalysis. II. Catalysis of Imino-esters. JULIUS STIEGLITZ (*Amer. Chem. J.*, 1908, 39, 166—183. Compare this vol., ii, 29, and preceding abstract).—It was stated in the earlier paper that the catalysis of an imino-ester may take place in either of two ways: (1) $\text{R}\cdot\text{C}(\text{NH})\cdot\text{OR}' + \text{H}_2\text{O} \rightarrow \text{R}\cdot\text{CO}_2\text{R}' + \text{NH}_3$, and (2) $\text{R}\cdot\text{C}(\text{NH})\cdot\text{OR}' \rightarrow \text{R}\cdot\text{C}\text{:N} + \text{R}'\cdot\text{OH}$. The former reaction is enormously accelerated by acids, and the latter by alkali hydroxides. Evidence was adduced to show that the reacting component in (1) is the positive imino-ester ion, $\text{R}\cdot\text{C}(\text{NH}_2^+)\cdot\text{OR}' \rightarrow \text{R}\cdot\text{CO}_2\text{R}' + \text{NH}_4^+$, and in (2) the negative ion, $\text{R}\cdot\text{C}(\text{N}^-)\cdot\text{OR}' \rightarrow \text{R}\cdot\text{C}\text{:N} + \text{OR}'^-$. A third reaction takes place in the absence of acid or alkali, involving the decomposition of the imino-ester according to (2), and, in this case, the reacting component is the non-ionised imino-ester itself. Each of these reactions proceeds with its characteristic velocity constant.

A further study of the subject has led to the following conclusions. Imino-esters resemble acid esters in being decomposed much more rapidly by alkali hydroxides than by acids. The decomposition in aqueous solution cannot be accounted for by the decomposition of the negative ion by a process of autocatalysis, or by assuming that it is produced by ionisation due to its amphoteric character; the reacting mass is the non-ionised ester.

The acceleration of the decomposition according to (1) being greatly

accelerated by acids, it was thought possible that the reacting component was not all the imino-ester salt, but only its positive ion. It has been found, however, that a second accelerating force is involved, and that the imino-ester salt itself, as an electrolyte, exerts a "salt effect" in its own catalysis. This effect is probably concerned with an increase in the ionisation of water.

The salts of those imino-esters which are the weakest bases have the greatest velocity of decomposition.

A series of analogies between imino-esters and acid esters is given, and it is shown that the chief point of difference between the two classes of substances lies in the more pronounced basic properties of the former, and the formation of salts which are comparatively little hydrolysed.

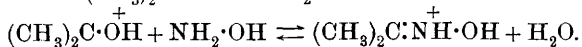
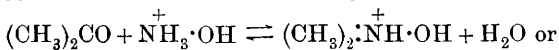
E. G.

Catalysis. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, **39**, 145—156).—Polemical. A reply to Stieglitz (this vol., ii, 29).

E. G.

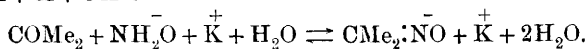
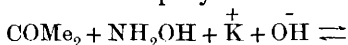
Catalysis. VII. Reaction of Carbonyl Compounds with Hydroxylamine and Hydroxylamine Hydrochloride. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, **39**, 300—309. Compare Acree and Johnson, *Abstr.*, 1907, ii, 856).—This paper has been written in view of the recent work of Abel (this vol., ii, 26), Lapworth (*Trans.*, 1907, **91**, 1133), Landrien (*Abstr.*, 1905, ii, 445), and Euler (*Abstr.*, 1907, ii, 1098).

The data obtained by Acree and Johnson indicate that acetone and hydroxylamine in aqueous solutions combine readily and nearly completely, thus: $(\text{CH}_3)_2\text{CO} + \text{NH}_2\cdot\text{OH} \rightleftharpoons (\text{CH}_3)_2\text{C}:\text{N}\cdot\text{OH} + \text{H}_2\text{O}$, and that the velocity of the reaction is accelerated by acids owing to the formation of cations which are more reactive than the free bases:

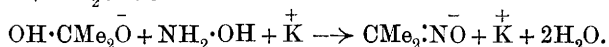
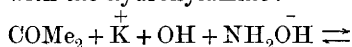


The quantitative results seem to show that the free bases, hydroxylamine, and acetoxime, as well as their cations, enter into the reaction. In this and in other cases, the question as to whether the free base, dissociated salt, or non-dissociated salt undergoes transformation depends simply on the relative activity of each in the particular reaction. If a quantity of acid is added which is not sufficient to use up all the base, the non-catalysed and catalysed reactions take place side by side each with measurable rapidity, and in this case the velocity of the reaction cannot be proportional to the concentration of the catalysing agent. In the presence of alkali hydroxide, the reaction is greatly accelerated, and proceeds nearly to completion.

The alkali probably forms small amounts of NH_2O^- ions, which react much more rapidly with acetone than hydroxylamine does:



The acetone may, however, form a salt, the anions of which react with the hydroxylamine:



The equilibrium point for the non-catalysed reversible reaction between acetone and hydroxylamine in concentrations of 1 gram-mol. per litre is different from that of the catalysed reversible reaction in which the concentrations of the acetone, hydroxylamine, and hydrochloric acid are also each 1 gram-mol. per litre, and the equilibrium in the latter case varies greatly with the variation in the amount of hydrogen ions of the catalyst.

A catalysing agent may influence the velocity of a reaction physically by condensing the reacting substances on the surfaces of solids, thus increasing the effective concentration, or by imparting energy to, or withdrawing it from, the solution. A catalyst may also change the velocity chemically by altering the concentration of some substance taking part in the reaction, or by forming some new substance which yields the same end-products. In some cases, side-reactions may be developed or suppressed by the addition or removal of the catalysing agent.

E. G.

Landolt's Experiments on Change of Weight in Chemical Transformation. T. H. LABY (*Chem. News*, 1908, 97, 1—3).—A summary and discussion of Landolt's results (Abstr., 1906, ii, 528).

G. S.

Observations and Deductions obtained from a Consideration of the Numbers given for the Atomic Weights of the Elements by the International Committee (1905), which lead to a Rational Determination of the Constitution and Structure of each Element. HAWKORTH COLLINS (*Chem. News*, 1907, 96, 176—177).—Certain relationships between the approximate numbers which represent the atomic weights of the twenty-eight elements with atomic weights below 60, as exact multiples of that of hydrogen, are noted. Deductions involving the assumption that the elements contain protyle are made.

H. M. D.

Reciprocal Displacement of the Constituents of Molecular Compounds and their Relative Stability. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1548—1565. Compare Abstr., 1907, ii, 751).—To determine the ability of one substance to replace another in a molecular compound, the latter is dissolved in a small quantity of the desired organic compound and the mixture left in a desiccator. The resulting crystals are then decomposed by water and the products analysed. The following is the order of relative stability of the molecular compounds formed by magnesium bromide and iodide with organic substances. Carbamide; water; aniline, acetamide, ethyl carbamate, formic acid; methyl alcohol; ethyl alcohol; acetonitrile, acetic anhydride; acetic acid; propionic acid; ethyl acetate, acetone; ethyl orthoformate, benzaldehyde; methyl acetate;

acetal, acetyl chloride; methylal; ethyl ether; anisole; anethole (which does not yield a compound).

The substances separated only by commas form molecular compounds of very nearly equal stability and do not replace one another. The substances at the close of the list yield the most unstable compounds, and are readily replaced by those before them.

In general, substances with a high dielectric constant, and also those with a high coefficient of association, form the most stable compounds with the magnesium halides, but there seems to be no direct quantitative relation between the stability and the physical properties of the organic constituent. Of the substances containing oxygen, the most stable compounds are formed by those containing the hydroxyl group, next come those with a carbonyl group, and finally substances of the type $R \cdot O \cdot R$. Compounds containing an amino-group are as stable as those containing an hydroxyl group, and, contrary to Werner's statement, it is highly probable that the constituents of a molecular compound containing both an NH_2 and a $C=O$ group are connected to one another by means of the nitrogen atom. Qualitative experiments show that, whilst little heat is developed in the formation of the unstable molecular compounds, considerable quantities are developed in the case of the more stable compounds.

Z. K.

Lecture Experiments with Ozone. CARL D. HARRIES (*Ber.*, 1908, 41, 42—43).—(1) A stoppered cylinder about 30 cm. long is filled with ozonised oxygen; the presence of ozone in the cylinder is shown by introducing a piece of potassium iodide starch-paper. About 50 c.c. of turpentine oil are poured quickly into the cylinder, which is then well shaken; if a piece of potassium iodide starch-paper is now placed in the cylinder, it will not turn blue, but does so when dipped in the ozonised turpentine oil.

(2) A strip of absorbent paper is saturated with turpentine oil, the excess removed by pressing between drying paper, and the strip then placed in a long, wide cylinder full of ozonised oxygen; in a few seconds, the turpentine oil ignites and burns with a luminous, smoky, dull red flame.

W. H. G.

Balances with Non-metallic Pans. ERNST BORNEMANN (*Chem. Zeit.*, 1908, 32, 125—126).—Attention is called to the trouble occasionally experienced in accurate weighings of glass utensils when using a balance with glass pans. The author finds this is caused by electric disturbances, and advises covering the pans with a disc of sheet copper.

L. DE K.

Inorganic Chemistry.

Slow Combination of Chlorine and Hydrogen under the Influence of Heat. HEINRICH SIRK (*Zeitsch. physikal. Chem.*, 1908, **61**, 545—565).—Mixtures of hydrogen and chlorine in different proportions, occasionally with hydrogen chloride in addition, were heated in glass vessels in a thermostat at 242.5°. After different intervals, the contents of the glass vessels were analysed. The reacting gases were protected from light throughout.

The combination of hydrogen and chlorine under the influence of heat is a very complicated problem, and for some of the author's observations no explanation can be suggested. The initial rate of combination is proportional to the chlorine concentration (c), and is independent over a wide range of the concentrations of hydrogen and hydrogen chloride. At the same time, the reaction is not a unimolecular one throughout, for the value of $k = 1/t \cdot \log.c/(c-x)$ diminishes as the reaction proceeds. If the chlorine, or the mixture of chlorine and hydrogen, has been heated previously, the combination of the two gases is accelerated (compare Burgess and Chapman, *Trans.*, 1906, **89**, 1399); a similar effect is produced by previous exposure of the chlorine to light. The activity of a mixture of hydrogen and chlorine is diminished by contact with concentrated sulphuric acid, but this apparently has nothing to do with the removal of traces of moisture. One experiment, made at 258°, indicates that the temperature-coefficient of the rate of combination of hydrogen and chlorine is 1.6 for a rise of 10°.

J. C. P.

Decomposition of Hydrogen Iodide in Light. MAX BODENSTEIN (*Zeitsch. physikal. Chem.*, 1908, **61**, 447—448).—The author found previously (*Abstr.*, 1897, ii, 252) that the decomposition of hydrogen iodide in the dark at high temperatures was a bimolecular reaction, whereas the decomposition in light was a unimolecular reaction. The suggestion that this difference is only an apparent one, and that the lowering of the order of the reaction might be due to the absorption of the active rays by the surface layer of the hydrogen iodide, has been tested by experiment. The glass tubes containing the hydrogen iodide were surrounded by wider tubes, containing in some cases air, in other cases hydrogen iodide, and were then exposed to sunlight. The decomposition in the inner tubes was practically equal under the two sets of conditions; hence the suggested explanation is disproved.

J. C. P.

Action of Oxygen on Metals. EDUARD JORDIS and W. ROSENHAUPT (*Zeitsch. angew. Chem.*, 1908, **21**, 50—66).—A complete account of work already partly published (this vol., ii, 98, 107). It is now found that above 145°, air attacks copper more energetically than does oxygen. The greater oxidising power of air and of moist oxygen, as compared with that of dry oxygen, is ascribed to the participation in the reaction of oxidation products of nitrogen and water. The course of the oxidation depends on the behaviour of the surface layer

of the metal; progressive oxidation is possible only if the oxide first formed does not act as a protective coating. An oxidisable surface may be the result of (a) the solution of the oxygen in the metal as such or as an alloy of copper and oxygen; (b) the diffusion of the oxygen through the layer of oxide which may dissolve the oxygen or be merely porous to it; (c) the alternate formation of lower and higher oxides, or (d) the layer of oxide scaling off from the metal. Examples of each case are given. During the oxidation, metallic filings shrink together and form a mass. With suitable apparatus, it would be possible to judge from the surface colours as to the ratio M : O in the outermost layer of the metal. G. Y.

[Formation of Ozone, Nitrogen Peroxide, and Hydrogen Peroxide in Reactions in Air which Develop High Temperatures, &c.]. EDWARD H. KEISER and LEROY MCMASTER (*Amer. Chem. J.*, 1908, 39, 101—104).—See this vol., ii, 223.

Presence of Sulphur in some of the Hotter Stars. SIR NORMAN LOCKYER (*Proc. Roy. Soc.*, 1907, 80, A, 50—57).—Certain lines in the spectrum of a star (Rigel) have been found to coincide in wave-length with prominent lines in the spark-spectrum and vacuum-tube spectrum of sulphur. There are, however, in that part of the spectrum in which comparison is possible, at least two well-defined lines ($\lambda = 4253\cdot8$, $4285\cdot1$, and possibly $4295\cdot0$) in the spark-spectrum of sulphur which are not present in the spectrum of Rigel, but these two lines are present in certain stars hotter than Rigel. The evidence for the presence of sulphur in stars is therefore regarded as conclusive. G. S.

Behaviour of Thiosulphuric Acid and its Use in Volumetric Analysis. ANGELO CASOLARI (*Gazzetta*, 1907, 37, ii, 601—608).—The decomposition of thiosulphuric acid begins immediately the acid is liberated from its salts, but titration of acidified solutions of sodium thiosulphate with iodine shows that the decomposition occurs slowly in dilute solutions. Sodium thiosulphate is hence capable of giving exact results when titrated with acid solutions (compare this vol., ii, 222). The opalescence appearing in solutions of sodium thiosulphate in presence of acid is due to the presence of a small proportion of free sulphur, which, probably owing to a change of state, has assumed the molecular form. Such opalescent liquids become clear when sulphite ions are added to them or hydrogen ions are removed, thiosulphuric acid being regenerated. When solutions of thiosulphuric acid are rendered alkaline and then faintly acidified, they yield an appreciable odour of hydrogen sulphide; the same is the case with the thionic acids which liberate sulphur. T. H. P.

Action of Carbonates on Tetrathionates. V. AUGUST GUTMANN (*Ber.*, 1908, 41, 300—307. Compare Abstr., 1905, ii, 384, 813; 1906, i, 149; 1907, ii, 862).—The action of alkali carbonates on sodium tetrathionate is different from that of alkali hydroxides; in addition to sodium thiosulphate, sulphate is formed instead of the sulphite obtained in the latter case. The experiments were carried

out with sodium, potassium, and lithium carbonates, as well as ammonia, the solutions being boiled for half an hour. Quantitative experiments carried out either by the author's method (Abstr., 1907, ii, 812), or by direct titration of the excess of carbonate, show that the reaction takes place in accordance with the equation: $4\text{Na}_2\text{S}_4\text{O}_6 + 5\text{Na}_2\text{CO}_3 = 7\text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + 5\text{CO}_2$, or $4\text{S}_4\text{O}_5 = 7\text{S}_2\text{O}_2 + 2\text{SO}_3$.

When, however, the carbonates of barium, strontium, and calcium were examined, it was found that the thiosulphate could not be determined by the cyanide and silver nitrate method as silver sulphide was precipitated, notwithstanding the fact that there was no sulphide in the solution before treatment with cyanide. This accords with Drechsel's suggestion that thiosulphate may have the isomeric forms $\text{O}=\text{S}<\begin{smallmatrix} \text{ONa} \\ \text{SNa} \end{smallmatrix}$ and $\text{S}=\text{S}<\begin{smallmatrix} \text{ONa} \\ \text{ONa} \end{smallmatrix}$.

An aqueous solution of sodium tetrathionate on boiling forms sodium sulphate, sulphur dioxide, and sulphur, not trithionate and sulphur as stated by Kessler (*Ann. Phys. Chem.*, 1848, [ii], 74, 253).

W. R.

Synthesis of Ammonia. HERMANN C. WOLTERECK (*Compt. rend.*, 1908, 146, 124—125. Compare Abstr., 1904, ii, 115; Brunel and Woog, this vol., ii, 34).—When a mixture of nitrogen (1 vol.) and hydrogen is passed over reduced iron, spread in thin layers on asbestos fibre, and heated at 550° , small quantities of ammonia are formed. The yield is increased slightly by substituting the oxide for the metal, but in both cases the reaction stops after a time. Similar results are obtained with the oxides of nickel, cobalt, copper, cadmium, silver, lead, bismuth, chromium, and iron, the last three giving the best yields. The reaction is made continuous by replacing the nitrogen by air, and the results are improved by introduction of water vapour, whilst the hydrogen can be replaced by coal gas freed from nitrogenous products. Passage of 100 litres of a mixture of hydrogen (1 vol.) and air (78 vols.) through water kept at 80° , and then over iron oxidised and reduced by carbon monoxide before the experiment, gave at different temperatures the following amounts of ammonia: $260\text{--}300^\circ$ 0.0803 gram, $300\text{--}350^\circ$ 0.204 gram, $350\text{--}400^\circ$ 0.119 gram, $400\text{--}450^\circ$ 0.0134 gram, $450\text{--}550^\circ$ 0.0411 gram, $550\text{--}650^\circ$ 0.0236 gram, all the experiments occupying 4.5 hours. These results show that $300\text{--}350^\circ$ is the most favourable temperature. Diminishing the velocity of the gas, that is, prolonging its contact with the iron, diminishes the yield. Other oxidisable materials which can be substituted for the reduced iron are coke and wood-charcoal, but better results are obtained with peat. A series of comparative experiments using sugar-charcoal and varying the temperature, and the volume and velocity of the mixed gases, show that the best results are obtained at 450° with 40 litres of gas passing in six hours, in which case 0.9 gram of ammonia is formed per 100 grams of charcoal burned.

E. H.

Electrolytic Reduction of Hydroxylamine at Copper Cathodes. JULIUS TAFEL and HANS HAHN (*Zeitsch. anorg. Chem.*, 1908, 56, 375—384).—In a previous paper (Abstr., 1902, ii, 559), it

was shown that hydroxylamine sulphate, dissolved in water containing a large proportion (20—50%) of sulphuric acid, is not reduced at a copper cathode, whilst Flaschner (Abstr., 1907, ii, 454) has observed a certain amount of reduction in dilute sulphuric acid solution. It is now shown that reduction always takes place when the sulphuric acid concentration in the layer of electrolyte in contact with the cathode is reduced beyond a certain point; and when there is no excess of acid; in other words, when hydroxylamine sulphate itself is electrolysed, the reduction is quantitative. These results are most readily accounted for on the view that only free hydroxylamine (produced in this case by partial hydrolysis of the sulphate), but not the hydroxylammonium ion, NH_3OH^+ , is reduced at a copper cathode. G. S.

Analysis of the Oxides of Nitrogen by means of their Ultra-red Absorption Spectra. EMIL WARBURG and G. LEITHÄUSER (*Sitzungsber. k. Akad. Wiss. Berlin*, 1908, 148—153).—The absorption spectra of the oxides of nitrogen and of ozone for ultra-red radiation between the wave-lengths 2.7μ and 7μ have been determined. The apparatus consisted of a Nernst lamp as the radiating source, a mirror spectrometer provided with a fluorspar prism, and a vacuum-bolometer as the receiving instrument. The maxima of absorption are very different for the various oxides of nitrogen; the wave-length values and the angles of minimum deviation corresponding with these absorption maxima are tabulated for N_2O_5 , N_2O_4 , NO_2 , NO , N_2O , and O_3 . The wave-lengths characteristic of the N_2O_4 and NO_2 molecules were determined by observations on nitrogen peroxide at different temperatures.

The data are applied to the examination of the products formed when electric discharge takes place in air. It is found that the action of the silent discharge, in the Siemens' ozoniser, not only yields ozone, but also nitrous oxide and nitrogen pentoxide. Spark discharge through air between platinum electrodes yields nitrogen peroxide and nitrous oxide. Alternating arc discharge at high potential in dry air yields only nitrogen peroxide. H. M. D.

Preparation of Pure Nitrites from Nitrous Fumes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 188188).—Inasmuch as the oxidation of nitric oxide to nitrogen trioxide is known to occur very rapidly, whilst the further oxidation to nitrogen peroxide proceeds relatively slowly, it has been recently suggested by Raschig that if the oxides from atmospheric nitrogen could be absorbed in about one second after their production in the electric arc it would be possible to prepare in this way pure nitrous acid or nitrites. It has now been found that this inconveniently rapid absorption of the gas is unnecessary if only the gaseous mixture containing chemically combined nitrogen and oxygen in the proportion $\text{N}_2:\text{O}_2$ is heated at 300° until absorption occurs. In these circumstances, the further oxidation to nitrogen peroxide is almost entirely inhibited, and pure nitrites can be prepared on a technical scale by absorbing with alkali hydroxides or carbonates, or even with the hydroxides of the alkaline earths. As the absorption of the heated gas leads to the generation of steam, solutions of low vapour pressure are employed in order that the action

may not be retarded owing to dilution of the gases with steam. With this end in view, strong solutions of nitrites are employed as absorbents.

G. T. M.

Heteromorphic (Allotropic) Modifications of the [Elements of the] Phosphorus-Arsenic Group. GOTTLOB E. LINCK (*Zeitsch. anorg. Chem.*, 1908, 56, 393—400).—The paper contains a summary of the progress of knowledge as to the allotropic modifications of the elements of the phosphorus group since the author's former publication on the subject (*Abstr.*, 1899, ii, 415). The work of Reppert (*Diss. Halle*) on the modifications of arsenic is adversely criticised in some respects.

The crystals of red phosphorus (Hittorf's phosphorus) are biaxial and probably monoclinic.

G. S.

Hittorf's Phosphorus. ALFRED STOCK (*Ber.*, 1908, 41, 250—251. Compare Linck, preceding abstract).—Largely polemical. Stock and Johannsen (*Diss. Berlin*, 1904) found that Hittorf's crystalline, red phosphorus, described as crystallising in the hexagonal hemihedric system, in reality forms reddish-brown, transparent plates, which appear violet-red in reflected light; these are biaxial and probably belong to the monoclinic system.

E. F. A.

Transformation of Solutions of White Phosphorus into Red Phosphorus. ALBERT COLSON (*Compt. rend.*, 1908, 146, 71—73. Compare this vol., ii, 35).—The velocity of the change of white into red phosphorus depends on the temperature and on the pressure of the vapour, and in the present paper the author shows that similar factors regulate the transformation of white phosphorus in solution into red phosphorus; the velocity of the change varies with the temperature and with the concentration of the solution. The experiments were conducted on solutions of phosphorus in oil of turpentine or carbon disulphide placed in sealed tubes, and, in order to avoid inequalities of temperature, these were placed in solutions of phosphorus in turpentine and heated to the required temperature. A solution of phosphorus in oil of turpentine, containing 23 grams per litre, remained clear after heating for fifty-two hours at 230—235°, but gave a thick deposit of red phosphorus after heating for eight to ten hours at 285—290°.

A solution containing 20 grams of phosphorus in a litre of oil of turpentine, deposited red phosphorus after heating for fifty-five hours at 260—265°, whilst a solution of phosphorus in carbon disulphide, containing 90 grams per litre, deposited red phosphorus after heating for fifteen hours at the same temperature. Three tubes containing respectively 150, 125, and 10 grams of phosphorus in 100 grams of carbon disulphide were heated at 225—230°; at the end of four hours the first tube contained a large quantity of red phosphorus, the second tube contained traces of the red phosphorus, whilst the contents of the third tube were unaltered.

M. A. W.

Action of Arsenic Hydride on Solutions of Halogens, Halogen Acids, and other Oxidising Agents. HANS RECKLEBEN and GEORG LOCKEMANN (*Zeitsch. anal. Chem.*, 1908, 47, 105—125).—Arsenic hydride is oxidised quantitatively to arsenic acid by iodine,

bromine, and chlorine in presence of water; hypochlorites and hypobromites act in a less satisfactory manner. In presence of a catalyst, the oxidation may be carried out by iodic acid and iodates, also by bromic acid and bromates. Chloric acid oxidises it to arsenious acid, but chlorates are quite inactive. Perchlorates in acid solution and in presence of a catalyst (a trace of iodine, for instance) act but very slowly. Periodates act like iodates, but much more slowly. Permanganates in neutral or acid solution, also alkaline ferricyanide (very slowly) and potassium dichromate in sulphuric acid solution, absorb the arsenic hydride completely. Nitric acid, sulphuric acid, solutions of persulphate, chromate, dichromate, and neutral ferricyanide absorb arsenic hydride very slowly and incompletely, whilst solutions of metallic nitrites, nitrates, hydrogen sulphates, and arsenious and arsenic acids are still less active.

Hydrogen peroxide acts very slowly; at first, arsenic is deposited, which is then gradually oxidised to arsenious or arsenic acid. In contact with potassium or sodium hydroxide and air, a separation of arsenic is noticed.

L. DE K.

Constitution of the Carbon Molecule from the Standpoint of Thermo-chemistry. H. STANLEY REDGROVE (*Chem. News*, 1908, 97, 37).—An attempt to elucidate the constitution of the carbon molecule from a consideration of the heat values of the different types of carbon linkings (compare Abstr., 1907, ii, 446, 604, 929). The formula recently suggested by Dewar (*Chem. News*, 1908, 97, 19) is not in agreement with thermochemical data.

H. M. D.

Density of Graphite. HENRY LE CHATELIER and S. WOLOGDINE (*Compt. rend.*, 1908, 146, 49—53).—The belief in the existence of the numerous polymerides of carbon is based on their difference in density; thus the density of amorphous carbon varies from 1 to 1.6, of graphite from 1.8 to 2.6, whilst that of the diamond is practically constant at 3.50 to 3.51. The authors have redetermined the density of graphite from eight different sources, natural or artificial, using a mixture of tetrabromoethane and ethyl ether, in which the graphite floated at any height. Preliminary experiments showed that the discrepancies in the densities of the different specimens were due to the presence of traces of impurities not removed by treatment with nitric acid, or to air in the pores of the graphite which was not completely eliminated in a vacuum. When, however, the graphite was fused with potassium hydroxide, after preliminary treatment with warm fuming nitric acid, washed, and then boiled with hydrochloric acid, D 1.12, dried at a dull red heat, and finally subjected to a pressure of 5000 kilos. per square centimetre, each specimen of graphite had D₄¹⁵ 2.255.

M. A. W

Relation Between the Composition of Coal and the Amounts of Carbon Monoxide and Dioxide contained in Gas Distilled from it. LEO VIGNON (*Bull. Soc. chim.*, 1908, [iv], 3, 109—114).—The object of the investigation was to determine what

relationship existed between the amount of oxygen in the coal and that in the oxygenated gases produced on its distillation.

Five samples of coal were used, and in these the amounts of calcium carbonate, carbon, hydrogen, nitrogen, sulphur, and oxygen (by difference) were determined, and finally the washed gases produced by their destructive distillation at 900° were analysed.

The results, which are given in detail in the original, show that the more oxygen the coal contains the larger are the amounts of carbon monoxide and dioxide produced on its distillation, and that the quotient of the total oxygen in these two gases, produced on distillation, by the oxygen originally present in the coal ranges from 0.292 to 0.314, that is, rather less than one-third is evolved in these two forms. The relative proportions of the two gases vary with the conditions, and at temperatures above 900° there is a tendency for carbon dioxide to be replaced by the monoxide.

T. A. H.

Dissociation of Carbonyl Chloride. MAX BODENSTEIN and GEORGE DUNANT (*Zeitsch. physikal. Chem.*, 1908, **61**, 437—446).—Carbonyl chloride or a mixture of carbon monoxide and chlorine in equivalent proportions was passed through a heated tube and the issuing gas was analysed. At 800° , carbonyl chloride is completely decomposed; at 603° , it is dissociated to about 91%; at 553° , to about 80%, and at 503° , to about 67%. From the corresponding equilibrium constants, the heat effect of the reaction $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ is calculated to be about 23,000 cal., a figure in rough agreement with the calorimetric determinations of Thomsen and Berthelot, and with Nernst's theory (see Nernst, *Abstr.*, 1906, ii, 727; Brill, *Abstr.*, 1907, ii, 233).

Some experiments on the rate of formation and decomposition of carbonyl chloride have been made at 503° , and the results obtained are best represented by the formulæ which Bodenstein and Wolgast have suggested (see this vol., ii, 162).

J. C. P.

Dissociation of Fused Silicates. CORNELIO DOELTER (*Monatsh.*, 1907, **28**, 1313—1379. Compare *Abstr.*, 1906, ii, 665).—An investigation of the extent to which silicates in the fused state are electrolytically dissociated, if at all, has been undertaken as a knowledge of this subject is necessary for the elucidation of the results obtained from the general study of fused silicates. In view of the experimental difficulties met with in the course of the work, the results now published must be regarded only as provisional.

It is found that the conductivity of the silicates depends chiefly on the temperature; silicates which in the solid state are almost non-conductors have a conductivity approaching that of dilute salt solutions when raised to a sufficiently high temperature. As at high, but varying, temperatures the different silicates examined have approximately the same conductivity, comparisons must be made only at a given temperature interval above or below the melting points, which are represented on the temperature-resistance curve by a break or by a gradual bend. If the conductivity is measured during cooling, a sharp break occurs in the curve for silicates which crystallise, but

there is no break in the curve for those which solidify to a glass.

The increase in the conductivity with rise of temperature may depend on increasing dissociation or on an increase in the mobility of the ions. It is concluded that a gradual change in the conductivity in the neighbourhood of the temperature of solidification must depend at least partly on a diminution of the dissociation, but that a sharp break results chiefly from the marked loss of mobility of the ions which must occur on crystallisation, since such wandering of the ions as may be possible in an amorphous solid cannot take place in a crystalline substance. In connexion with this, the author discusses the relation between the coefficient of internal friction and the conductivity of fused salts.

From the comparison of the results obtained with the different silicates examined, it is concluded that at high temperatures all silicates are electrolytically dissociated; at medium temperatures, orthoclase is dissociated to a greater, labradorite to a smaller, extent than augite or hornblende. Of two silicates, that which melts at the higher temperature is dissociated to the less extent at a given medium temperature. In agreement with this are the results of experiments which show that, whilst simple silicates such as olivine, enstatite, augite, and also labradorite always separate after fusion, other silicates are not reformed.

G. Y.

Colloidal Sodium Chloride. CARL PAAL and GUSTAV KÜHN (*Ber.*, 1908, 41, 51—57).—Relatively stable organosols of sodium chloride, similar to those described previously (*Abstr.*, 1906, ii, 749), are obtained by the action of ethyl chloroacetate, chloroacetone, and phenacyl chloride on ethyl sodioethylmalonate in benzene or ether. The colloidal solution obtained by acting on ethyl sodioethylmalonate with ethyl chloroacetate in benzene, when heated for some time, becomes more viscid, remaining, however, quite liquid and apparently homogeneous. This product, when poured into a glass vessel, deposits a gel on the sides of the vessel, and, when filtered through a filter paper, separates into a gel, which remains on the filter, and into a benzene solution of the organic compounds formed in the reaction, which passes through the filter and is almost free from sodium chloride. The authors propose to name such products *liquid gels*.

The action of sulphuryl chloride on ethyl sodioethylmalonate in benzene, results in the formation of a sodium chloride sol which rapidly changes into the liquid gel.

W. H. G.

Colloidal Sodium Bromide and Iodide. CARL PAAL and GUSTAV KÜHN (*Ber.*, 1908, 41, 58—61. Compare preceding abstract).—Organosols and gels of sodium bromide are obtained by using ethyl sodioethylmalonate instead of ethyl sodiomalonate (*Abstr.*, 1906, ii, 749), and are similar to those previously described (*loc. cit.*). When ether is employed as the solvent, the organosol of sodium bromide changes into a *gel*, which is not gelatinous, but consists of large aggregates of small, transparent, amorphous globules.

It has also been found possible by acting on ethyl sodioethylmalonate with ethyl β -iodopropionate in benzene or ether to obtain an *organosol* of sodium iodide, which is, however, exceedingly unstable, and rapidly changes into a *gel*. The sodium iodide, previously inaccurately described as crystalline (*loc. cit.*), when examined under a microscope, is found to consist of aggregates of amorphous, transparent globules. W. H. G.

Percarbonates. RICHARD WOLFFENSTEIN and ERICH PELTNER (*Ber.*, 1908, 41, 280—297. Compare this vol., ii, 183; Constam and von Hansen, *Abstr.*, 1897, ii, 550; von Hansen, 1898, ii, 23; Tanatar, 1899, ii, 482; 1903, ii, 208; Willstätter, 1903, ii, 537; Kasanezky, 1903, ii, 366; Bauer, D.R.-P. 145746).—The investigation of the action of carbon dioxide on peroxide of sodium has led to the preparation of sodium percarbonates containing, in general, water of crystallisation, but not hydrogen peroxide of crystallisation. This is shown by a study of the analytical results and by the mode of preparation, the first product being the normal salt, and the second the hydrogen salt or its anhydride.

Sodium dioxide carbonate, $\text{Na}_2\text{CO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, is best prepared by first hydrating $\frac{1}{2}$ gram-mol. of sodium peroxide with 50 grams of ice, and then slowly passing a current of carbon dioxide over the mass. The temperature is kept below 0° , and, as soon as the mass becomes pasty, another $\frac{1}{2}$ gram-mol. of sodium peroxide is added in portions. The action is finished when 1 gram-mol. of carbon dioxide has been absorbed. The unstable salt is washed with alcohol and ether, and dried in a vacuum. *Sodium dioxide dicarbonate*, $\text{Na}_2\text{C}_2\text{O}_6$, is obtained when the gas can no longer be absorbed. It is more stable than the normal carbonate.

When a similar series of experiments were carried out with Tafel's sodyl hydroxide (*Abstr.*, 1894, ii, 448), it was found that the dry substance was not acted on by carbon dioxide, but in the presence of a trace of moisture action occurs, the mass becoming warm and decomposing. Sodyl hydroxide containing 26—30% water is kept below 0° , and treated carefully with carbon dioxide, solid or gas, when *sodium trioxide dicarbonate*, NaHCO_4 or $\text{Na}_2\text{C}_2\text{O}_7$, results. It is very unstable. The preparation of a *sodium trioxide hydrate*, $\text{Na}\cdot\text{O}\cdot\text{O}\cdot\text{H}$, isomeric with Tafel's sodyl hydroxide, $\text{O}\cdot\text{Na}\cdot\text{OH}$, is accomplished by treating sodium ethoxide with a mixture of 30% hydrogen peroxide (1 mol.) and absolute alcohol, when it is precipitated. From this material, an isomeric *sodium trioxide dicarbonate*, NaHCO_4 or $\text{Na}_2\text{C}_2\text{O}_7$, is obtained in the above way. Washing the product with alcohol and ether removes hydrogen peroxide, but analysis of the washed material agrees with the formula. It is shown that the sodium trioxide hydrate, as above prepared, contains hydrogen peroxide of crystallisation. The dicarbonate is much easier to prepare than its isomeride, is much more stable, and behaves differently towards heat. *Sodium trioxide carbonate*, Na_2CO_5 , is formed on treating sodium trioxide hydrate with the calculated quantity of carbon dioxide; it is less stable than the dicarbonate. W. R.

Preparation of Sodium Hydrogen Percarbonates. EMANUEL MERCK (D.R.-P. 188569).—At low temperatures, hydrated sodium

peroxide furnishes sodium percarbonate, Na_2CO_4 , on treatment with solid, liquid, or gaseous carbon dioxide. A substance containing a greater proportion of CO_2 is obtained by adding 20 parts of ice to 39 parts of sodium peroxide, and then treating the sodium peroxide hydrate thus produced with 33 parts of carbon dioxide, the mixture being stirred until the reaction is complete. *Sodium hydrogen percarbonate*, $4\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{CO}_3$, finds employment as a disinfectant and in the preparation of hydrogen peroxide. G. T. M.

Constitution of Sodium Hyposulphite. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1588—1617).—See this vol., i., 132.

Rubidium Dichromate. GREGOIRE WYROUBOFF (*Bull. Soc. chim.*, 1908, [iv], 3, 7—10. Compare *Bull. Soc. chim.*, 1901, [iii], 25, 105; Abstr., 1901, ii, 149, and Stortenbeker, Abstr., 1907, ii, 764).—The author reiterates his opinion that the monoclinic and triclinic forms of this salt have practically the same solubility, and attributes the greater solubility, observed by Stortenbeker, for the monoclinic form to the fact that this investigator did not render his preparation of the monoclinic form anhydrous by melting it, to eliminate occluded water. Further, he cannot confirm Stortenbeker's observation that the monoclinic form disintegrates slowly in contact with a solution containing excess of the salt and still more slowly when dry. Crystals of the two forms in his experience can be kept for months in contact with a saturated solution of the salt without showing any tendency to transformation, whilst crystals have been kept in a dry state for eighteen years without showing any change in form. T. A. H.

Ammonium Nitrite. JULIUS MEYER and EMIL TRUTZER (*Zeitsch. Elektrochem.*, 1908, 14, 69—76).—The decomposition of ammonium nitrite in aqueous solution has been studied. The discrepancies in the results of previous observers appear to be due to the use of impure water and impure ammonium nitrite. A trace of carbon dioxide in the water was found to increase the rate of decomposition by about 30%. The ammonium nitrite was purified by fractional precipitation of an alcoholic solution with ether. The dry salt decomposes when kept, ammonia and oxides of nitrogen being formed; these are absorbed by the salt, which becomes yellow. The rate of decomposition of the solutions increases nearly in proportion to the age of the salt. A sample of the salt three months old decomposes almost explosively at 60° . The rates of decomposition of solutions of salt up to eight weeks old were measured and velocity constants calculated. The results are well represented by the equation of the unimolecular reaction, but the velocity constant instead of being independent of the initial concentration of the solution is proportional to it. This is regarded as indicating that the change is due to the catalytic action of the acid decomposition products contained in the dry salt, and this view is also in accordance with the increase of the constants with the age of the salt.

Colloidal platinum appears to accelerate the reaction.

T. E.

Ammonium Syngenite. JOH. D'ANS (*Ber.*, 1908, 41, 187—189).—Replying to Bell and Taber (*Abstr.*, 1907, ii, 867), the author shows that the double sulphate of calcium and ammonium which has not been treated with 50% alcohol, but freed from mother liquor by the use of a hydraulic press, or by washing first with absolute alcohol and then with ether, has the composition represented by the formula $\text{CaSO}_4(\text{NH}_4)_2\text{SO}_4\cdot\text{H}_2\text{O}$ (compare *Abstr.*, 1906, ii, 751).

W. H. G.

The Reduction of Silver Oxide by Hydrogen: Colloidal Silver. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1908, 14, 49—63).—In order to throw light on the apparent volatilisation of metals in vacuum tubes, the formation of silver films in the reduction of silver oxide by hydrogen has been studied.

The perfectly dry substances do not react; in presence of a trace of moisture, the reaction takes place even at the ordinary temperature. The presence of larger quantities of water retards the change, which always begins at the points of contact of silver oxide and glass. If a little silver oxide dust is distributed over the walls of a flask, which is then filled with hydrogen nearly saturated with aqueous vapour, minute drops of water can be caused to condense round the silver oxide particles by cooling one side of the flask. The reduction takes place in these drops much more rapidly than in the dry particles, and, when the drops are evaporated, a film of silver is left on the glass. The film consists of colloidal silver; it does not conduct electricity at first, but soon passes into the ordinary form of the metal.

When a suspension of silver oxide in pure water is reduced by hydrogen, the reaction takes place almost exclusively in the contact surface of glass and solution, the solid oxide being unattacked; the reduced silver is obtained partly as a mirror and partly as a hydrosol. The rate of reduction of the silver oxide increases with the ratio (glass surface)/(volume of solution), whilst the ratio hydrosol/mirror diminishes. The nature of the hydrosol obtained depends on the kind of vessel used. Ordinary glass and quartz glass give yellowish-brown solutions, Jena glass yields red, blue, or violet solutions, whereas platinum gives no hydrosol, all the silver separating as a crystalline deposit on the platinum. The solutions contain dissolved silver hydroxide in addition to the colloidal silver. The latter is estimated by precipitation with potassium nitrate solution. The conductivity of a solution is only slightly larger than that of a solution of silver hydroxide of the same strength. By passing a current of hydrogen through a solution of hydrosol and silver hydroxide contained in a platinised platinum basin, the silver hydroxide is reduced, leaving a solution of the pure hydrosol. The conductivity of the purified solution is about one-tenth of the original conductivity, and about three times that of the pure water used, so that the removal of electrolytes is very complete. The quantity of colloidal silver in the purified solutions is always less than that in the original solution; calling the difference Δ , and the quantity in the purified solution Ag , the ratio Ag/Δ is usually not very far from unity for all the yellowish-brown solutions, whilst it varies from 3 to 20 for the blue or violet

solutions. This is the only difference found between the two kinds of solution; the quantity and quality of dissolved glass does not affect the result; a solution of ordinary glass in a Jena flask gave a blue hydrosol and not a brown one. The author thinks that the original hydrosol molecule is a compound of silver and silver hydroxide; the treatment with hydrogen in a platinum vessel removes both the combined and the dissolved silver hydroxide; the brown solutions would, therefore, contain molecules having $\text{Ag}:\text{AgOH}=1$, whilst in the violet solutions this ratio is much larger. If a trace of silver is brought into a borax bead, a brown or violet coloration is obtained as the bead cools, which is probably due to the separation of colloidal silver. The reduction of silver oxide by carbon monoxide also yields silver hydrosols. T. E.

Some Effects of Sunlight on Colourless Glass. ROSS AIKEN GORTNER (*Amer. Chem. J.*, 1908, 39, 157—162).—It has been shown by Crookes (*Chem. News*, 1905, 91, 73), Avery (*Abstr.*, 1905, ii, 589), Simpson (*Chem. News*, 1905, 91, 236), and Rueger (*Abstr.*, 1905, ii, 709) that certain specimens of glass assume a violet colour on exposure to sunlight for a considerable time. Fischer (*Abstr.*, 1905, ii, 320) has found that the same change can be effected in glass containing manganese by exposing it to the ultra-violet rays from a quartz-mercury lamp. In only one case (Alway and Gortner, *Amer. Chem. J.*, 1907, 37, 1) has the time necessary to produce the coloration been recorded.

Several specimens of glass from various sources have been exposed to the direct action of the sun, and the following observations have been made. Glass which is relatively rich in manganese (about 0.2—0.3%) becomes coloured in less than a month, the degree of coloration being proportional to the manganese present. Most specimens of glass containing only a small quantity of manganese become coloured in less than a year, and the colour becomes deeper if the time of exposure is increased. The production of this violet coloration is a proof of the presence of manganese, but some specimens of glass, although containing this element, do not become coloured. Rueger's suggestion (*loc. cit.*) that glass may become coloured by lying in the proximity of manganese or its ores is untenable. A violet background is more favourable to the action of the ultra-violet rays than one of any other colour. White, yellow, blue, and red act alike, and seem to have no effect on the rate of coloration, whilst brown and black appear to have a retarding action. E. G.

Barium Percarbonate [Barium Dioxide Carbonate]. RICHARD WOLFFENSTEIN and ERICH PELTNER (*Ber.*, 1908, 41, 275—280).—According to Duprey (*Compt. rend.*, 1862, 55, 736) and Balard (*ibid.*, 738), the action of carbon dioxide on barium dioxide in water is to form barium carbonate and hydrogen peroxide. A re-investigation of the reaction according to Duprey's conditions shows that, at the beginning, the hydrogen peroxide formed corresponds with the barium peroxide used, but after some time the action ceases. If instead of using carbon dioxide in excess, barium dioxide is employed

in considerable excess, then no separation of hydrogen peroxide occurs, although the carbon dioxide is absorbed. Continued saturation of this solution with the gas leads, however, to the formation of hydrogen peroxide, and in a short time all the active oxygen exists as hydrogen peroxide. The reaction therefore occurs in two stages, and, in order to separate the intermediate compound, *barium dioxide carbonate*, BaCO_4 , particular care must be taken to avoid the presence of too much water on the one hand, otherwise hydrogen peroxide is liberated, or of too little water on the other, as that leads to the development of heat and decomposition of the compound. It is best prepared by cooling 30% barium dioxide solution to 0° , and slowly saturating the solution with carbon dioxide. The compound is light yellow, and does not lose hydrogen peroxide quickly in cold water, or on washing with ether or alcohol, so that, although the compound has not been obtained free from water, it does not contain hydrogen peroxide of crystallisation. W. R.

False Equilibria. ERNST H. BÜCHNER (*Zeitsch. Elektrochem.*, 1908, 14, 63—64).—The reaction $\text{MgCO}_3 \cdot 3\text{H}_2\text{O} + \text{KHCO}_3 + n\text{H}_2\text{O} \rightleftharpoons \text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O} + (n-1)\text{H}_2\text{O}$ has been stated by Engel to yield solutions of different composition when the double salt is digested with water, on the one hand, and when magnesium carbonate is digested with a solution of potassium hydrogen carbonate on the other. The experiments have been repeated at 20° and 30° , allowing the reaction to go on for twenty-four to thirty-two days, instead of for a few hours. It appears that the same solution is obtained, but that from four to eight days elapse before equilibrium is reached. T. E.

Magnesium Silicide. PAUL LEBEAU and ROBERT BOSSUET (*Compt. rend.*, 1908, 146, 282—284. Compare Gattermann, Abstr., 1889, 342; Winckler, Abstr., 1890, 1372; Vigouroux, Abstr., 1899, ii, 211).—Alloys of magnesium and silicon have been prepared, those containing 0—45% of silicon by heating fragments of magnesium with a mixture of magnesium filings and potassium silicofluoride, and those containing more than 45% by fusing magnesium filings with crystallised silicon and a small quantity of potassium silicofluoride. Metallographic examination of the polished surfaces of these shows (1) in the alloy containing 0.38% of silicon, grains of magnesium surrounded by a eutectic, but no crystals of the silicide; (2) in alloys containing 6—8% of silicon, well-defined crystals of the silicide in the midst of a eutectic very rich in magnesium; (3) that an alloy containing 40% of silicon is composed mainly of crystals of the silicide and a eutectic differing from the former and containing free silicon, and (4) crystals of free silicon in alloys containing more than 50% of that element. The pure silicide cannot be isolated by treating the alloys with any aqueous reagent, owing to the decomposing action of water, but the magnesium is dissolved away from an alloy containing 25% of silicon by means of ethyl iodide and ether, leaving brilliant, slate-blue, octahedral crystals of magnesium silicide, the analysis of which corresponds accurately with the formula Mg_2Si . Magnesium silicide slowly decomposes water at the ordinary temperature, giving hydrogen,

but no silicon hydride; it is vigorously attacked by cold hydrochloric acid, evolving hydrogen and spontaneously inflammable silicon hydrides, and is completely dissociated when heated in a vacuum or in a current of hydrogen at 1100—1200°.

Analyses of alloys containing free silicon show that in every case the ratio of the magnesium to the combined silicon is that required by the formula Mg_2Si . The conclusion is drawn that by the direct action of magnesium on silicon only the single definite compound Mg_2Si is produced. E. H.

The System: Zinc Oxide-Carbon Dioxide-Water. HANS MIKUSCH (*Zeitsch. anorg. Chem.*, 1908, **56**, 365—374).—As there is much uncertainty with regard to the number of basic carbonates of zinc, the question has been investigated on the basis of the phase rule. Neutral zinc carbonate was hydrolysed progressively with water at 25°, 50°, and 100°, and the composition of the liquid phase and of the residue determined from time to time; conversely, zinc carbonate was formed by the progressive action of carbon dioxide on the hydroxide, and the solid and liquid phases analysed from time to time. In both cases, sodium acetate was added to the liquid phase (compare Hawley, *Abstr.*, 1906, ii, 854) to dissolve sufficient of the carbonate and hydroxide to allow of analysis.

The results indicate that only the compound $5ZnO, 2CO_2, 4H_2O$ exists; the other basic salts described in the literature are solid solutions of zinc oxide and carbonate. G. S.

Direct Production of Dry Zinc Hyposulphite. CHEMISCHE FABRIK GRÜNAU, LANDSHOFF, and MEYER (D.R.-P. 184564).—Hitherto zinc hyposulphite has only been obtained in the form of the sodium double salt, but by means of suitable concentrations employed at definite temperatures it has been found possible to isolate the simple salt ZnS_2O_4 in a dry state. One hundred parts of zinc dust mixed with 150 to 200 parts of water were treated at 45—50° with a rapid stream of sulphur dioxide until the metal had entirely dissolved. The viscid, greyish-yellow mass thus produced, when cooled to the ordinary summer temperature, set to a stiff paste, which was collected and drained in an inert atmosphere.

A large excess of sulphur dioxide must be avoided, as this oxide reacts with the zinc hyposulphite, giving rise to polythionic acids.

G. T. M.

Specific Gravity of Aqueous Solutions of Cadmium Chloride. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1502—1506).—The specific gravity of cadmium chloride solutions of various concentrations has been redetermined, and on the basis of the three most accurate determinations the following formula has been deduced: $10^4 \cdot D_{20}^{20} = 9983 + 87.144p + 0.474p^2 + 0.00991p^3$ (where p = percentage concentration of the solution in question). The results calculated by means of this formula agree well with the experimental values and also with those obtained by other investigators. Z. K.

Alloys of Copper and Magnesium. G. G. URAZOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1566—1581).—The curve expressing the relation between the composition of the copper magnesium alloys and their freezing points consists of six branches, and is characterised by two maxima at 570° and 799° , corresponding with the compounds Mg_2Cu and MgCu_2 , and by three eutectic points at 480° and 16 at. % Cu, 555° and 41.5 at. % Cu, and 725° and 78 at. % Cu. Neither the metals nor the compounds form solid solutions. The eutectic and melting points observed by Boudouard (Abstr., 1903, ii, 78, 480) differ from those given here, it is also improbable that there is such a compound as MgCu (compare Guillet, Abstr., 1905, ii, 712). Photographs of the microstructure of various alloys are given and agree completely with the results deduced from the freezing-point curve. Z. K.

Heat Treatment of Copper-Zinc Alloys. GUY D. BENGOUGH and O. F. HUDSON (*J. Soc. Chem. Ind.*, 1908, 27, 43—52).—An alloy containing 60.43% of copper and 39.21% of zinc (Muntz metal) was cast and hard-rolled, and the effect of annealing on the structure and properties was studied. The relations of the α and β solid solutions were found to be in agreement with Shepherd's diagram (Abstr., 1904, ii, 662). By coating fractured surfaces with electrolytic copper and cutting sections, it was found that the fracture passes by preference through the β areas, but the mineralogical hardness of the two constituents is about the same. C. H. D.

Alloys of Copper with Cobalt, Iron, Manganese, and Magnesium. R. SAHMEN (*Zeitsch. anorg. Chem.*, 1908, 57, 1—33).—The investigation was carried out by Tammann's method of thermal analysis, controlled by microscopic observations. All the pairs of metals are completely miscible in the fused state. Only magnesium and copper enter into chemical combination, forming the compounds Cu_2Mg , m. p. 797° , and CuMg_2 , m. p. 570° .

Copper-Cobalt Alloys.—These metals form two series of mixed crystals, from 0—10% and 95.5—100% by weight of copper respectively. There is a break in the cooling curve at 1100° from 10—95% copper, below which the alloy completely solidifies to a conglomerate of the two series of mixed crystals.

On cooling, β -cobalt, which is non-magnetic, changes to magnetic α -cobalt. The transition temperature is lowered from 1115° (for pure cobalt) to 1050° by the addition of 10% of copper, remains constant at 1050° up to 90% of copper, and then falls with further addition of copper. Alloys containing 99% of copper are still magnetic.

Copper-Iron Alloys (compare Pfeiffer, Abstr., 1906, ii, 358).—The cast-iron employed contained less than 0.3% of impurities. The equilibrium diagram is very similar to that for copper-cobalt alloys. There are two series of mixed crystals, from 0—3.5% and 97.3—100% by weight of copper respectively. There is a break in the cooling curve from 3—97% of copper, below which the alloy is completely solidified to a conglomerate of mixed crystals.

The transition from γ - to β -iron has been followed thermally. By the gradual addition of copper up to 4% (saturated mixed crystals), it

is lowered from 878° to 715° , and remains constant on further addition of copper. If, however, the solidified alloy is heated for some time at 900° to 1000° and again cooled, the transition takes place at 790° . The change from β - to α -iron has been followed by magnetic observations. It occurs about 790° , and is not influenced by the presence of copper, so that the latter is not miscible in the solid state with α -iron.

The colour of the polished surface of the alloys varies gradually from red to grey as the proportion of iron increases. The tensile strength of the alloys was not determined.

Copper-Manganese Alloys (compare Schemtschuschny, Urasoff, and Rykowski (Abstr., 1907, ii, 777).—The freezing-point curve of these alloys falls from the melting points of both metals, and has a minimum at 866° and 65% by weight of copper. The deduction, from the form of the curve, that the metals form a continuous series of mixed crystals is confirmed by microscopic observations, but the alloys only become completely homogeneous when heated for some time below their melting point.

All the alloys up to 80% of copper are grey in colour. The alloy containing 2% of copper is about as hard as manganese, with further increase of the former metal they become softer, and between 10% and 100% of copper are not much harder than that metal.

Copper-Magnesium Alloys (compare Boudouard, Abstr., 1903, ii, 78, 480).—The freezing-point curve shows two maxima, at 797° and 33.3 atom. % and 570° and 66.7 atom. % of magnesium respectively, corresponding with the compounds Cu_2Mg and CuMg_2 , and three eutectic points, at 730° and 21.5 atom. %, 555° and 56 atom. %, and 465° and 85 atom. % of magnesium respectively.

On the etched surface of the alloys, the compound Cu_2Mg appears as polygonal crystals, and CuMg_2 in long, rod-shaped crystals. Both compounds are very brittle and of the same colour as magnesium.

The author's results differ in several respects from those of Boudouard (*loc. cit.*). The paper is illustrated by 17 photomicrographs. G. S.

Ammonio-cuprous Sulphate. ALBERT BOUZAT (*Compt. rend.*, 1908, 146, 75–77).—Ammonio-cuprous sulphate, $\text{Cu}_2\text{SO}_4 \cdot 4\text{NH}_3$ (compare Joannis, Abstr., 1898, ii, 221; 1903, ii, 371; 1904, i, 644; Péchard, Abstr., 1903, ii, 293; Foerster and Blankenberg, Abstr., 1907, ii, 89), is precipitated as a white, crystalline powder on the addition of alcohol to a solution of cuprous oxide and ammonium sulphate in aqueous ammonia at 50° in an atmosphere of hydrogen. Ammoniacal cuprous oxide, like the corresponding cupric compound (Abstr., 1902, ii, 490, 550), is therefore a sufficiently strong base to displace ammonium from its salts. M. A. W.

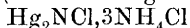
Interaction of Mercury with Alloys of other Metals. JOHN W. MALLETT (*Proc. Roy. Soc.*, 1908, 80, A, 83–87).—The action of mercury on certain alloys at the ordinary temperature has been examined. An alloy of tin and platinum, corresponding with the formula Sn_2Pt , is not acted on by mercury, but if a very small quantity of sodium is added to the mercury, a amalgamation takes place at once. The soft amalgam was strained by squeezing it through chamois leather

and the fluid portion found to contain very small quantities of both platinum and tin. A silver platinum alloy, corresponding with the formula Ag_4Pt , amalgamates with mercury. The fluid obtained by squeezing through chamois leather contains both silver and platinum, but the proportion of silver is greater than in the solid alloy. A copper-tin alloy, corresponding approximately with the formula Cu_4Sn , amalgamates very slowly with mercury, and the strained fluid contains only very small quantities of the two metals.

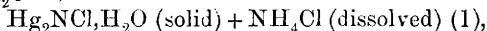
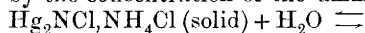
The experiments show that platinum prevents the amalgamation of tin, that silver causes platinum to pass into solution, and that by alloying copper and tin, the readiness and extent with which they unite with mercury, when separately exposed to its action, is greatly diminished.

H. M. D.

Dissociation by Water of the Double Chlorides of Ammonium and Dimercuriammonium. H. GAUDECHON (*Compt. rend.*, 1908, 146, 177—180).—The decomposition of the double chlorides, $\text{Hg}_2\text{NCl}, \text{NH}_4\text{Cl}$ (Rammelsberg and Pesci) and

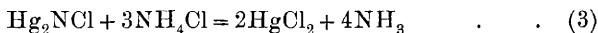


("white precipitate"), by water at the ordinary temperature is limited by the concentration of the ammonium chloride. The equation:



comprising three components in four phases, constitutes a univariant system. At 15° , the concentration of the liquid phase in equilibrium is 0.011 molecule of NH_4Cl per 100 molecules of water, whilst at 27° the concentration is 0.20. This increase in the decomposition is in accordance with the law of the displacement of equilibrium with variations in temperature, and it is shown that ammonium chloride combines with $\text{Hg}_2\text{NCl}, \text{H}_2\text{O}$ with a notable development of heat. The decomposition of $\text{Hg}_2\text{NCl}, 3\text{NH}_4\text{Cl}$ by water also constitutes a univariant system: $\text{NH}_2\text{Cl}, 3\text{NH}_4\text{Cl} (\text{solid}) \rightleftharpoons \text{Hg}_2\text{NCl}, \text{NH}_4\text{Cl} (\text{solid}) + \text{NH}_4\text{Cl} (\text{dissolved}) \quad (2)$. At 14° , the concentration of the liquid phase in equilibrium is 0.65 molecule per 100 molecules of water, and at 27° the concentration has increased to 0.84 molecule, which again agrees with the law of displacement of equilibrium, and the constant concentration at a given temperature establishes the non-existence of the compound $\text{Hg}_2\text{NCl}, 2\text{NH}_4\text{Cl}$. In the system (1) there is only a trace of mercury in solution, but in the system (2) the liquid contains a small quantity of the metal as Hg_2NCl or its compounds with NH_4Cl . At 15° , the compound $\text{Hg}_2\text{NCl}, 3\text{NH}_4\text{Cl}$ does not combine further with ammonium chloride.

At 100° , the decomposition of the two chlorides proceeds according to reactions which are the converse of those representing their formation, thus:



The reactions are really more complicated, it being necessary to dissolve the chlorides in ammonium chloride solution, but the quantities of ammonia, mercuric chloride, and mercuric oxide here represented are actually produced.

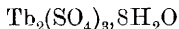
The conclusions are drawn that at the ordinary temperature in the presence of water the two chlorides behave as true double salts, although combination of NH_4Cl with Hg_2NCl to form $\text{Hg}_2\text{NCl}, \text{NH}_4\text{Cl}$ develops an unusually large amount of heat, and that in presence of boiling water the radicle Hg_2N tends to re-form its generators, ammonia, mercuric chloride, and mercuric oxide. E. H.

Neo-Erbium. KARL A. HOFMANN and O. BURGER (*Ber.*, 1908, 41, 308—312).—Neo-erbium oxide, prepared by Wilson and Cleve's method, contains thulium, holmium, and dysprosium as impurities. Fractional precipitation with aniline hydrochloride (Krüss, *Abstr.*, 1903, i, 376) is of no value for purification, as the holmium cannot be removed by this process. The methods adopted were (1) treatment of the salts with concentrated potassium sulphate solution, (2) evaporation to dryness with excess of sodium nitrite and extraction with water, when most of the erbium hydroxide is insoluble, (3) crystallisation of the formates, (4) gradual fractional precipitation with dilute ammonia, (5) Urbain's method of crystallising the ethyl sulphate (*Abstr.*, 1900, ii, 346; 1906, ii, 360).

Welsbach's method of crystallising the double oxalate (this vol., i, 26) is very effective for separating holmium and erbium.

The purified material appeared to be homogeneous, and repeated purification did not alter it. The atomic weight determined by the sulphate method, using Brauner's precautions (*Trans.*, 1902, 81, 1243) was found to be 167.43 (four determinations, O = 16, S = 32.06). The absorption spectrum of a 10% nitrate solution has bands λ 653, 523, 487, 450, 442. J. J. S.

Some Compounds of Terbium and of Dysprosium. GEORGES URBAIN and G. JANTSCH (*Compt. rend.*, 1908, 146, 127—129).—*Terbium peroxide* has a composition corresponding exactly with the formula Tb_4O_7 so long as too high a temperature has been avoided in its preparation by calcination of a terbium salt. The peroxide loses oxygen at a white heat, and consequently the composition of the product of calcining the sulphate at 1600° contains a variable quantity of oxygen, as estimated by dissolving in a sulphuric acid solution of ammonium ferrous sulphate and determining the excess of the latter by permanganate. Terbium peroxide dissolves in nitric acid diluted with a small quantity of water (8 : 1), giving colourless, monoclinic needles of *terbium nitrate*, $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, which give an aqueous solution neutral to litmus, and when heated in a sealed tube melt in their water of crystallisation at 89.3° . Terbium sulphate,



(Urbain, *Abstr.*, 1905, ii, 711), is also obtained as a crystalline powder of micaceous lamellæ by precipitation of a solution of terbium containing sulphuric acid by alcohol. *Terbium chloride*, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, formed by dissolution of the peroxide in hydrochloric acid, forms colourless, transparent, prismatic crystals, which are extremely hygroscopic and give an aqueous solution neutral to litmus.

Dysprosium does not form a peroxide, the oxide, Dy_2O_3 , remains unchanged when heated in either an oxidising or a reducing atmosphere. Under the conditions in which the hexahydrated terbium

nitrate is formed, dysprosium gives the pentahydrated *dysprosium nitrate*, $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, resembling bismuth nitrate. This loses water in a dry atmosphere, gives a neutral aqueous solution, and has m. p. 88.6° (in water of crystallisation). Dysprosium sulphate, $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (Urbain and Dementitroux, *Abstr.*, 1906, ii, 855), closely resembles the terbium salt. *Dysprosium chloride*, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$, is prepared similarly to the terbium chloride, to which it is analogous, but is less deliquescent. E. H.

Bromates of the Rare Earths. I. New Method for the Separation of the Yttrium Earths. CHARLES JAMES (*Chem. News*, 1908, 97, 61—62. Compare *Abstr.*, 1907, ii, 467).—The author briefly points out the disadvantages of the methods for the separation of the yttrium earths employed by Urbain (*Abstr.*, 1898, ii, 518; 1899, ii, 28; 1901, ii, 160), Demarçay (*Abstr.*, 1896, ii, 475; 1900, ii, 347), von Welsbach (*Abstr.*, 1907, ii, 26), Muthmann and Rolig (*Abstr.*, 1898, ii, 518), and Muthmann and Böhm (*Abstr.*, 1900, ii, 209), and, after examining the solubilities of the salts of a large number of inorganic and organic acids, recommends the fractional crystallisation of the bromates.

The rare earth material, generally in the form of the oxalates, is made into a paste with concentrated sulphuric acid, and heated until fumes cease to be evolved. The residue is powdered, dissolved in water at 0° , and the solution poured over an excess of barium bromate, the operation being performed on the water-bath with efficient stirring. When the double decomposition is completed, the filtered liquid is evaporated to such a concentration that about half the substance in solution crystallises out on cooling.

After six series of crystallisations, the spectroscope shows that a separation is being effected. After twenty operations, the least soluble fraction is colourless and consists mainly of yttrium bromate the absorption spectrum showing, however, that some dysprosium, and in a smaller degree, samarium and holmium are present. The brown colour of the oxide also indicates that terbium collects in this fraction. The more soluble fractions become yellower, those exhibiting the strongest colour showing very intense bands of dysprosium and holmium. Succeeding fractions attain a rose pink colour, and show only erbium bands. Then thulium begins to appear, and finally the most soluble fraction is reached, consisting largely of ytterbium.

The bromates of the rare earths arrange themselves in the following order of increasing solubility: samarium (europium?, gadolinium?), terbium, yttrium, dysprosium, holmium, erbium, thulium, and ytterbium. This order is not quite the same as that of the ethyl sulphates; the bromate method, in conjunction with Urbain's, should prove very valuable for the separation of yttrium from dysprosium and holmium, and possibly of thulium from ytterbium. C. S.

Action of Finely-divided Metals on Water. WILLEM VAN RYN (*Chem. Weekblad*, 1908, 5, 1—5. Compare Birnie, *Abstr.*, 1907, ii, 469).—The author has investigated the action of finely-divided aluminium, zinc, magnesium, nickel, copper, and lead on pure distilled

water at the ordinary temperature and at 100°. The lead and nickel were obtained by reduction of the oxalates in a current of hydrogen, and the copper by reduction of cuprous oxide. The oxalates of the other metals could not be reduced, so that finely-powdered commercial samples were employed.

Aluminium has no action on cold or boiling water, but addition of a small quantity of mercury produces an evolution of hydrogen which is increased by heat. Zinc decomposes cold water slowly, boiling water rapidly, the presence of mercury producing no effect. Magnesium resembles zinc, but addition of mercury causes a greater evolution of hydrogen than with aluminium. Nickel, copper, and lead, with or without mercury, do not liberate hydrogen at temperatures up to 100°.

A. J. W.

Formation of Certain Precious Stones of the Family of the Aluminides. FRÉD. BORDAS (*Compt. rend.*, 1908, 146, 21—24. Compare Abstr., 1907, ii, 956; this vol., ii, 8).—When a yellow corundum artificially coloured by the action of radium bromide is heated on a bath of a lead-tin alloy, maintained constant at 300° by means of a Schlösing regulator, the colour becomes paler at the end of three hours, and after four hours the stone regains its original colour and transparency. A similar result is obtained with an oriental topaz, the yellow colour disappearing. If a sapphire is exposed to the action of radium, it gradually becomes green, usually a disagreeable cabbage-green colour, but by careful heating as above it can be converted to the beautiful green of the oriental emerald. The conclusion is drawn that oriental topazes were not coloured at the time of their formation, but became yellow subsequently by the radio-activity of the sun, and that an oriental emerald is simply a sapphire in which the blue colour has been exactly neutralised by the yellow resulting from the same radioactive influence.

By means of a modification of the apparatus described by d'Arsonval and Bordas (*Compt. rend.*, 1906, 143, 567), in which precautions are observed to prevent a rise in temperature of the stone treated, the author has submitted corundums to the cathodic rays, and finds that the colourless stones do not become yellow, whilst the yellow corundum retains its colour. Thus the cathodic rays, like the β -rays from radium and unlike the X-rays, have no action on corundum.

E. H.

Dissociation Temperatures of Manganese Dioxide (MnO_2) and Dimanganese Trioxide (Mn_2O_3) in Air and Oxygen. RICHARD J. MEYER and KURT RÖTGERS (*Zeitsch. anorg. Chem.*, 1908, 57, 104—112).—Pure manganese dioxide was prepared by prolonged heating of the nitrate at 500°. The experiments were made in an electric furnace, the chemical changes being followed by weighing and also by estimating the products iodometrically.

The change $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ begins in air at 530°, and is complete (under the conditions of the experiment) in eighty-six hours; the change $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ begins about 940°, and is complete in twelve hours. The oxide, Mn_3O_4 , is stable in air up to 1300°, and does not re-absorb oxygen from the air on cooling. In dry oxygen at

atmospheric pressure, the reaction $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ begins at 565° , and the reaction $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ at 1090° . In oxygen at 650 – 900° , the tetroxide is reconverted into the oxide, Mn_2O_3 . G. S.

Spontaneous Combustion of Manganese Sulphide. O. BINDER (*Zeitsch. anal. Chem.*, 1908, 47, 144).—A precipitate of hydrated manganese sulphide, placed in a watch-glass and covered over with a larger one, was found to have become ignited in two or three places. The space between the glasses was filled with fumes.

L. DE K.

Constitution of Cast-irons containing Manganese. LÉON GUILLET (*Compt. rend.*, 1908, 146, 74–75).—The chemical and micrographical examination of an extensive series of white cast-irons containing increasing quantities of manganese (0.86% to 42.22%) shows that, contrary to the conclusion drawn from earlier experiments (Abstr., 1907, ii, 875), γ -iron is present in cast-irons containing high percentages of manganese, and these also contain a carbide. The cast-iron containing 3.6% of carbon and 15% of manganese, when cooled sufficiently slowly, consists of the pure eutectic mixture carbide- γ -iron. The addition of manganese to a grey cast-iron causes the production of γ -iron before the graphite has disappeared.

M. A. W.

Iron Sulphide. HANS MALFATTI (*Zeitsch. anal. Chem.*, 1908, 47, 133–140).—Experiments showing that the precipitate formed in ferric iron solutions by ammonia and ammonium sulphide is a ferric compound. So long as the supernatant liquid contains not less than 0.5% of NH_3 , the precipitate consists of the compound FeS_2NH_4 . On adding ammonium chloride, or by prolonged washing with water, the ammonia is removed and Fe_2S_3 is left behind. The same substance is formed by the action of hydrogen sulphide on ferric hydroxide.

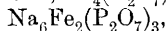
L. DE K.

The Reducing and Oxidising Power of Salts of Iron. ERICH MÜLLER and FRIEDRICH KAPPELLER (*Zeitsch. Elektrochem.*, 1908, 14, 76–82).—The reducing power of a solution containing ferrous and ferric ions increases with the ratio $\text{Fe}^{++}/\text{Fe}^{+++}$. Three examples of this are studied: (1) Atmospheric oxygen does not oxidise an acid solution of ferrous sulphate, but is quickly absorbed if an alkali is added. In the former, the ratio cannot much exceed 10^3 , whereas in presence of normal alkali it is 1.5×10^{22} , owing to the greater solubility of ferrous hydroxide. (2) Solutions of ferrous and cupric sulphates do not react, but cuprous oxide is precipitated if potassium fluoride is added to the neutral mixture, and metallic copper if it is added to the acid solution. In this case, the ratio is increased by the conversion of ferric ions into complex ions containing iron and fluorine. In neutral solution, the cuprous ions produced by the reduction separate as hydroxide, whilst in acid solution, owing to the higher concentration reached, they yield metallic copper and cupric ions. (3) The oxidation of hydriodic acid to iodine by ferric ions, $2\text{I}^- + 2\text{Fe}^{+++} = \text{I}_2 + 2\text{Fe}^{++}$, is reversed by the addition of potassium fluoride, the explanation being the same as that given above.

T. E.

Some Complex Iron Salts in which the Iron is Masked.

P. PASCAL (*Compt. rend.*, 1908, 146, 231—233).—The solubility of ferric pyrophosphate in the corresponding sodium salt is due to the formation of a new complex salt, $\text{Fe}_4(\text{P}_2\text{O}_7)_3, 3\text{Na}_4\text{P}_2\text{O}_7$, or



analogous to the ferricyanides, for which it is suggested that the name *ferripyrophosphate* be reserved.

Sodium ferripyrophosphate, $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3, 9\text{H}_2\text{O}$, is slowly deposited as a pale violet, microcrystalline precipitate at 30° from a 15% solution of sodium pyrophosphate, saturated with ferric pyrophosphate, and yields by double decomposition the *silver* salt, $\text{Ag}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3, 4\text{H}_2\text{O}$, which is greenish-yellow, or the *copper* salt, $\text{Cu}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3, 12\text{H}_2\text{O}$, which is greenish-blue. The complex acid, $\text{H}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3, 7\text{H}_2\text{O}$, is obtained as a white solid when ferric pyrophosphate is heated for twelve hours at 50° with two-thirds of its weight of syrupy pyrophosphoric acid dissolved in acetone.

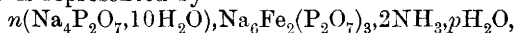
By similar methods, the author has prepared *sodium ferropyrophosphate*, $\text{Na}_3\text{Fe}_2(\text{P}_2\text{O}_7)_3$, the corresponding *ferro-* and *ferri-metaphosphates*, $\text{Na}_4\text{Fe}(\text{PO}_3)_6$ and $\text{Na}_3\text{Fe}(\text{PO}_3)_6$, and also the corresponding salts, in which the iron is replaced by cobalt, chromium, or nickel. M. A. W.

A New Series of Ammonio-ferric Salts in which the Iron is Masked.

P. PASCAL (*Compt. rend.*, 1908, 146, 279—282).—Addition of ammonia to a ferripyrophosphate solution (preceding abstract) does not precipitate ferric hydroxide, but colours the solution reddish-yellow. When ammonia (29° Baumé) is added to the solution at 10° , obtained by mixing 15% solutions of sodium pyrophosphate and ferric chloride, the liquid is coloured red, and there are produced (1) a crystalline precipitate equal to one-third of the sodium pyrophosphate used; (2) at the junction of the two liquids initially separate, a layer of red clots surmounted by one of yellow, and (3) in the upper layer of the liquid, a mass of long, felted, silky needles. All three compounds are ammonio-ferric salts, in which the iron is masked. The compound (1) contains sodium pyrophosphate which has carried down with it varying proportions of ammonia and iron, the ratio between the quantities of the two latter having one of two values. When much ammonia is present, the precipitate consists of short, thick, orange-coloured needles, containing iron and ammonia, in the ratio $\text{Fe}:\text{NH}_3 = 1:1.5$. It can be represented as a combination of sodium pyrophosphate and ammoniacal ferripyrophosphate, thus:



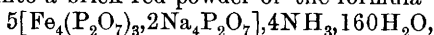
Values are obtained for n 4, 2.5, and 18, and for p 8, 15, and 25. On the other hand, in the presence of but little ammonia, the precipitate is composed of small, rectangular, yellow plates, often having broken corners. In these, the ratio $\text{Fe}:\text{NH}_3$ equals unity, and their constitution is represented by



the values found for n being 18 and 9, and for p 50 and 60.

When removed from the liquid and exposed to the air, the red clots (2) liquefy, becoming deep violet-red in colour, and losing water and ammonia. If dried in an atmosphere of dilute ammonia, which

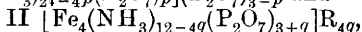
prevents dissociation, they have a composition corresponding with $\text{Fe}_4(\text{P}_2\text{O}_7)_3, 2\text{Na}_4\text{P}_2\text{O}_7, 4\text{NH}_3, 68\text{H}_2\text{O}$. The substance dissolves in water to a red solution, which is alkaline towards phenolphthalein, gives a rusty precipitate with silver salts, but does not exhibit the characteristics of ferric salts except towards ammonium hydrosulphide. On prolonged contact with dry air, the salt loses water and ammonia, and is transformed into a brick-red powder of the formula



the iron still being masked.

When the red liquid, obtained by adding ammonia to the ferripyrophosphate solution, is slowly evaporated, a precipitate is formed in two layers, the upper one being red, and the lower yellow. The latter is a very easily dissociated ammoniacal derivative, the former, however, is a stable compound of the composition $\text{Fe}_4(\text{P}_2\text{O}_7)_3, 8\text{NH}_3, 32\text{H}_2\text{O}$, which dissolves in water to a neutral solution, giving a pale yellow precipitate with silver salts. All the constituent radicles of this salt seem to be masked.

These new derivatives may be members of series having the general formulæ: I $[\text{Fe}_4(\text{NH}_3)_{24-4p}(\text{P}_2\text{O}_7)_p](\text{P}_2\text{O}_7)_{3-p}$ and



comparable to the cobaltammines. Ferriphosphates have been prepared having the formula II in which $q=3$, whilst the red clots correspond with the same formula when $q=2$. E. H.

Alloys of Nickel with Tin, Lead, Thallium, Bismuth, Chromium, Magnesium, Zinc, and Cadmium. G. Voss (*Zeitsch. anorg. Chem.*, 1908, 57, 34—71).—The thermal and microscopic examination of the alloys mentioned in the title show that the following compounds exist: Ni_3Sn_2 , Ni_3Sn , Ni_4Sn ; NiBi , NiBi_2 ; Ni_2Mg , NiMg_2 ; NiZn_3 ; NiCd_4 . Nickel does not enter into chemical combination with lead, thallium, or chromium. The magnetic properties of the alloys have also been investigated.

Nickel-Tin Alloys (compare Gautier, *Bull. Soc. Encour.*, 1896, i, 1293; Heycock and Neville, *Trans.*, 1890, 57, 376).—The behaviour of these metals is remarkable, inasmuch as they separate into two layers in the fused state from 3·5—18% and 26—45% of nickel. There are no distinct maxima on the freezing-point curve, but there are three breaks and two eutectic points, at 1135° and 68·5% and 229° and 1·3% of nickel respectively.

Between 30% and 45% nickel, the two liquid layers react at 1262° to form the compound Ni_3Sn_2 .

A break in the cooling curve at 1162° corresponds with the formation of the compound Ni_3Sn (long needles) from the compound Ni_3Sn_2 and a fused mass containing 65% of nickel. Between 60% and 85% nickel, there is a break in the cooling curve at 855°, due to the formation of the compound Ni_4Sn by interaction of Ni_3Sn and the mixed crystals. From 42·5—60% of nickel, a slight thermal effect at 837° (sometimes lower owing to supercooling) appears to indicate the breaking down of the compound Ni_3Sn into Ni_3Sn_2 and Ni_4Sn . There is one series of mixed crystals from 0—15% of tin.

Only alloys up to 60% of nickel are magnetic. The temperature at

which the magnetic property disappears on heating falls from 350° for pure nickel to 145° for 62% of that metal. From 67—65% of nickel, the fall is 60° (190° — 130°), corresponding with the disappearance of the mixed crystals.

Nickel-Lead Alloys.—These alloys are not miscible in the fused state between 16% and 72% of nickel. There is a series of mixed crystals which, when saturated, contain 4% of lead; at 1338° , these are in equilibrium with the two liquid layers. The solubility of the mixed crystals in lead decreases very rapidly with fall of temperature, and at its melting point pure lead separates.

All the alloys are magnetic. The transition temperature of non-magnetic to magnetic nickel is raised about 5° by the addition of 4% of lead, and remains constant at 350° on further addition of lead.

Nickel-Thallium Alloys.—These metals are not miscible in the fused state from 0—90% of nickel. Nickel retains in solid solution up to about 3% of thallium; these mixed crystals are in equilibrium at 1386° with the two liquid layers. The transition temperature of non-magnetic to magnetic nickel is lowered 15° by the addition of sufficient thallium to form the saturated mixed crystals, and remains constant on further addition.

Nickel-Bismuth Alloys.—These metals are completely miscible in the fused state. The freezing-point curve consists of three branches, without maxima or minima. There is one series of mixed crystals containing up to 0.5% of bismuth. At 638° , the saturated mixed crystals react with a fused mass containing 32% of nickel to form the compound NiBi ; the latter reacts at 472° with the fused mass containing 11% of nickel to form a second compound, NiBi_2 . These compounds could not be obtained pure, even on prolonged heating in the neighbourhood of their temperatures of formation.

The transition temperature of magnetic to non-magnetic nickel is lowered 20° by the addition of sufficient bismuth to form the saturated mixed crystals, and then remains constant at 325° up to a composition of 32% of nickel, beyond which point the alloys are no longer magnetic.

Nickel-Chromium Alloys.—The freezing-point curve of these alloys consists of practically two branches; from 0—42% of nickel, mixed crystals, rich in chromium, separate, and from 42.5—100% of nickel mixed crystals rich in the latter metal. There is a very short break in the miscibility from about 42.0% to 42.5% of nickel.

Alloys containing less than 90% of nickel are non-magnetic. The transition temperature is lowered 100° by the addition of 2% of chromium.

Nickel-Magnesium Alloys.—These metals are completely miscible in the fused state. The freezing-point curve shows a flattened part (not a true maximum) at 1145° from 75—83% nickel, which, from other indications, corresponds with the compound Ni_2Mg (thin leaflets), two eutectic points at 1082° and 89% nickel (nickel and Ni_2Mg) and 512° and 34% nickel (NiMg_2 and magnesium) respectively, and a break at 768° . At the latter temperature, Ni_2Mg and the fused mass containing about 45% of nickel react to form the second compound, NiMg_2 .

The magnetic transition temperature of nickel at 350° is not altered by the addition of 17% of magnesium. From 83—55% of nickel, the transition takes place at 235° , and alloys containing less than 55% are not magnetic.

Nickel-Zinc Alloys (compare Heycock and Neville, Trans., 1897, 71, 383).—Only alloys up to 23% of nickel were investigated. From 14.5—23% of nickel, mixed crystals of a compound, NiZn_3 , and zinc separate, but between 0% and 14.5% of nickel these mixed crystals are insoluble in zinc. These results agree well with those of Tafel (this vol., ii, 105), except that the latter found the saturation point of the mixed crystals at 12.5% of nickel.

At room temperature, these alloys were non-magnetic.

Nickel-Cadmium Alloys.—Owing to the volatility of cadmium, these alloys could only be investigated up to 15% of nickel. At 501° , a compound of unknown composition reacts with the fused mass to form a compound, NiCd_4 . Nickel is insoluble in solid cadmium at the melting point of the latter.

The alloys with zinc and cadmium are not magnetic.

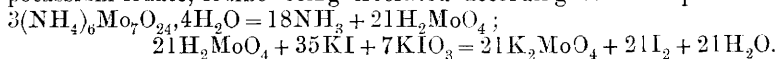
The paper is illustrated by thirty-four photomicrographs. G. S.

Sulphide Compounds of Nickel and Cobalt. ITALO BELLUCCI and LILIO BELLUCCI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 18—29).—By fusing at a high temperature a mixture of a nickel salt with sulphur and an alkali, the crystalline double sulphides, $3\text{NiS}, \text{K}_2\text{S}$ and $4\text{NiS}, \text{BaS}$, may be obtained. Under similar conditions, cobalt salts yield only the sesquisulphide, Co_2S_3 ; in one case, in which the mixture was kept at a white-red heat for a long period, a crystalline product, approximating in composition to Co_3S_4 , was obtained. Thus nickel behaves analogously to its homologues palladium and platinum, whilst the sulphur compounds of cobalt, in which the trivalent type predominates, are in accord with those of rhodium and iridium. These facts confirm the position of nickel in the periodic system after cobalt and before copper. T. H. P.

Chromic Acid as an Oxidising Agent. II. KARL SEUBERT and J. CARSTENS (*Zeitsch. anorg. Chem.*, 1908, 56, 357—364. Compare Abstr., 1906, ii, 617).—In dilute hydrochloric acid solution, hydrazine is oxidised quantitatively by chromic acid to nitrogen and water. The chemical dynamics of the reaction have been investigated at 20° , its progress being followed by withdrawing a portion of the mixture from time to time, mixing with acidified potassium iodide solution, and titrating the iodine liberated with thiosulphate.

The reaction is extremely rapid; in a solution 1/8000 and 1/16000 molar with regard to hydrazine and chromic acid respectively, and 1/200 molar with regard to hydrochloric acid, it is complete in about an hour. The rate is proportional to the concentrations of chromic acid and hydrazine respectively in the presence of excess of hydrochloric acid, and is also proportional to the concentration of the latter. The mechanism of the reaction cannot be fully elucidated, owing to the want of knowledge of the constitution of chromate solutions, but the ionic equation $\text{Cr}_2\text{O}_7^{2-} + \text{N}_2\text{H}_5^+ = 2\text{CrO}_2 + \text{N}_2 + 2\text{H}_2\text{O} + \text{OH}^+$ is in agreement with the kinetic measurements. G. S.

The Hydrolysis of Ammonium Molybdate in the Presence of Iodides and Iodates. SETH E. MOODY (*Amer. J. Sci.*, 1908, [iv], 25, 76—78. Compare Glasmann, Abstr., 1905, ii, 209).—Ammonium molybdate is completely hydrolysed in presence of potassium iodide and potassium iodate, iodine being liberated according to the equations:



On distilling, the free ammonia acts on three-sevenths of the iodine unless prevented by acidifying. The decomposition of ammonium molybdate is not a partial one as supposed by Glasmann.

R. J. C.

Preparation of Silicotungstic Acids. HIPPOLYTE COPAUX (*Bull. Soc. chim.*, 1908, [iv], 3, 101—109).—Marignac described three acids of this type, namely, silicotungstic acid, $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} + 31\text{H}_2\text{O}$, in quadratic crystals; tungstosilicic acid, $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} + 22\text{H}_2\text{O}$, in triclinic crystals, and silicodectungstic acid, $10\text{WO}_3 \cdot \text{SiO}_2 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O}$, amorphous and unstable. The present paper deals mainly with methods of preparing these substances.

Three methods are available for the preparation of silicotungstic acid, and the simplest and most expeditious consists in treating sodium tungstate with sodium silicate in presence of acetic acid.

Tungstosilicic acid may be most easily made by adding sodium silicate to a faintly acid solution of sodium tungstate, making the mixture slightly acid with sulphuric acid, and heating at 100° until, on adding sulphuric acid and ether, oily drops separate. In addition to tungstosilicic acid, some silicotungstic acid is formed, and the two may be separated by fractional crystallisation of the potassium salts, the silicotungstate separating first. Both salts are isomorphous, similarly hydrated, have the same electrical conductivity, and may be equally well used as alkaloidal reagents. Contrary to Marignac's statement, potassium tungstosilicate slowly passes into the silicotungstate when heated with water in a closed vessel at 150° .

A slight improvement in Marignac's method of preparing silicodectungstic acid may be effected by adding ammonia in great excess to a solution of silicotungstic acid and boiling the mixture, the latter being shaken constantly. The ammonium salt so obtained crystallises in orthorhombic prisms, and on solution in water and evaporation yields the required acid. The methods employed for the analysis of these substances have been described already (compare Copaux, Abstr., 1906, ii, 170, Friedheim, Henderson and Pinagel, Abstr., 1905, ii, 614).

T. A. H.

Heterogeneous Colloidal Hydroxides of Uranyl, Thorium, Zirconium, Lead, Yttrium, Iron, and Copper. BÉLA SZILARD (*J. Chim. phys.*, 1907, 5, 636—646).—Colloidal solutions are often prepared by dissolving an insoluble hydroxide in a solution of a salt with a common ion. The author has modified the method by employing hydroxides and electrolytes without a common ion, and terms the products heterogeneous colloids.

Such colloids containing thorium, lead, zirconium, and uranyl have

been prepared, and their properties are described. Isomeric colloids of different behaviour, prepared, for example, from thorium hydroxide and uranyl nitrate on the one hand, and from thorium nitrate and uranyl hydroxide on the other, are of particular interest.

In these colloids, it is not, in general, possible to displace one component by another directly. They do not give the ordinary chemical reactions for the elements present, but a colloid containing lead was found not to be typical in this respect, as it gives the reactions for the metal.

G. S.

Stannic Acids. HUGO KÜHL (*Pharm. Zeit.*, 1908, 53, 49).—The stannic acid obtained by treating a hot solution of sodium stannate with sulphuric acid, when freshly prepared, is completely soluble in 5% hydrochloric acid and concentrated sulphuric acid; the solution in the latter deposits prismatic crystals when heated. The stannic acid, kept as a paste for ten days, is soluble in 5% hydrochloric acid only on boiling, and is only partly soluble in concentrated sulphuric acid; the insoluble gelatinous portion is not completely soluble in strong hydrochloric acid, neither is the gelatinous stannic acid precipitated on heating the sulphuric acid solution.

The stannic acid, obtained by carefully adding dilute sulphuric acid to a cold solution of sodium stannate when freshly prepared, is readily soluble in 2% hydrochloric acid and strong sulphuric acid; the solution in sulphuric acid gives no deposit when heated. The acid loses its solubility in sulphuric acid, but not in hydrochloric acid, when kept for some time in a pasty condition.

The stannic acid, obtained from a freshly prepared solution of sodium stannate, is readily soluble in 2% hydrochloric acid and 2% potassium hydroxide, whereas that obtained from the same solution after being kept for twelve days is not soluble in solutions containing less than 6% of potassium hydroxide and 5% of hydrogen chloride. W. H. G.

So-called Amorphous Antimony. ERNST COHEN and J. OLIE (*Zeitsch. physikal. Chem.*, 1908, 61, 588—595. Compare Abstr., 1904, ii, 345; 1905, ii, 170, 532).—Hérard's experiments (Abstr., 1888, 1256), on which is based the existence of amorphous antimony, are subjected to a critical examination. It is shown that when pure antimony and pure nitrogen are used, the phenomena described by Hérard are not to be observed. If, on the other hand, the nitrogen is insufficiently purified, these phenomena are reproduced. What Hérard described as "amorphous antimony" appears to be nothing else than the ordinary stable antimony contaminated with more or less trioxide.

J. C. P.

Compounds of Antimony, Sulphur, and Chlorine. HERMAN J. TAVERNE (*Chem. Weekblad*, 1908, 5, 19—28. Compare Ruff, Abstr., 1905, ii, 22; Bertrand and Finot, Abstr., 1881, 239; Ouvrard, Abstr., 1893, ii, 533; Hensgen, Abstr., 1891, 1160; and Walden, Abstr., 1901, ii, 11).—A review of previous work on compounds of antimony with sulphur and chlorine, and an account of two derivatives prepared by the author are given. When dry hydrogen sulphide is passed into a

solution of antimony trichloride in dry carbon disulphide or tetrachloride, or in a mixture of these solvents, there is formed a white precipitate, which is converted by a little water into antimony trisulphide. On continued passage of hydrogen sulphide, the colour of the white compound changes to yellow, yellowish-red, orange, and finally dark red. The end-product is crystalline, and has the formula $\text{Sb}_4\text{S}_6\text{Cl}_2$. It is identical with that obtained by Ouvrard. The author gives reasons supporting the view that it results from replacement of one S-atom in two molecules of antimony trisulphide by two Cl atoms. A light orange, crystalline intermediate product, $\text{Sb}_5\text{S}_6\text{Cl}_3$, has also been isolated. A. J. W.

So-called Amorphous Bismuth. ERNST COHEN and J. OLIE (*Zeitsch. physikal. Chem.*, 1908, **61**, 596—598).—The results described by Hérard (Abstr., 1889, 572) can be obtained only with imperfectly purified nitrogen. What Hérard refers to as amorphous bismuth is the ordinary form of the metal contaminated with more or less trioxide. J. C. P.

Bismuthous Compounds. II. WALTER HERZ and ARTHUR GUTTMANN (*Zeitsch. anorg. Chem.*, 1908, **56**, 422—428. Compare Abstr., 1907, ii, 274).—The freezing-point curve of the system bismuth trichloride-bismuth shows a maximum corresponding with the composition of bismuthous chloride, BiCl_2 , and the formation of this compound is confirmed by the fact that its density, 4.85—4.88, is lower than that of a mixture of bismuth trichloride and bismuth of corresponding composition. It occurs in thick, lustrous, black needles, m. p. 163° ; the black colour may be due to a trace of impurity.

Bismuthous bromide and the corresponding *iodide* are formed by heating the bismuthic compounds with the calculated amount of bismuth; the former occurs in greyish-black, crystalline leaflets, D 5.9, m. p. 198° , the latter in crystals with metallic lustre, D 6.5, which decompose below their melting point.

An unsuccessful attempt was made to prepare the chloride and bromide by leading the corresponding halogen acid over heated bismuthous oxide.

The authors now admit that, contrary to their previous statement and in agreement with Aten (Abstr., 1906, ii, 11), there is no evidence of the existence of bismuthous sulphide, BiS . G. S.

Chemical Decomposition of Platinum by means of an Alternating Current. THEODOR GROSS (*Chem. Zentr.*, 1907, ii, 1729; from *Elektrochem. Zeitsch.*, 1907, **14**, 146—147).—When potassium carbonate containing a little potassium nitrate is treated in a platinum crucible at a yellow heat with an alternating current (50 alternations per second, 120 volts, 35 amperes), the platinum is attacked and needles resembling graphite are formed on and in the fused mass. The brown residue, obtained on extracting the fusion with water, is attacked by hydrogen only with difficulty, is soluble in hot hydrochloric acid, or, after ignition, in *aqua regia*, and gives a dark brown precipitate with hydrogen sulphide. The filtrate from this, on evaporation, yields

a red powder, which does not contain platinum, dissolves in hydrochloric acid, is precipitated by potassium hydroxide, and, after ignition, is soluble only when first disintegrated by means of an alkali. The needles, formed during the electrolysis, behave in the same manner as the brown residue, after solution in *aqua regia*. It is considered that the red powder is the hydrate of a new substance. After ignition, the hydrogen sulphide precipitate from the whole of the products weighs 15% less than the loss of platinum from the crucible and electrodes. Ordinary platinum cannot be detected in the electrolysed fused mass. The electrolysis of potassium hydroxide and of a mixture of nitric and sulphuric acids in platinum gives similar results. G. Y.

Rhodium. ALEXANDER GUTBIER and A. HÜTTLINGER (*Ber.*, 1908, 41, 210—216).—The double halogen salts of rhodium described were prepared with the object of finding a material suitable for atomic weight determinations. When heated in a stream of hydrogen they all give up the halogen attached to rhodium as halogen hydride, and can therefore be analysed by the method described by Gutbier, Trenkner, and Ransohoff (*Zeitsch. anorg. Chem.*, 1905, 45, 166, 243). *Potassium rhodipentachloride*, $K_2RhCl_5 \cdot H_2O$, prepared either by heating potassium chloride and rhodium in a stream of chlorine or by concentrating a solution of the components in molecular proportions, forms small, glistening, dark red plates. *Sodium rhodi-hexachloride*, $Na_3RhCl_6 \cdot 12H_2O$, forms a rose-coloured powder. *Ammonium rhodi-hexachloride*, $(NH_4)_3RhCl_6 \cdot 1\frac{1}{2}H_2O$, forms dark red crystals, whilst the *rhodipentachloride*, $(NH_4)_2RhCl_5 \cdot H_2O$, separates in glistening, dark red crystals.

Cæsium and *rubidium rhodipentachlorides* could not be prepared by heating cæsium or rubidium chlorides with rhodium in a stream of chlorine, but were obtained (with $1H_2O$) as sparingly soluble, brilliant, rose-coloured products by the alternative method.

The corresponding rhodibromides were obtained from the potassium salt (the only one accessible) by heating a mixture of finely-divided rhodium and the alkali bromide in a stream of bromine. *Potassium rhodipentabromide*, K_2RhBr_5 , forms brilliant, dark green, irregular plates; *ammonium rhodipentabromide*, $(NH_4)_2RhBr_5$, is black with a green shade; the *cæsium* and *rubidium* compounds, which are sparingly soluble, have a brilliant green colour. E. F. A.

Mineralogical Chemistry.

Sodium Fluoride in Nepheline-Syenite from Los Islands.
ALFRED LACROIX (*Compt. rend.*, 1908, 146, 213—216).—The Los Islands, off the West Coast of Africa, are composed entirely of nepheline-syenites, which vary from fine-grained to pegmatitic in texture, and contain the

following minerals: microcline, albite, nepheline, bright blue sodalite, ægirite, arfvedsonite, astrophyllite, biotite, lāvenite, eudialyte, fluorite, and analcite. The analcite occurs as an original constituent in limpid masses the size of the fist. A fine-grained, grey rock from the island of Ruma is spotted with a crimson mineral, which was found to be essentially sodium fluoride (with traces of potassium, calcium, and possibly zirconium); $D\ 2.79$; $H < 3$. This new mineral, called *villiaumite*, is tetragonal and pseudo-cubic, with three perfect cleavages at right angles to one another. The refractive index ($n_{Na} = 1.328$) is lower than that of any other mineral and less than that of water; the birefringence is very feeble, and no interference-figure is seen in convergent polarised light. A striking feature is the very strong pleochroism, the colours being crimson and golden for vibrations respectively perpendicular and parallel to the vertical axis. The colour and pleochroism were thought to be possibly due to the presence of a trace of manganese, but this element could not be detected. At a red-heat, the colour is destroyed and the mineral fuses to a colourless, mobile liquid. The mineral is soluble in water, and from the solution sodium fluoride crystallises as cubes, or octahedra, with cubic cleavages, and $D\ 2.76$, $n_D = 1.327$. Boiling water extracts from the rock 0.35% of soluble salts, consisting mainly of sodium fluoride with some sodium chloride. The new mineral is present as a primary constituent of the nepheline-syenite. The minerals most closely related to it are the alkali aluminium fluorides, cryolite, cryolithionite, and chiolite. L. J. S.

Magnesium-pectolite from the Diabase of Burg, Hesse-Nassau. E. REUNING (*Centr. Min.*, 1907, 739—741).—Pectolite occurs in crevices of the diabase at Burg, near Herborn, as white masses with a radially fibrous structure. Analysis by M. Dittrich gave:

										H ₂ O.	
SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	<110°.	>110°.	CO ₂ .	Cl.	Total.	Sp. gr.
54.11	0.64	24.84	5.54	6.63	0.21	1.78	5.32	0.82	trace	99.89	2.688

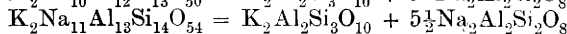
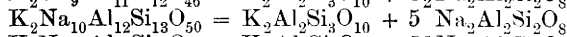
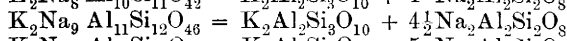
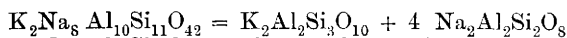
These results, besides showing an abnormal amount of magnesia, differ appreciably from other analyses of pectolite, and no simple formula is deducible from them. The material is no doubt impure, since it is not always completely decomposed by hydrochloric acid. The mineral is largely altered, apparently to prehnite. L. J. S.

Composition of Nepheline. JÓZEF A. MOROZEWICZ (*Bull. Acad. Sci. Cracow*, 1907, 958—1008).—Nepheline is completely soluble in a $N/4$ solution of hydrochloric acid, and this gives a method of readily separating enclosed impurities (felspars, mica, hæmatite, &c.), which in earlier analyses must have been weighed with the silica. In the following new analyses, each the mean of two determinations, special precautions were observed; the alkalis, for example, were not determined at the end of the analysis, since their amount would be increased by the accumulation of impurities from the reagents. I, is of grey, porphyritic crystals from mariupolite (*Abstr.*, 1902, ii, 668);

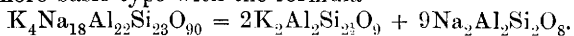
D 2·631 (not allowing for 12% of enclosed albite). II, a large mass of elæolite also from mariupolite, with 9·8% insoluble material (albite, ægirite, beckelite, &c.). III, grains of red elæolite from mariupolite, enclosing 50% of perthite and hæmatite. IV, elæolite from Mias, Urals; D 2·645; the powdered mineral gives an alkaline reaction in water, and, after digestion for twelve hours, 0·45% is dissolved. V, well-formed crystals of nepheline from Vesuvius; D 2·64. VI, small, prismatic crystals from Vesuvius, with 0·5% insoluble enclosures:

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	43·65	0·10	33·12	0·48	0·49	—	5·69	15·91	0·74	100·18
II.	43·46	0·07	32·82	0·75	0·31	—	5·55	16·12	0·89	99·97
III.	43·55	0·03	32·96	0·66	0·25	—	6·09	16·00	0·33	99·86
IV.	42·71	0·04	33·83	0·40	0·32	trace	5·86	16·46	0·18	99·86
V.	42·53	0·01	33·92	0·30	1·97	0·07	5·82	15·12	0·13	100·11
VI.	43·34	trace	33·75	0·50	2·20	0·24	4·34	15·66	0·23	100·26

In all these analyses, the molecular ratio of (Al,Fe)₂O₃:(Na₂,K₂,Ca)O = 1:1; but the ratio of (Si,Ti)O₂:(Al,Fe)₂O₃ varies from 2·11:1 to 2·21:1 (being 2·21:1 in analyses I—III). The ratio of K₂O:(Na₂O+CaO) varies from 1:4·06 to 1:5·6, being usually 1:4·4. These and previous analyses are discussed in detail, and evidence is adduced to show that potassium (which is invariably present in nepheline) and sodium do not replace each other isomorphously. Most analyses may be referred to the following series of normal nephelines:



These formulæ represent double compounds of a potassium aluminotrisilicate (comparable with the silicate portion of sodalite, &c.) with a sodium aluminodisilicate (analogous to natrolite minus water). A few analyses (amongst them IV and V now given) represent a slightly more basic type with the formula



L. J. S.

Mineralogy of Iron Mine Hill, Rhode Island. B. L. JOHNSON and CHARLES HYDE WARREN (*Amer. J. Sci.*, 1908, [iv], 25, 1—38).—In an account of the geology and petrography of Iron Mine Hill, near Cumberland in Rhode Island, a detailed description is given of the ultra-basic igneous rock called cumberlandite, which consists of olivine (46%), labradorite (9%), magnetite (20½%), and ilmenite (18%), with some spinel (3½%) and metallic sulphides (1%). Analysis I of the olivine shows it to be the iron-rich variety hyalosiderite. Analysis II is of the fresh, unaltered cumberlandite. Chloritic (anal. III), actinolitic, and serpentine (anal. IV) types of alteration of the cumberlandite are distinguished. The altered rock is traversed by narrow veins of secondary minerals, which are mainly actinolite (anal. V), clinocllore, and hortonolite (VI):

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.	Sp. gr.
I.	37.16	0.07	—	0.12	31.38	0.40	31.16	trace	—	—	—	100.63*	3.728
II.	22.35	10.00	5.26	14.05	28.84	0.43	16.10	1.17	0.10	0.44	0.42	99.26†	3.92-4.0
III.	20.89	9.57	6.93	17.81	26.04	—	15.65	0.96	nil	trace	2.71	100.54	3.80-3.85
IV.	19.98	9.76	6.75	19.25	21.42	0.40	16.83	n. d.	trace	trace	4.77	99.32	3.56-3.65
V.	56.00	trace	1.00	0.10	7.14	0.10	20.52	14.03	trace	0.50	0.80	100.19‡	3.062
VI.	33.27	trace	—	0.37	49.32	1.50	16.08	—	—	—	n. d.	100.54	4.054

* Also, insoluble felspar 0.34%.

† Also (not included in total), V₂O₅, 0.18; Cr₂O₃, trace; CO₂, 0.02; P₂O₅, 0.02; S, 0.38; Zn, 0.71; Cu, 0.08; Co+Ni, 0.08; Pb, trace.

‡ Also, trace of fluorine(?).

This analysis of actinolite gives ratios agreeing closely with those of Penfield (Abstr., 1907, ii, 102). The hortonolite is a dark resinous mineral with distinct cleavages in two directions at right angles; in small fragments, it is pale yellow by transmitted light. The occurrence of this rare member of the olivine group as a secondary vein mineral is of interest.

L. J. S.

The Volcano of Siroua, in the Morocco Atlas. LOUIS GENTIL (*Compt. rend.*, 1908, 146, 185-187).—A description is given of this extinct volcano, the rocks of which belong to two series, trachytic and phonolitic. Analyses are given of a biotite-trachyte and of a haüyne-ægirite-phonolite.

L. J. S.

Origin of Laterite. JEAN CHAUTARD and PAUL LEMOINE (*Compt. rend.*, 1908, 146, 239-242).—The products of decomposition of rocks are different in temperate and in tropical regions; in the former they consist of aluminium and iron hydroxides, and in the latter of aluminium silicates (clays). The products in tropical regions consist of bauxite and laterite, which are analogous in constitution, and are of importance as ores of aluminium and iron respectively. Twelve analyses by F. Pisani are given of rocks and their decomposition products from Guinea; the following are selected as examples. I and II are of fresh diabase, and Ia and IIa of the laterite which has been derived from the same rocks:

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	P ₂ O ₅ .	Loss on ignition.	Total.
I.	51.80	1.56	13.83	—	9.80	11.21	7.85	0.68	2.27	0.06	0.50	99.56
Ia.	12.60	3.24	34.71	22.78	1.26	0.63	0.16	0.32	0.14	—	23.70	99.54
II.	48.51	2.96	14.18	2.40	10.35	8.00	6.05	0.67	4.51	0.13	3.12	100.75
IIa.	5.52	9.05	34.10	27.13	1.26	—	0.65	0.26	0.25	—	22.50	100.72

Assuming the titanium dioxide to be the most stable and constant constituent, it will be seen from these analyses that the decomposition has resulted in the removal of the calcium, magnesium, and alkalis, a removal of about four-fifths of the silica, and a slight removal of aluminium and iron; the percentage amounts of the latter being relatively increased. The aluminium is present as minutely crystallised hydrargillite (Al₂O₃·3H₂O), and the silica is free. The process of lateritisation therefore consists in the removal of certain constituents, and in the oxidation and hydration of others.

L. J. S.

The Williamstown Meteorite. EDWIN E. HOWELL (*Amer. J. Sci.*, 1908, [iv], 25, 49-50).—This meteoric iron was found on 25th April, 1892, near Williamstown, Grant Co., Kentucky. It weighed about 31 kilos., with D 8.1. The structure is that of a typical octa-

hedrite of medium coarseness. Bands of kamacite, t enite, and plessite are visible on the etched surfaces, with here and there nodules of troilite, some of which enclose carbonaceous matter and are surrounded by a skin of schreibersite. Analysis by W. Tassin gave :

Fe.	Ni.	Co.	Cu.	Cr.	P.	S.	C.	Si.	Total.
91.54	7.26	0.52	0.03	0.05	0.12	0.17	0.004	trace	99.694

L. J. S.

The Ainsworth Meteorite. EDWIN E. HOWELL (*Amer. J. Sci.*, 1908, [iv], 25, 105—107).—This meteoric iron, which weighed 10.65 kilos., was found in the winter of 1906–7 near Ainsworth, in Brown Co., Nebraska. The structure is octahedral, with very wide bands on the surface of which a minute, octahedral structure is also evident. Troilite and schreibersite are present. Analysis by W. Tassin gave :

Fe.	Ni.	Co.	Cu.	P.	S.	Cr.	Si.	C.	Sp. gr.
92.22	6.49	0.42	0.01	0.23	0.07	0.01	0.05	0.09	7.85

L. J. S.

Physiological Chemistry.

Cheyne-Stokes Respiration. MARCUS S. PEMBREY (*J. Pathol. Bacteriol.*, 1908, 12, 258—265).—This type of breathing is not necessarily pathological, but is a sign of decreased excitability of the nervous system. Carbon dioxide increases, and oxygen diminishes, until the depressed cells of the respiratory centre are stimulated to produce shallow and inefficient respiratory efforts, so that the increase of carbon dioxide and decrease of oxygen in the blood still continue; this in time increases the respiratory efforts, and culminates in dyspnoëic breathing, which sweeps out the carbon dioxide and increases the oxygen taken in; the stimulation of the centre wanes, and finally apnoëa sets in until the same series of events is repeated. This view is supported by analyses, and numerous tracings of the respiratory movements are given.
W. D. H.

Equilibrium between the Cell and its Environment, with Special Reference to Red Blood Corpuscles. BENJAMIN MOORE and HERBERT E. ROAF (*Bio-Chem. J.*, 1908, 3, 55—81).—The membrane theory fails to explain many phenomena, such as the difference in composition of the electrolytes within and without the cell, and the variations they undergo in different media. The view is advanced that adsorptates, or chemical combinations, are formed within the cell between the electrolytes and the proteins. These constituents undergo reversible changes of association and dissociation with alterations of osmotic pressure; the range varies for each constituent, and within it labile changes are alone possible. Drugs, toxins, and other agencies produce other adsorptates or compounds which upset cell-metabolism, on account of their stability at given osmotic pressures.
W. D. H.

Proteic Acids in Blood. J. BROWIŃSKI (*Zeitsch. physiol. Chem.*, 1908, 54, 548—549).—The proteic acids of Bondzyński and others, which are discoverable in human urine, occur also in the urine of the horse. They can also be detected in the blood-serum of the horse after proteins have been removed by acidification, boiling, and filtering. They are not identical with urochrome. W. D. H.

Researches in Phagocytosis. HARTOG J. HAMBURGER and E. HEKMA (*Proc. k. Akad. Wetensch. Amsterdam*, 1907, 10, 144—166).—The activity of the cells was determined by counting the percentage which took up carbon particles. The addition of water lessens this activity, but replacement of the cells in their own serum restores it either wholly or partly. A heightening of the concentration of the serum by salt similarly damages the cells, and again restoration occurs when they are returned to their own serum. In solutions of 0.9% sodium chloride, the phagocytic power is about equal to that in serum. In some cases, chemical action rather than osmotic changes alters phagocytic power; thus Ca ions and also OH ions increase it. Na ions are not harmful to leucocytes, although Loeb found they were to larvæ, heart muscle, &c. W. D. H.

Variations in the Proteolytic Activity of Pancreatic Juice. LUCIEN CAMUS and EUGÈNE GLEY (*J. Physiol. et Pathol. gén.*, 1907, 987—998).—The juice secreted under the influence of secretin is not always without action on proteins. When the secretion ceases after the first injection, the first portion of that secreted as a result of a second injection is slightly active, digesting egg-white more or less completely in thirty-six to forty-eight hours. If the second injection is made before the effect of the first has passed off, the juice is inactive. The juice which is secreted under the influence of an injection of Witte's peptone, or pilocarpine, is always slightly active, the secretion of active juice alternating with periods of the secretion of inactive juice. The addition of potassium oxalate to the juice, sufficient in amount to precipitate all its calcium salts, hinders, but does not abolish, its proteolytic activity. W. D. H.

Calcium Metabolism. S. W. PATTERSON (*Bio-Chem. J.*, 1908, 3, 39—54).—A diet of oatmeal and maize produces calcium starvation in rabbits, but the blood undergoes no loss of calcium. The bones, however, lose calcium. In experiments on rabbits and men, the conclusion is drawn that the bones are the seat of calcium storage. W. D. H.

Fate of Carbon Acids in the Dog. I. Normal *dl*- α -Amino-acids. II. Methylated *dl*- α -Amino(Normal)-acids. III. Methylated *dl*- α -Amino-acids containing Side-Chains. IV. Dimethylated *dl*- α -Amino(Normal)-acids. V. Synthesis of Acetoacetic Acid by Perfusion through the Liver. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 151—157, 158—176, 177—193, 194—201, 202—213).—Dogs were fed by the mouth on the various acids, and the urine examined for the substances given; the

C:N ratio was also taken as a guide as to whether the materials administered had passed into the urine. I. Glycine, *dl*-alanine, *dl*-amino-*n*-butyric acid, *dl*-amino-*n*-valeric acid, and *dl*-amino-*n*-hexoic acid were given. Thirteen % of the last-named substance passed into the urine; the remaining acids were almost completely broken down in the body.

II. In the second series, sarcosine, *dl*- α -methylamino-propionic, -butyric, -valeric, and -hexoic acids were given. The first two were found in the urine to about one-third of the amount given. The last three left the body almost unchanged.

III. In the third series, *dl*- α -aminoisobutyric acid, *dl*- α -methylamino-isovaleric acid, *dl*- α -methylamino- β -methylvaleric acid, and *dl*- α -methylamino- γ -methylvaleric acid were given. The presence of a second tertiary hydrogen atom increases the ability of the organism to decompose the acid given; this is still more the case when the tertiary hydrogen atom is in the β -position to the carboxyl group.

IV. Dimethylaminoacetic, *dl*- α -dimethylamino-*n*-propionic, *dl*- α -dimethylamino-*n*-butyric, *dl*- α -dimethylamino-*n*-valeric and *dl*- α -dimethylamino-*n*-hexoic acids were given. On the average, about 50% of the substance administered was excreted as such. The introduction of the second methyl group does not therefore increase the difficulty of the organism to deal with the acids.

V. This research is on rather different lines to the four which precede it. The liver was perfused with a mixture of Ringer's fluid and blood to which various substances were added (alcohols, aldehydes, organic acid, &c.); many of these lead to the appearance of acetone in the issuing fluid. Of those investigated, only acetaldehyde and aldol led also to the appearance of acetoacetic acid. In the case of the first of these, aldol is probably first formed as a condensation product.

W. D. H.

Production of Fat from Proteins. Estimation of Fat. ELLY A. BOGDANOFF (*J. Landw.*, 1908, 56, 53—87).—The results of experiments with pigs indicated that mixed foods very rich in proteins had very slight fattening effect. It is, however, considered probable that a certain amount of fat can be formed from protein.

In estimating the amounts of fat, the substance, cut thin and dried at 97—100°, is first kept in contact with ether for some hours. It is then cut into smaller pieces, and again extracted. The residue is then finely ground, extracted with ether for two days in a Soxhlet apparatus, after which it is treated with boiling alcohol for two days or longer. The residue obtained by distilling the alcoholic extract is extracted with ether, and all the ether extracts united. The substance is practically free from fat after the above treatment. Traces of fat can, however, be obtained by Dormeyer's artificial digestion method, followed by extraction with ether.

N. H. J. M.

Parenteral Nitrogenous Metabolism. I. LEONOR MICHAELIS and PETER RONA (*Pflüger's Archiv*, 1908, 121, 163—168).—In a dog in nitrogenous equilibrium, half of the milk in the diet used during the first period of the research was withdrawn, and a subcutaneous injection of the corresponding quantity of caseinogen substituted. There was a

great increase in nitrogenous excretion, although no caseinogen as such passed into the urine. The injected protein is believed to have been katabolised, and at the same time some of the nitrogenous breakdown is attributed to a toxic action; the animal gave indications of this by a rise of temperature and other symptoms. The most noteworthy effect, which was subsequently confirmed on other animals, was a swelling of the mammary glands, leading in some cases to actual milk formation. This suggests that the mammae do not actually form caseinogen, but are merely the seat of its excretion. W. D. H.

Protein Synthesis in Animals. VALDEMAR HENRIQUES (*Zeitsch. physiol. Chem.*, 1908, 54, 406—422).—If animals are fed with the abiuretic products of protein cleavage obtained by the action of trypsin and erepsin, they remain in nitrogenous equilibrium, or may even put on nitrogen. If these products are boiled for six hours with 20% sulphuric acid, they retain this property; but after seventeen hours' boiling they lose it. What this means exactly, it is impossible to say. It was, however, noticed that the tryptophan reaction remained unchanged in the products capable of utilisation. W. D. H.

The Value of Amides in Carnivora. W. VÖLTZ and G. YAKUWA (*Pflüger's Archiv*, 1908, 121, 117—149. Compare Abstr., 1907, ii, 109).—A mixture of ammonium acetate, acetamide, and glycine increases the absorption of nitrogenous material; asparagine does not influence nitrogenous katabolism until after its administration ceases, and then it is lessened; acetamide increases nitrogenous katabolism, and ammonium acetate has a still more marked effect; glycine has no effect. W. D. H.

Chemical Studies on Growth. IV. Transformation of Glycogen by Enzyme Action in Embryonic Tissues. LAFAYETTE B. MENDEL and TADASU SAIKI. **V. Autolysis of Embryonic Tissues.** VI. Purines, Pentose, and Cholesterol of Eggs. VII. Catalase in Embryonic Tissues. VIII. Lipase in Embryonic Tissues. IX. Embryonic Muscular and Nervous Tissues. LAFAYETTE B. MENDEL and CHARLES S. LEAVENWORTH (*Amer. J. Physiol.*, 1908, 21, 64—68, 69—76, 77—84, 85—94, 95—98, 99—104. Compare Abstr., 1907, ii, 895).—Embryo pigs were used throughout.

IV. The embryonic muscle contains glycogen at an earlier date than the liver, and when digested with glycogen causes more of it to disappear than in the case of the liver. In later embryonic life, the liver acquires its characteristic capacities, and overtakes the muscles in efficiency. These organs were not freed from blood, but in all cases the glycogen digesting power of the blood is relatively small.

V. Experiments on autolysis were confined to the liver; autolysis in the foetal liver is less rapid than that in the adult; this is not due to lack of autolytic ferments, but to the want of development of acid, which in its turn may be attributable to scarcity of carbohydrate. If the acidity is artificially equalised in the two cases, autolysis proceeds at an equal velocity in both.

VI. The figures given adduce further evidence of the progressive synthesis of purines during embryonic growth, and, as in adult and embryo organs already examined, guanine and adenine predominate. The yield of pentose (absent in fresh eggs) increases as nucleo-proteins are elaborated. There is no evidence that a synthesis of cholesterol occurs in the development of the chick; that present in early stages appears like other lipoids of the yolk to disappear, acting as sources of energy in growth.

VII. Any difference in the amount of oxygen liberated from hydrogen peroxide by embryonic, as compared with adult, organs appears to be due to extraneous causes (for example, the inhibiting influence of acid) rather than to an absence of catalase in the embryonic tissues.

VIII. Lipase is present at an early stage in the embryonic liver and intestine; but the action of extracts is less pronounced than that of those obtained from full-grown animals.

IX. Embryonic tissues are relatively rich in water. Creatine is present in the embryonic muscle, but in less amount than in the adult. Among the purine bases, adenine and guanine preponderate as in other tissues. Hypoxanthine is free in the tissue as in the adult.

W. D. H.

Importance of Calcium Salts for the Growing Organism.

HANS ARON and ROBERT SEBAUER (*Biochem. Zeitsch.*, 1908, 8, 1—28).—The amount of lime required by a growing mammal is at least 1.2% of the increase in body weight. The same diet may at one time contain enough lime, when given in small quantity, so as to produce but little growth, and at another time, when given in large rations, it may not contain enough lime, on account of the more rapid increase in body weight. The body as a whole is not affected by a shortage of lime; the effects are limited to the skeleton (possibly the brain is also affected to some extent). The bones do not weigh less, but contain less organic substance and more water than normal ones. The dry substance of the skeleton of lime-starved animals also contains a smaller percentage of ash than that of normal animals, but the proportion of calcium in the ash is not appreciably decreased. These chemical changes agree with those observed in rachitic bones.

G. B.

Nitrates in Vegetable Foods, Cured Meats, and Elsewhere.

WILLIAM D. RICHARDSON (*J. Amer. Chem. Soc.*, 1907, 29, 1757—1767).—The results of a large number of determinations of nitrates in different foods (fruits, vegetables, and cured meats), showed that with a diet consisting of fresh vegetables, the equivalent of 1 to 2 grams of sodium nitrate could be consumed daily. Smaller amounts of nitrates could be consumed with a diet consisting partly of cured meats, so that the quantities of nitrates in the latter must be considered harmless.

N. H. J. M.

The Substitution of Bromine by Chlorine in the Animal Body. M. BÖNINGER (*Chem. Zentr.*, 1907, ii, 1539; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 414—418).—In absolute chlorine hunger in the

dog, bromine can take its place; even in the blood serum, chlorides are replaced by bromides. Cumulation of the halogen was not observed.

W. D. H.

The Cell and its Medium. III. Inorganic Salts of the Protozoan Cell and its Medium. AMOS W. PETERS (*Amer. J. Physiol.*, 1908, 21, 105—125).—*Paramaccia* were placed in pure distilled water which was frequently changed, the organisms being at each change separated by the centrifuge. Mere centrifugalising was found to produce no injury. In spite of this, the animals contaminated the water; this was due to the diffusion outwards of the salts of the cells, and this led to loss of movement and, finally, death. Moderate withdrawal of the salts is harmless.

W. D. H.

[Amount of] Arginine, Lysine, and Histidine in the Hydrolytic Products of Various Animal Tissues. ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1908, 4, 119—147).—Variations occur in the yield of these three substances from different tissue proteins. The group (or groups) in the protein molecule which yield the bases is large in the case of muscle, and small in that of the kidney; but in the same organ of different species of animal, the variations are very small. In pathological organs, even when gross changes occur, as in acute atrophy of the liver, the composition of the liver protein is not essentially changed so far as the amount of, and proportion between, the bases is concerned, and the amount of histidine is least influenced by degenerative changes.

W. D. H.

The Work of the Intestinal Muscle. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1908, 54, 461—480).—The production of carbon dioxide in the normal movements of the intestine is from 20 to 36 mg. per 100 grams of muscle per hour. This is about one-tenth of that found in striped muscle, and from 1/20 to 1/70 of that produced by glandular activity. The movements were made to occur by placing the intestine in oxygenated Ringer's solution.

W. D. H.

Formation of Dextrorotatory Lactic Acid in Autolysis. III. In Muscle. KATSUJI INOUE and K. KONDO (*Zeitsch. physiol. Chem.*, 1908, 54, 481—500).—During autolysis of rabbit's and bird's muscle, there is, as in rigor mortis, a formation of sarco-lactic acid, even in the presence of chloroform water. Later (about the seventh day of autolysis), the amount diminishes. In the muscles of cold-blooded animals (fish), the same occurs, but the increase is not so marked. The same occurs in filtered extracts of the muscles, and therefore the acid cannot be a product of cellular activity. The action is regarded as due to a ferment, and the source of the acid to be both carbohydrate and protein.

W. D. H.

Vagus Inhibition and the Output of Potassium from the Heart. WILLIAM H. HOWELL and W. W. DUKE (*Amer. J. Physiol.*, 1908, 21, 51—63. Compare Abstr., 1907, ii, 110).—If the isolated mammalian heart is perfused with Locke's fluid and the vagus

stimulated, the increase in potassium of the fluid may amount to as much as 29%. It is believed that the inhibiting influence of the vagus is due to the liberation of potassium in diffusible form, and it is the potassium which inhibits the heart. The amount of calcium in the circulating fluid does not alter. Stimulation of the accelerator nerves causes no increase in the amount of potassium in the circulating fluid.

W. D. H.

Carbon Dioxide in the Regulation of the Heart Rate. YANDELL HENDERSON (*Amer. J. Physiol.*, 1908, 21, 126—156).—In dogs under artificial respiration, the development of shock is dependent, not upon the extent of injury, or the intensity of stimulation of afferent nerves, but on the rate of pulmonary ventilation. Diminution in the amount of carbon dioxide in arterial blood increases the heart rate up to cardiac tetanus, and by regulation of the rate of pulmonary ventilation the heart can be adjusted to any desired rate of beat. The hypothesis is presented that acapnia (this is, diminution of carbon dioxide in the blood and tissues resulting from hyperpnea and from exhalation of carbon dioxide from exposed viscera) is the cause of surgical shock.

W. D. H.

The Iron of the Liver. V. SCAFFIDI (*Zeitsch. physiol. Chem.*, 1908, 54, 448—460).—One hundred grams of rabbit's liver contains 9 mg. of iron; there are on the average 19 mg. of iron para-nucleinates in the whole liver. The nucleo-protein contains from 0.18% to 0.44% of iron. In animals treated with iron para-nucleinate, this rises to 1.1%. The quantity of iron in the nucleo-protein is, however, not proportional to the total iron of the liver. Although the amount of iron in the nucleo-protein is thus variable, the percentage of phosphorus is constant.

W. D. H.

Nature of the Fat in Normal and Pathological Human Livers. PERCIVAL HARTLEY and A. MAVROGORDATO (*J. Path. Bact.*, 1908, 12, 371—377).—The iodine value of the higher fatty acids from adipose tissue is 65; that from the normal liver 115—120. When the amount of fat in the liver is abnormally great, the iodine value falls. Whether this is due to fat transported from the adipose tissue or to excessive formation of fat from carbohydrate is discussed, but left uncertain.

W. D. H.

Perfusion of Excised Kidneys. IX. Effects of Poisons. TORALD SOLLMANN and ROBERT A. HATCHER (*Amer. J. Physiol.*, 1908, 21, 37—50).—The ureter-flow in excised kidneys depends mainly on glomerular pressure, and the various poisons investigated are regarded as having their effect rather on the vessels than on the renal epithelium. Chloral, *Hydrastis*, hydrocyanic acid, and juniper cause vaso-dilation and increase of ureter flow; adrenaline, sodium arsenate, digitalis, mercuric chloride, and picric acid have the reverse effect. Alcohol, caffeine, cantharidin, carbon dioxide, carbon monoxide, ergot, formaldehyde, hydrastinine, and sodium thiocyanate in the concentrations used have no effect. The effect of the drugs on the intact kidney *in vivo* in cases where the comparison is capable of being made, is stated to be the same as in the excised organ.

W. D. H.

The Occurrence of Scatole in the Human Intestine. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1908, 4, 101—109).—Scatole is by no means always present in the lower gut in either children or adults. When intestinal putrefaction is excessive, it is present, and this is sometimes accompanied with increased formation of indole. When indole is absent in the fæces, indican is present in the urine; hence the scatole is probably produced later in the intestine. Its formation is due mainly to putrefactive anaërobic bacteria. Certain strains of the bacillus of malignant œdema and of *B. putrificus* form scatole; but *B. coli communis* forms indole, and usually little or no scatole. The conditions giving rise to the two products are thus different. The formation of indoleacetic acid is perhaps a necessary step in the production of scatole, most bacteria attacking it with difficulty if at all.

W. D. H.

Constituents of Ox Bile. I. KURT LANGHELD (*Ber.*, 1908, 41, 378—385).—A new method is described for treating the acids of ox bile, which allows of the isolation of more than 80% of the crude product in the form of definite chemical compounds. The crude acids are treated directly with alcohol, which leaves the cholic acid undissolved, and after separation of the fatty acids the remainder is esterified by Fischer's method. The substances isolated are obtained in the following percentages: cholic acid, 50·8; palmitic and stearic acids, 5·4; deoxycholic acid, from the esters soluble in light petroleum, 1; deoxycholic acid, from the insoluble esters, 20·7. The last is a mixture of deoxycholic acid, m. p. 172—173°, $[\alpha]_D^{20} + 53\cdot28^\circ$, and its isomeride, Mylius's choleic acid, m. p. 187—188°, $[\alpha]_D^{20} + 47\cdot97^\circ$, the existence of which, although denied by Latschinoff (*Abstr.*, 1887, 682) and Lassar-Cohn (*Abstr.*, 1893, ii, 220), is now confirmed. Myristic acid was not found in the bile.

G. Y.

The Protein Hydrolysis of Cows' Milk. ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1907, 21, 434—458).—The author finds that a 3% solution of iodoform in acetone is the most suitable reagent for use in studying the enzymes of milk. The addition of 3·3 c.c. of this solution to 25 c.c. of milk sterilises the latter completely without interfering with the action of the enzyme. It is shown that the proteolytic enzyme present in cows' milk is capable of digesting about two-thirds of the proteins present in the milk; the action is limited, and does not appear to be influenced by the age of the cow or by the quantity of milk yielded by the cow. The activity of the enzyme bears no relation to the period of lactation.

W. P. S.

Parent Substance of the Hippuric Acid Produced in Animals. HARALAMB VASILIU (*Bied. Zentr.*, 1908, 37, 29—32; from *Mitt. Landw. Inst. Univ. Breslau*, 1906).—The chief source of hippuric acid seems to be phenylalanine. The fact that carnivorous animals, notwithstanding the considerable amounts of phenylalanine present in meat, eliminate only small amounts of hippuric acid in the

urine is shown, by an experiment made by the author on himself, to be probably due to the combustion of the benzene ring.

N. H. J. M.

The Relation of Nitrifying Bacteria to the Urorosein Reaction of Nencki and Sieber. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1908, 4, 239—251).—The urorosein reaction sometimes (perhaps always) depends for its development, when the reaction is induced by adding hydrochloric acid to the urine, on the presence of bacteria in that fluid. The bacteria can be isolated, and a pure culture obtained; if this is added to sterile urine, the typical urorosein reaction can then be obtained. These bacteria are capable of forming nitrites, and the reaction depends on the liberation of nitrous acid.

Doubtless the urorosein chromogen would be more frequently detected if nitrites were employed; the action is probably due to oxidation, and not to the formation of a nitroso-compound. Urorosein is distinct from scatole-red, and its chromogen occurs quite independently of the absorption of scatole from the intestine. The urorosein chromogen is indoleacetic acid, but further evidence of this is postponed.

W. D. H.

A Thermosoluble Protein said to be that of Bence-Jones. L. GRIMBERT (*J. Pharm. Chim.*, 1908, [vi], 27, 97—101).—The proteins from urine, described by various authors as the albumose of Bence-Jones, are not identical, and chiefly resemble each other in being redissolved on heating. The solubilities of the protein in a case observed by the author are compared with those observed by other French investigators (compare Patein, *Abstr.*, 1904, i, 954). G. B.

Excretion of Urochrome in Man. ST. DOMBROWSKI (*Zeitsch. physiol. Chem.*, 1908, 54, 390—397).—Urochrome is precipitated as a compound with cuprous oxide. The nitrogen in this was determined, and from this was subtracted the nitrogen due to the presence of purine substances in the precipitate. Normal urine contains from 0.45 to 0.47 gram in the twenty-four hours. In pneumonia (1 case), the amount was 0.78; in typhoid fever (4 cases), it rose to 0.76—1.05.

W. D. H.

Changes in the Bile Occurring in some Infectious Diseases. HELEN BALDWIN (*J. Biol. Chem.*, 1908, 4, 213—220).—Although the method used (Ritter's) for the estimation of the cholesterol is not considered absolutely accurate, the following facts were noted: the increase in the cholesterol of the bile is slight in cholecystitis if there is free drainage, and but little disintegration of epithelium cells is present. The increase is marked when the bile flow is obstructed, and the bile filled with masses of degenerating cells. Most of the increase is in suspension rather than solution. Cholecystitis is a common complication not only in typhoid fever as is well known, but also in pneumonia and suppuration in various parts.

W. D. H.

Prosecretin in Relation to Diabetes Mellitus. FRANCIS A. BAINBRIDGE (*Bio-Chem. J.*, 1908, 3, 82—86).—The yield of secretin from the duodenal mucous membrane is almost or quite as great in diabetic as in non-diabetic people. It is doubtful if the absence of prosecretin has any causal relationship to diabetes. In the cases where observers have failed to find it, it is suggested that its disappearance is due to rapid post-mortem changes. W. D. H.

Production of Glycosuria in Rabbits by Intravenous Injection of Sea-water made Isotonic with the Blood. THEO. C. BURNETT (*J. Biol. Chem.*, 1908, 4, 57—62).—The magnesium in sea-water is responsible for the glycosuria that follows its injection. W. D. H.

Metabolism, Nitrogenous and Inorganic, in Pancreatic Diabetes in Dogs. W. FALTON and JAMES LYMAN WHITNEY (*Beitr. chem. Physiol. Path.*, 1908, 11, 224—228).—After extirpation of the pancreas there is an enormous increase in protein katabolism, which cannot be ascribed to fever (as it partly may in phloridzin diabetes), nor to accidental occurrence of infectious disease. This is accompanied by a relatively large increase in the mineral constituents of the urine, and also a rise in endogenous uric acid formation. The tissue breakdown appears to be particularly great, for the tissue proteins are richer in saline material than reserve proteins. It is possible that bone atrophy may contribute to the result. W. D. H.

Lactic Acid in Eclampsia. JULIUS DONATH (*Zeitsch. physiol. Chem.*, 1908, 54, 550).—It is pointed out that A. ten Doesschate's view (this vol., ii, 122) that lactic acid is the result and not the cause of convulsions has been advanced previously by the author. W. D. H.

The Purgative Inefficiency of Saline Cathartics when Injected Subcutaneously or Intravenously. JOHN AUER (*J. Biol. Chem.*, 1908, 4, 197—212).—MacCallum (Abstr., 1903, ii, 742; 1904, ii, 63, 191, 755) stated that saline purgatives have the same action whether they are introduced into the alimentary canal, or injected subcutaneously or intravenously. This was disputed by the present author (Abstr., 1906, ii, 876), but confirmed by Bancroft. The present paper is a reply to the latter, and reaffirms the author's previous contentions. W. D. H.

The Behaviour of Calcium Formate and Acetate in the Organism. ATTILIO BONANNI (*Chem. Zentr.*, 1907, ii, 1803; from *Arch. Farm. sper.*, 1907, 6, 419—443).—The urine of dogs and rabbits contains normally minute quantities of formic and acetic acids. After intravenous or subcutaneous administration of the calcium salts of these acids, the amount increases, but the quantity excreted is not so great as that given. The actual quantities vary in the two animals. Numerical details are given. W. D. H.

Behaviour of Quinine in the Body. PAUL GROSSER (*Biochem. Zeitsch.*, 1908, 8, 98—117).—Great discrepancies as to what happens to quinine in the body occur in previous writings on the subject.

Phosphotungstic acid precipitates it quantitatively in the urine, and in albuminous solutions, such as extracts of organs, the loss is almost 2% if protein material is removed by the kaolin method of Rona and Michaelis. The present observations were made on people suffering from malaria. The faeces contain at most 1% of the amount of quinine administered. If given by the mouth, or injected into the muscles, a quantity varying from 8% to 46% is recoverable in the urine. The causes of this extreme variation is far from clear. The remainder does not accumulate in the tissues, but is destroyed there. Perfusion of the liver by Brodie's method with Ringer's solution containing quinine shows that the issuing fluid contains less than that which enters, and the liver has the power of decomposing quinine. W. D. H.

Is Arsenious Anhydride, Introduced into the Animal Organism, Eliminated Unchanged or as Arsenic Acid? MARIO TONEGUTTI (*Boll. chim. farm.*, 1907, 46, 899—908. Compare Abstr., 1907, ii, 908).—Arsenious acid, when introduced into the organism either by ingestion or intravenously, reappears unchanged in the urine, and is transformed into arsenic acid when the urine is treated with magnesia mixture. T. H. P.

The Influence of Potassium Cyanide on Protein Metabolism. ALFRED N. RICHARDS and GEORGE B. WALLACE (*J. Biol. Chem.*, 1908, 4, 179—196).—There is an increase in the excretion of total nitrogen, which is due partly to the increased muscular work associated with the convulsions, and partly to the dyspnoea, but mainly to a specific influence of the poison on cell metabolism. The urea excretion runs parallel with that of total nitrogen, in spite of interference with respiration. This affords evidence that urea formation is not oxidative. The ammonia output varies within normal limits. There is a distinct increase in preformed creatinine; creatine was also found in the urine. The undetermined nitrogen varies considerably, but there is no evidence that any significant excretion of amino-acids occurs. Small doses of cyanide cause a greater increase in oxidised sulphur excretion than large doses, and probably in the latter case the increase in "neutral sulphur" occurs at the expense of sulphur which would otherwise be oxidised. W. D. H.

The Influence of Hydrazine on the Intermediary Metabolism of the Dog. FRANK P. UNDERHILL and ISRAEL S. KLEINER (*J. Biol. Chem.*, 1908, 4, 165—178).—In inanition, the dog excretes urine, in which the ammonia-nitrogen is slightly increased in proportion to the urea-nitrogen. The excretion of creatinine varies, and there is a large output of creatine. Allantoin also is a constant constituent of such urine. In hydrazine poisoning, the partition of urinary nitrogen and sulphur is only slightly different from that which obtains during inanition. It has no specific action in causing an elimination of allantoin. It causes fatty degeneration of the liver. Emphasis is laid on the protective adaptation of the liver during hydrazine poisoning. W. D. H.

Comparison of the Hæmolytic and Toxic Action of Eel's Serum on the Marmot. LUCIEN CAMUS and EUGÈNE GLEY (*Arch. internat. Pharmacodyn. Thér.*, 1905, 15, 159—169).—Eel's serum is globulicidal and also toxic towards the rabbit and guinea-pig. The pigeon, on the other hand, is very resistant to both actions. There are, however, animals, such as the marmot, in which the hæmolytic action is slight, and yet the serum is very toxic. Moreover, a temperature sufficiently high to destroy the hæmolytic power of eel's serum, only lessens its poisonous action. Not only are toxic actions elective, but the same is true for immunity. W. D. H.

Lecithid Formation. PRESTON KYES (*Biochem. Zeitsch.*, 1908, 8, 42—46. Compare Abstr., 1907, ii, 569).—Polemical. A reply to Michaelis and Rona, (Abstr., 1907, i, 667); and Morgenroth and Carpi (Abstr., 1907, ii, 570).—The author adheres to the views he has expressed. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Further Studies on Putrefaction. LEO F. RETTGER (*J. Biol. Chem.*, 1908, **4**, 45—56).—Real putrefaction is the work of anaërobes. *Bacillus tetani* has little or no putrefactive action on native proteins. *B. aërogenes capsulatus* attacks proteins slightly, but the change is not genuine putrefaction. *B. putrificus* and *B. maligni œdematis* are present in normal fæces in small amount, and probably in spore form only. As spores, they are able to resist the unfavourable conditions of the human intestine.

W. D. H.

Fermentation of Formic Acid by *Proteus vulgaris*. HARTWIG FRANZEN and GEORG BRAUN (*Biochem. Zeitsch.*, 1908, **8**, 29—39).—The same amount of formic acid is fermented in a given time and at a given concentration, whether the acid is present as potassium or as sodium salt. The velocity of the reaction is increased by increasing the concentration of the formate.

G. B.

Sugar Formation and other Fermentative Processes in Yeast. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, **54**, 398—405. Compare Abstr., 1889, 1027).—On autolysis of yeast in chloroform water, a fermentable sugar is formed from the carbohydrate material of the cells. The fluid, however, is lævorotatory, but this action is not necessarily due to the fermentable sugar, for the fluid contains a mixture of numerous substances, such as gum, dextrin, pentoses, purine bases, tyrosine, lysine, leucine, peptone, and sometimes succinic acid. The sugar was identified as dextrose by separating it as a diphenylhydrazone compound.

W. D. H.

Constitution of Aqueous Solutions, and the Influence of Salts on Alcoholic Fermentation. ALBERT J. J. VANDEVELDE (*Chem. Zentr.*, 1907, ii, 1435; from *Bull. Assoc. Anciens Élèves del' Inst. Brasserie, Gand*, 13, 83—94).—The velocity of the fermentation of sugar in presence of various inorganic salts has been followed gravimetrically, and the results are expressed in tables in terms of the number of hours required for the decomposition of three-fourths of the sugar, termed the "fermentation energy." Within concentrations of 2—10%, barium chloride, ammonium sulphate, magnesium sulphate, and zinc sulphate appear to be without influence on the velocity of the fermentation, but the numerous other inorganic salts investigated retard the fermentation, in some cases to an extent approximately proportional to the increase in the osmotic pressure of the solution.

G. Y.

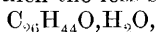
Influence of Micro-organisms on the Utilisation of the Insoluble Phosphates by Higher Plants. SANTE DE GRAZIA and A. CERZA (*Bied. Zentr.*, 1908, 37, 85—86; from *Staz. sper. agrar. ital.*, 1906, 39, 817).—Experiments with *Aspergillus niger*, *Penicillium glaucum*, and *P. brevicaulis* showed that the moulds have a dissolving action on tricalcium phosphate.

N. H. J. M.

Chemistry of the Higher Fungi. I. *Trametes suaveolens*. JULIUS ZELLNER (*Monatsh.*, 1908, 29, 45—54. Compare Abstr., 1904, ii, 679; 1905, ii, 550; 1906, ii, 572).—In continuation of his investigations into the chemistry of the fungi, the author has undertaken the study of some parasitic fungi, and now gives an account of the results obtained with *Trametes suaveolens*.

The fungus was gathered from willows in February and March, when full of sap, but still free from spores. The freshly-gathered fungus contains 65—67%, the air-dried material 7—9%, of water. When incinerated, the completely dried substance yields 2.9% of ash, consisting chiefly of potassium and calcium sulphates and carbonates, with smaller amounts of magnesium, phosphoric acid, and silica, and traces of sodium, iron, aluminium, and chlorine.

The light petroleum extract amounts only to 0.8%. The crude fat is yellow, deposits a crystalline substance, and gives the acid number 32.29—29.40, and the hydrolysis number 175.2—172.0; the small amount of fatty acid obtained has the acid number 186.1, and consists chiefly of oleic acid; the very small amount of solid fatty acids obtained has m. p. 74°. It is shown that the powdered fungus contains a lipolytic ferment. The soap from the crude fat, on extraction with ether, yields a substance, m. p. 158—167°, closely resembling the ergosterol obtained from fly agaric (Abstr., 1905, ii, 550); it is a mixture of two substances, of which the less soluble in alcohol,



has m. p. 165—167°.

The alcohol extract yields mycose and dextrose, but not mannose or trehalase (Bourquelot and Hérissé, Abstr., 1905, ii, 193). The resin from the alcoholic extract gives coloured precipitates with metallic acetates, and a brown coloration with ferric chloride.

The aqueous extract, 18—20%, contains dextrin or gum-like substances, pentosans in sufficient amount to give a strong furfuraldehyde reaction, a ferment which hydrolyses glucosides, a diastatic, and probably an inverting, ferment, and traces of proteins.

The fungus contains also amanitol, previously found in fly agaric, and, when distilled with very dilute sodium hydroxide, yields traces of ammonia and probably trimethylamine. The skeleton of the fungus does not give the lignin reactions. The grey colouring matter in old plants is insoluble.

G. Y.

Supposed Extracellular Photosynthesis of Carbon Dioxide by Chlorophyll. ALFRED J. EWART (*Proc. Roy. Soc.*, 1908, 80, B, 30—36).—A severe criticism of the work of Usher and Priestley (*Abstr.*, 1906, ii, 299, 881). All forms of commercial gelatin turn pink in the presence of decolorised rosaniline; it is on this reaction that Usher and Priestley mainly depended for the detection of formaldehyde in their gelatin chlorophyll films. Moreover, chlorophyll itself, when exposed to light, yields formaldehyde as a decomposition product, whether in the presence or absence of carbon dioxide.

There is no conclusive evidence that living plant cells ever contain hydrogen peroxide, the other product of this supposed photosynthesis; it is probably always destroyed by catalase. The author has also failed to detect the evolution of oxygen from gelatin chlorophyll films and from dead cells of *Elodea* and *Vallisneria* as described by Usher and Priestley. The simultaneous production of formaldehyde and of hydrogen peroxide in a gelatin film appears to be improbable from the experiments of Geisow (*Abstr.*, 1904, i, 289), who found that these substances interact with the formation of carbon dioxide, water, and hydrogen.

G. B.

Hydrogen Cyanide and the Assimilation of Nitrogen in Green Plants. CIRO RAVENNA and ARRIGO PELI (*Gazzetta*, 1907, 37, ii, 586—600).—The formation of hydrogen cyanide in *Sorghum vulgare* is traced to the indirect, simultaneous action of nitrates and carbohydrates, and, when these are removed, the proportion of the acid present diminishes rapidly. Light favours the formation of hydrogen cyanide, provided that the functions of the chlorophyll are not impaired. The acid seems to be the simplest substance which can be detected as taking part in the synthesis of proteins.

T. H. P.

Production and Physiological Rôle of Pentosans in Plants. G. A. CALABRESI (*Bied. Zentr.*, 1908, 37, 93—96; from *Staz. sper. agrar. ital.*, 1906, 39, 69).—Determinations of pentosans were made in the different parts of maize, beet, and beans at different periods of growth.

N. H. J. M.

Constant Composition of Vegetable Juices Obtained by Successive Extractions. GUSTAVE ANDRÉ (*Compt. rend.*, 1907, 145, 1349—1352).—Experiments made with leaves of *Valerianella olitoria* and carrots (roots) showed that the composition of the extracts, as indicated by the ratios N: extract and ash: extract, remained almost the same whatever the pressure employed.

N. H. J. M.

Nitrate-reducing Enzyme in Green Plants. ANNIE A. IRVING and RITA HANKINSON (*Bio-Chem. J.*, 1908, 3, 87—96).—The presence of a reducing enzyme in green plants is considered to be established. Asparagine is regarded as a stage in protein synthesis, but the centres for nitrate reduction and protein formation may be distinct. In ensilage the loss of nitrogen may be in part due to evolution of gaseous nitrogen, owing to the distribution of the enzyme becoming less localised. Normally, the only conditions necessary for nitrate reduction are the presence of the enzyme and a suitable carbohydrate. The latter condition suggests the leaf as the centre for reduction, and this agrees with the distribution of nitrates in the plant. Any hexose or polysaccharide is suitable for the supply of energy for nitrate reduction, not as in later stages of protein synthesis, where dextrose is the only carbohydrate which, together with asparagine, can provide the necessary basis for protein construction. W. D. H.

[Composition of] the Pulp of *Parkia Biglobosa*: "Farine de Netté." A. GORIS and L. CRÉTÉ (*Compt. rend.*, 1908, 146, 187—189).—The substance is produced in the fruits of *Parkia*, and at the period of maturity is dry and friable. The percentage composition was found to be as follows: water, 4.90; N, 0.624; ash, 4.96; P_2O_5 , 0.383; soluble in water, alcohol, and carbon disulphide, 72.00, 56.67, and 1.30, respectively. The pulp contains more sugar than any other known substance, the amount being sucrose, 25%, dextrose and lævulose, 20.5%. N. H. J. M.

Vegetable Phosphatides II. ERNST WINTERSTEIN and O. HIESSTAND (*Zeitsch. physiol. Chem.*, 1908, 54, 288—330. Compare Abstr., 1906, i, 478).—The phosphorus compounds soluble in absolute alcohol and ether (phosphatides), obtained from the following plants, have been examined. Cereals, *Avena sativa*, *Lupinus albus*, *L. luteus*, *Vicia sativa*, *Pinus cembra*, *Picea excelsa*, *Boletus edulis*, *Cantharellus cibarius*, also from the leaves of *Aesculus hippocastanum*, pollen of *Alnus viridis*, *Pinus montana*, and potato. The products obtained from all these sources, with the exception of *Pinus cembra*, when hydrolysed, gave carbohydrates. The actual amount of reducing carbohydrate varied with the different sources; thus *Triticum vulgare* gave 16%, *Lupinus albus* 13%, and *L. luteus* only 1%. Even the same material gave varying amounts. Lecithins were also isolated in addition to phosphatides. It is possible that the phosphatides, which gave only small amounts of reducing sugars, contained these in an adsorbed state.

Galactose has been isolated from cereal phosphatide, and the presence of dextrose has been proved, but it has not been settled whether these exist as such in the molecule or are derived from di- and polysaccharides. These phosphatides probably contain other nitrogenous residues in addition to choline. The ratio N : P in the phosphatides is practically the same as in lecithins. J. J. S.

Bio-chemistry of Barley. I. Amylase of Resting Barley. JOHN S. FORD and JOHN M. GUTHRIE (*J. Inst. Brewing*, 1908, 14, 61—85).—The diastatic activity of a barley extract is largely increased

when the digestion of the barley with water is carried out in presence of (1) a salt, such as sodium or potassium chloride, potassium sulphate, potassium dihydrogen phosphate, or calcium sulphate; (2) glycine, asparagine, or α -alanine, or (3) a proteolytic enzyme, such as bromelin, animal trypsin, or active or inactive papain. These substances apparently bring about the dissolution of an insoluble, partially occluded enzyme, whilst in the case of papain, with which the increase in diastatic activity is especially marked, the amphoteric proteins present tend to prevent the destruction of amylase, which takes place under other conditions of extraction.

It is further found that considerable increase of amylolytic activity is exhibited by the filtered extract of barley, digested for twenty hours with water containing an antiseptic at 30—35°, instead of for one hour at 18°, as in the ordinary aqueous extraction; this increased activity the authors term "autodigestion activity." The "aqueous extraction" and "autodigestion" values represent the algebraic sum of solution and destruction of the enzyme under the conditions employed, and are not a measure of the amylase, but rather of other substances in the barley. Various unsuccessful attempts have been made to produce a marked increase in the activity of barley extracts, but the results are insufficient to disprove the existence of a zymogenic or inactive soluble variety of translocation diastase.

By far the greater part of the amylase obtained by treatment of barley with active papain is derived from the endosperm, the embryos containing an insignificant quantity. The enzyme apparently permeates the entire amyliferous tissue, but its concentration is far greater in the peripheral zone and aleurone layer than in the innermost parts. The distribution of soluble salts in the barley corn is also irregular, the relative amounts, estimated by measuring the conductivity of their solutions in equal weights of the various parts, being: endosperm, including the aleurone layer, 1, embryo, 4, and husks, 3. Further, the salts in the different parts vary in character, since, in many barleys, the husks are distinctly alkaline to rosolic acid, whilst the reactions of the embryos and endosperms tend towards faint acidity.

When an aqueous extract of barley is shaken with solid starch, a portion of the translocation amylase present is adsorbed by the starch, the filtered extract exhibiting diminished diastatic activity.

The amylolytic activity of barley does not appear to be connected with the hordein or edestin contained in the barley. T. H. P.

Importance of Sodium for Sugar Beet. K. ANDRLÍK and JOSEF URBAN (*Zeitsch. Zuckerind. Böhm.*, 1908, 32, 208—216).—The percentage of sugar in the roots is high when the roots contain high amounts both of potassium and nitrogen to one of sodium. High amounts of potassium alone in relation to one of sodium are also generally coincident with high percentages of sugar; the relation of potassium to sodium, however, varies during growth. After sixty-six days, roots were found to contain less potassium than sodium, whilst after one hundred and seventy days the relation of potassium to sodium was 1.82:1.

The presence of large amounts of sodium in roots is coincident with lower amounts of sugar; it is, however, not established that the greater assimilation of sodium is the cause of diminished sugar production.
N. H. J. M.

Nutritive Value of Non-Proteins in Hay. OSCAR KELLNER (*J. Landw.*, 1908, 56, 49—52).—A criticism of Max Müller's results and conclusions (*Abstr.*, 1907, ii, 645).
N. H. J. M.

Humous Carbonate Soils and their Conversion into Grey Sand Soils. A. F. LEBEDEF (Bied. Zentr., 1908, 37, 60—61; from *J. exper. Landw.*, 1906, 2, 591).—Analyses are given of (I) humus-carbonate soils, and (II) transition soils, from humus-carbonate to grey sand, characterised by the complete washing out of the carbonates and by low amounts of humus:

	Humus.	KCl NaCl.	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .	CO ₂ .
I. {	1. 6.71	0.87	32.91	—	4.56	1.58	27.13	22.87
	2. 3.25	0.68	43.37	0.64	4.11	1.23	14.01	32.47
	3. —	0.38	50.85	0.65	2.11	0.65	4.89	40.26
II. {	4. 1.18	2.38	0.90	1.93	10.44		80.96	0.0
	5. 2.10	1.67	0.49	0.85	3.17	1.27	90.04	0.0

N. H. J. M.

Action of Calcium Cyanamide on Different Kinds of Soils. THEODOR REMY (*Bied. Zentr.*, 1908, 37, 91—93; from *Landw. Jahrb.*, 35, *Erg.-bd.*, iv., 114).—In pot experiments, 0.07 gram of nitrogen as calcium cyanamide per kilo. of soil was injurious to vegetation, and as little as 0.03 gram was temporarily injurious. In the field, a top dressing of 30 kilos. per hectare was distinctly injurious. The manure acts most favourably on clayey soils, and is then almost equal to sodium nitrate; even considerable amounts are without injurious effect on clay soils.

On sandy soils, the manure may be injurious to seeds, and its action is both slow and incomplete, comparable with that of blood meal.

Calcium cyanamide was found to be without action on the bacteria of heavy soils, whilst on light soils the manure was decidedly injurious.
N. H. J. M.

Calcium Cyanamide. CAMILLE ASCHMANN and J. P. AREND (*Bied. Zentr.*, 1908, 37, 62—63; from *Landw.*, 1906, No. 23).—Experiments with mangolds and barley showed that calcium cyanamide had no poisonous action, and that it acts most quickly on light soils.
N. H. J. M.

Decomposition of Calcium Cyanamide. F. LÖHNIS and A. SABASCHNIKOFF (*Centr. Bakt. Par.*, 1908, ii, 20, 322—332. Compare *Abstr.*, 1905, ii, 412).—Experiments on the decomposition of the two forms of the manure ("Kalkstickstoff" and "Stickstoffkalk") under different conditions gave almost identical results. The presence of

calcium chloride (in "Stickstoffkalk") has, however, some influence on the number of bacteria, other than those which produce ammonia.

Remy's results, indicating that calcium cyanamide has no retarding action on nitrification, were confirmed.

N. H. J. M.

Analytical Chemistry.

An Accurate Form of Gas Analysis Apparatus for Commercial and other Purposes. WILLIAM A. BONE and RICHARD V. WHEELER (*J. Soc. Chem. Ind.*, 1908, 27, 10—11).—A modification of Bone's apparatus (*Proc.*, 1898, 14, 134). The apparatus consists of a water-jacketed combination of measuring and pressure tubes communicating with a mercury reservoir, an absorption vessel standing over mercury in a mahogany trough, and an explosion tube fitted with wires and connected with a separate mercury reservoir. The connexions between the parts of the apparatus are of capillary bore, glass taps being provided where necessary. The principle of measurement adopted is that recommended by Regnault, namely, the measurement of the pressure of the gas under constant volume, and the length of the pressure tube provides for the proper dilution of the "explosive mixture" in an explosion analysis. The absorptions are carried out over mercury in the vessel provided, fresh quantities of the reagents being used for each analysis, and the reagents are removed from the vessel by means of an exhaust pump in connexion with the top of the vessel. The apparatus is particularly adapted to the analysis of mixtures of oxygen with hydrocarbons, and of producer gas, water gas, oil gas, coal gas, &c.

W. P. S.

A Problem of Gas Analysis. P. ANEMA and CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1908, 5, 65—74).—Examples of determinate and indeterminate problems in gas analysis are cited.

A. J. W.

Preparation of Normal Hydrochloric Acid with Gaseous Hydrochloric Acid. H. REBENSTORFF (*Chem. Zeit.*, 1908, 32, 99—100).—This is based on Moody's method (*Trans.*, 1898, 73, 658). Hydrogen chloride is evolved from ammonium chloride in lumps and sulphuric acid, and, after the air has been expelled, the dry gas is passed into a weighed flask containing an exact weight of water. The flask is placed in water, and, when sufficient gas has been absorbed, it sinks to a certain mark, which indicates that an approximately correct *N*-acid has been obtained. The flask is then re-weighed, and the increase equals the exact amount of hydrogen chloride absorbed. It is then brought to exact normal strength by suitable dilution.

L. DE K.

Estimation of Chlorates, Bromates, Iodates, and Periodates by means of Formaldehyde, Silver Nitrate, and Potassium Persulphate. HEINRICH BRUNNER and RUDOLF MELLET (*J. pr. Chem.*, 1908, [ii], 77, 33—42).—Grützner's method of estimating chlorates and bromates by heating the salts with formaldehyde, nitric acid, and silver nitrate (*Abstr.*, 1897, ii, 166) is extended to the estimation of iodates and periodates by adding potassium persulphate to the reaction mixture. This addition has the advantage in all cases that it prevents the evolution of free halogen, and hence removes the necessity of working in closed vessels. The analyses quoted show the method to give satisfactory results. A number of experiments are described, showing that chlorates, iodates, and periodates are not reduced by the persulphate in absence of formaldehyde, and that neither hydrogen peroxide nor potassium hydrogen sulphate can be employed in place of the persulphate. Contrary to Grützner's statement, iodates and periodates are reduced, only more slowly than chlorates or bromides, by formaldehyde alone. G. Y.

Estimation of Bromic and Iodic Acids by means of Thiosulphuric Acid. ANGELO CASOLARI (*Gazzetta*, 1907, 37, ii, 609—618. Compare this vol., ii, 173).—Bromic and iodic acids can be estimated in acid solutions with great exactness by means of sodium thiosulphate, the excess of which is determined by titration with iodine. This method may be applied to the determination of the titre of solutions of sodium thiosulphate and iodine, starting from that of potassium bromate or iodate solution of decinormal strength with reference to its oxidising power; it can also be used generally in the volumetric estimation of substances readily reducible in the cold. In the reaction which occurs, tetrathionic acid is formed in almost theoretical proportion; hydrogen sulphide is also evolved, as is the case when other oxidising agents are used. A polythionate containing m atoms of sulphur in the molecule generates m molecules of sulphuric acid when treated with hydrogen peroxide and sodium hydroxide; polythionates may be estimated by determining the amount of sulphuric acid formed in this way. T. H. P.

Rapid Estimation of Water in Articles of Food, &c. WILHELM THÖRNER (*Zeitsch. angew. Chem.*, 1908, 21, 148—150).—Ten to twenty-five grams of the substance are placed into a round-bottomed distilling flask fitted with a thermometer and connected with a small condenser, in turn connected with a vertical, narrow, graduated cylinder. Fifty c.c. of petroleum are added, and a few pieces of pumice stone are introduced; also, in the case of milk, butter, and cream, a little dry tannic acid. The whole is now distilled, and, when about 18 c.c. of petroleum have passed over, all the water has been expelled, and the volume may then be read off in the bottom part of the graduated tube. L. DE K.

Detection of Ozone, Nitrogen Peroxide, and Hydrogen Peroxide in Gas Mixtures. EDWARD H. KEISER and LEROY McMASTER (*Amer. Chem. J.*, 1908, 39, 96—104).—A method is

described for detecting ozone, nitrogen peroxide, and hydrogen peroxide in presence of one another in mixtures of gases.

If the gas is led through a solution of potassium permanganate, the nitrogen peroxide and hydrogen peroxide are destroyed, whilst the ozone passes through and can be detected by means of potassium iodide and starch. The presence of nitrogen peroxide can be ascertained by passing the gas through a tube containing manganese dioxide, ozone and hydrogen peroxide being decomposed by this reagent, whilst the nitrogen peroxide is not affected and can be detected by means of very dilute permanganate or by passing it into a solution of pure sodium hydroxide and testing for nitrites by the sulphanilic acid and α -naphthylamine method. The presence of hydrogen peroxide can be proved by passing the gas into a solution of potassium ferricyanide and ferric chloride, the solution being rendered first blue and then green by the action of the hydrogen peroxide.

It has been found that, when hydrogen is burnt in air, ozone and nitrogen peroxide are produced together with a very small quantity of hydrogen peroxide. If pure dry air or oxygen is passed through a Siemens' ozoniser, the ozonised gas does not contain either nitrogen peroxide or hydrogen peroxide. The gas produced by the action of strong sulphuric acid on barium dioxide contains ozone, but not hydrogen peroxide or nitrogen peroxide. Ozone and nitrogen peroxide are formed by the slow oxidation of phosphorus in moist air, but hydrogen peroxide is not produced. By the action of the flaming electric arc on air, nitrogen peroxide, a little hydrogen peroxide, and traces of ozone are formed. A sample of ordinary air which was examined was found to contain ozone, but neither nitrogen peroxide nor hydrogen peroxide was present. E. G.

Estimation of Sulphur in Iron and Steel. ÉMILE JABOULAY (*Chem. Zentr.*, 1907, ii, 1444—1445; from *Rev. gen. chim. pure. appl.*, 1907, 10, 193—195).—Five grams of the metal are dissolved in 100 c.c. of dilute hydrochloric acid (1 : 1) in a current of hydrogen, and the gas evolved is burnt in a mixture of air and oxygen. The sulphur dioxide formed is absorbed in a cylinder containing a known amount of hydrogen peroxide, and the excess of this may then be titrated with permanganate, or the sulphuric acid formed may be estimated gravimetrically. The hydrogen peroxide may be preserved by adding 20 c.c. of nitric acid to one litre of its 12% solution.

For exact details and figure of the apparatus, the original communication should be consulted. L. DE K.

Colorimetric Estimation of Nitrogen in Soils: the Nessler Test. D. CHOUGHAK and ISIDORE POUGET (*Bull. Soc. chim.*, 1908, [iv], 1, 1173—1180).—0.2—0.6 Gram of the carefully prepared sample is mixed with 0.02—0.03 gram of dried oxalic acid, and burnt in the ordinary way with soda-lime in a tube 25—30 cm. long and 0.8—0.1 cm. in diameter. The gases evolved are passed through a kind of small Peligot tube containing 2—3 c.c. of dilute hydrochloric acid. The liquid is then diluted to 50 c.c., and in 5 c.c. of this the ammonia is Nesslerised as usual.

The Kjeldahl process may be employed instead; 5 c.c. of sulphuric acid are used with additions of a small drop of mercury or, preferably, a few decigrams of reduced copper. When cold, the liquid is diluted to 50 c.c.; 5 c.c. are taken, diluted with 20 c.c. of water, and, if mercury has been employed, boiled with a little reduced copper. When cold, a sufficiency of aqueous sodium hydroxide is added and the ammonia is distilled off, the distillate being received in a tube containing a few c.c. of water. The ammonia is then Nesslerised.

In this process, extreme care should be taken to ensure the complete absence of ammonia from any of the reagents, also the absence of nitrates from the soda-lime.

L. DE K.

Microchemical Detection of Traces of Arsenic, Antimony, and Phosphorus. BOUWE SJOLLEMA (*Chem. Weekblad*, 1908, 5, 11—15).—A modification of Gutzeit's test is described, the silver nitrate solution (1:1) being placed on a microscope slide held over the test-tube, the reducing action of the filter-paper being thereby eliminated. With arsenic, three forms of lemon-yellow crystals are obtained, 0.005 mg. of As_2O_3 being recognisable. The results for antimony and phosphorus are also characteristic. Mercuric chloride can be substituted for silver nitrate.

A. J. W.

Estimation of Arsenic Hydride in Gaseous Mixtures. HANS RECKLEBEN and GEORG LOCKEMANN (*Zeitsch. anal. Chem.*, 1908, 47, 126—132).—*Gasometric Methods.*—These can be applied only to mixtures containing a large percentage of arsenic hydride. The gas is carefully measured before and after treatment with suitable absorbents (compare this vol., ii, 36). In the presence of methane, for instance, silver nitrate, iodic acid, or hypochlorite solutions may be used; in the presence of ethylene, silver nitrate or iodic acid should be employed, whilst in presence of acetylene, hypochlorite or iodic acid must be used. In presence of saturated and unsaturated hydrocarbons, iodic acid only must be employed.

Gravimetric Methods.—The gaseous mixture is treated with silver nitrate, which is then heated with excess of ammonia. The precipitated metallic silver may then be weighed or, better still, the solution, which now contains the arsenic as ammonium arsenate, may be used for estimating the same by the well-known gravimetric methods. Rohmer's distillation process with hydrocarbons and sulphurous acids (*Abstr.*, 1901, ii, 194) is recommended as a preliminary step.

Volumetric Methods.—The most satisfactory plan is to titrate the arsenious acid obtained by the distillation process by means of standard iodine after removing the sulphur dioxide present by means of a current of carbon dioxide. Traces of arsenic hydride are estimated by passing a measured volume of gas through bromine covered with water. The arsenic is then finally estimated with the Marsh apparatus.

L. DE K.

Detection of Arsenic in Sodium Fluoride by means of the Gutzeit and Flückiger Reaction and the Marsh Apparatus. WILLEM VAN RYN (*Pharm. Weekblad*, 1908, 45, 98—101).—Experiments showing that sodium fluoride may prevent completely the formation of

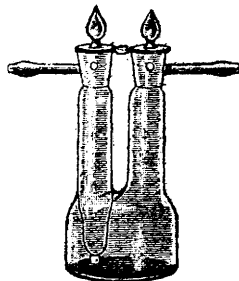
arsenical mirrors in the Marsh apparatus, although the hydrogen evolved may show positively the presence of arsenic by the Flückiger (mercuric chloride) test or by the Gutzeit (silver nitrate) reaction. L. DE K.

Estimation of Carbon. ISIDORE POUGET and D. CROUCHAK (*Bull. Soc. chim.*, 1908, [iv], 3, 75—80).—The authors state that in the ordinary method of estimating carbon by complete combustion in a current of air or oxygen in presence of an inorganic oxidising agent, the substitution of a volumetric method of determining the amount of carbon dioxide produced makes it possible to use much smaller quantities of the organic substance, and generally to simplify the operation (compare Loges, *Abstr.*, 1883, 247, 830).

The disposition of apparatus is similar to that usually employed, except that the tube is drawn out to a point at one end, and that the carbon dioxide is collected in a modified form of Winkler's aspirator containing a standard solution of baryta, and suitably connected to a reservoir of mercury so that the pressure can be adjusted during the progress of the combustion. When the whole of the carbon dioxide has been evolved, the pointed end of the tube is connected to a wash-bottle containing a concentrated solution of potassium hydroxide, the point is broken, and air is drawn through the apparatus to sweep the last traces of carbon dioxide into the aspirator. Finally, the baryta solution in the aspirator is titrated with *N*/50 sulphuric acid. Full details of the method of conducting the combustion are given in the original. The method is regarded as particularly suitable for the estimation of carbon in soils. T. A. H.

Estimation of Ash in Graphite. SAMUEL S. SADTLER (*Chem. Zentr.*, 1907, ii, 1445; from *J. Franklin Inst.*, 1907, 144, 201—203).—The powdered sample is placed into a platinum crucible, the top diameter of which is a little smaller than the bottom one. A small accurately-weighed quantity of ignited magnesium oxide is added, and the mixture is ignited gradually over the blowpipe in a slow current of oxygen. The addition of magnesium oxide serves to prevent the fusion and agglomeration of the ash. The crucible should be placed at an angle of 30°. L. DE K.

Rapid Estimation of Carbon Dioxide in Mineral Waters. J. STRÁNSKY (*Chem. Zeit.*, 1908, 32, 100—101).—The sample is collected by means of a capillary tube in a cylinder containing some ether, and the carbon dioxide is titrated as usual with *N*/10 potassium hydroxide with phenolphthalein as indicator. The capillary tube attached to the burette dips into the aqueous layer. Escape of carbon dioxide is thus prevented. L. DE K.



Soda-lime Apparatus for Organic Analysis and Carbon Dioxide Estimation. MAX DENNSTEDT (*Chem. Zeit.*, 1908, 32, 77).—The apparatus will be readily understood from the accompanying illustration. It may be made of thin glass, and its weight when empty need not exceed 50 grams. It is loosely filled with about 50 grams of granulated soda-

lime, which, if too dry, should be moistened with a few c.c. of water. L. DE K.

Estimation of Carbon Disulphide in Benzene. ISIDORE BAY (*Compt. rend.*, 1908, 146, 132).—The white, crystalline precipitate of phenylhydrazine phenylthiocarbazate, $\text{CS}_2(\text{NHPh}\cdot\text{NH}_2)_2$, obtained by addition of phenylhydrazine to carbon disulphide, is sufficiently stable to allow it to be employed as the basis of a method of estimating carbon disulphide.

The precipitation is complete in two to three hours. The precipitate is collected on a double tared filter, washed with benzene, and dried in a vacuum desiccator. The method gives very accurate results when estimating carbon disulphide in benzene, the greatest error observed being less than 0.5% of the amount determined, the values being always too high. E. H.

Use of Borax, &c., Beads in Analysis. OSCAR LUTZ (*Zeitsch. anal. Chem.*, 1908, 47, 1—36).—The author has compared the colorations produced by various elements when the latter are fused in the ordinary way on borax and phosphate beads, and finds that borax beads are only suitable for use in the case of basic elements, such as chromium, manganese, iron, cobalt, nickel, copper, tin, and cerium. For acid-forming elements, such as titanium, vanadium, molybdenum, tungsten, and uranium, phosphate beads give the better results. The bead reactions are at best only confirmatory tests, and in most cases better tests are available. W. P. S.

Electrolytic Analysis. ALEXANDER CLASSEN (*Zeitsch. Elektrochem.*, 1908, 14, 33—34). ARTHUR FISCHER (*ibid.*, 34—36).—Claims for priority in reference to several methods recently brought forward in papers dealing with this subject. T. E.

Volumetric Estimation of Zinc according to Schaffner. V. HASSREIDTER (*Zeitsch. angew. Chem.*, 1908, 21, 66—69).—A criticism of Schaffner's zinc titration process with sodium sulphide. The retention of zinc by the ferric hydroxide may be much lessened by washing the precipitate with dilute ammonia instead of water. Excess of ammonia has been supposed to have an injurious effect when applying the spot-test on lead-paper, but the author thinks this is caused by too high a temperature of the solution, also by a large excess of ammonium salts. The analysis of the ore and the checking of the sodium sulphide solution should be carried out simultaneously with the aid of two separate burettes. It also appears that the richer the ore the less chance there is of discrepancies in duplicate commercial analyses. L. DE K.

Electrolytic Separation of Silver and Copper. HORACE W. GILLET (*J. Physical Chem.*, 1908, 12, 26—27).—Silver may be determined satisfactorily in presence of copper if the following conditions are observed: total silver and copper about 0.25 gram in the form of nitrates, 7 grams of tartaric acid, 25 c.c. of ammonia,

D 0.9, water up to 120 c.c., voltage 1—1.35. The electrolysis may be carried out either at 70° or 20°, but at the lower temperature a very rapid rotation of the anode is necessary so as to get a firmly adhering deposit.

From the liquid the copper may be precipitated as sulphide, which is then redissolved in nitric acid and deposited by electrolysis in the usual way. L. DE K.

Electrolytic Estimation of Minute Quantities of Copper. E. E. FREE (*J. Physical Chem.*, 1908, 12, 28—29).—The author states that it is possible to estimate fractions of a milligram of copper with accuracy by electrolysis if care is taken to work with a small electrode weighing about 0.3 gram, and with the aid of a delicate assay-balance. The electrode is weighed after the copper has been deposited, and then again after its removal by means of nitric acid.

Good results are obtained by using 25 c.c. of copper solution acidified with 2—4% of nitric acid and a few drops of sulphuric acid. The electrolysis should last overnight with a current of about 1.8 volts and 0.01 ampere. The usual precautions are taken. L. DE K.

Volumetric Estimation of Mercury in its Ores. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1908, [iv], 1, 1169—1173).—A quantity of the powdered ore, representing about 1 gram of metal, is dissolved in nitro-hydrochloric acid at a gentle heat and then evaporated to dryness at 50°. The residue is dissolved in hot water, 50 c.c. of 20% potassium iodide are added, and then a solution of sodium carbonate so long as a precipitate is formed. After adding a slight excess of 20% aqueous sodium hydroxide, the liquid is filtered, the residue is again extracted a few times with alkaline potassium iodide solution, and finally well-washed with hot water; when cold, the solution is made up to 100 c.c.

Ten c.c. of the solution are then placed in a stoppered flask, 20 c.c. of 20% aqueous sodium hydroxide are added, also 20 c.c. of 35% formaldehyde, and the whole is kept for twenty hours at 25°. This causes the precipitation of metallic mercury, which is carefully washed with alcohol and dissolved in a known measure of standard iodine solution. The excess of iodine is titrated with standard thio-sulphate.

Gold or platinum should be absent, as they are also reduced by formaldehyde. L. DE K.

Volumetric Estimation of Lead [as Sulphide]. HUGO KOCH (*Chem. Zeit.*, 1908, 32, 124—125).—Lead may be estimated with sufficient accuracy by titrating the dilute solution with standard sodium sulphide until no further precipitate is formed. Addition of carbon tetrachloride causes a rapid separation of the precipitate, leaving the aqueous layer quite colourless. Lead sulphate should be dissolved in solution of ammonium acetate.

Sodium sulphide solution keeps well in an atmosphere of coal-gas. L. DE K.

Red Leads and their Examination. ALFRED PARTHEIL (*Arch. Pharm.*, 1907, 245, 683).—The author's results (this vol., ii, 69) have,

for the most part, already been obtained by Reinsch (*Apoth.-Zeit.*, 1907, 195).
G. B.

Assay of Red Lead. JULIUS F. SACHER (*Chem. Zeit.*, 1908, 32, 62—63).—The sample is digested with water and a sufficiency of nitric acid with addition of formaldehyde until the lead peroxide is decomposed; hydrogen peroxide may also be used, but sugar, oxalic acid, alcohol, and lactic acid cannot be recommended, as they may lead to the formation of insoluble lead oxalate. The solution is then evaporated to dryness, the lead nitrate is dissolved in water, and the insoluble matter is collected and weighed.
L. DE K.

Assay of Red Lead. ERNST PIESZCZEK (*Pharm. Zeit.*, 1908, 53, 87—88).—A criticism of Sacher's process (preceding abstract). The author cannot recommend the reduction by means of formaldehyde as the action is too violent. Hydrogen peroxide causes no such inconvenience, and it is not necessary, as recommended by Sacher, to remove the excess of nitric acid by evaporation, as red lead is not likely to contain lead sulphate. The solution should be tested also for calcium.
L. DE K.

Volumetric Estimation of Manganese in Steel. LUIGI SACERDOTI (*Chem. Zentr.*, 1907, ii, 1448; from *L'Industria Chimica*, 1907, 7, 258—259).—A modification of Deshay's process. 0.2 Gram of borings is boiled with 45 c.c. of nitric acid, D 1.18, until no more nitrous fumes are evolved, 40 c.c. of water are added, and, after heating to boiling, 1.5—2 grams of lead peroxide are added. After boiling for another two minutes, the liquid is rapidly cooled, diluted to exactly 100 c.c., and filtered through asbestos. Fifty c.c. of the filtrate are then diluted with 50 c.c. of water, and the permanganate present is titrated with standard solution of sodium arsenite, which has been checked by means of a steel containing an accurately known percentage of manganese.
L. DE K.

Titration with Permanganate in Presence of Hydrochloric Acid. THOMAS W. HARRISON and F. MOLLWO PERKIN (*Analyst*, 1908, 33, 43—47).—Owing to the reducing action of hydrochloric acid on permanganate, the authors find that the latter cannot be used for the titration of solutions of ferrous salts containing even small quantities of this acid. The addition of substances, such as potassium sulphate, magnesium sulphate, borax, sodium acetate, mercuric sulphate, manganous sulphate, and phosphoric acid, some of which have been stated to have a retarding action on the reduction due to the hydrochloric acid, had no effect on the results, except in the case of manganous sulphate. This salt appeared to have a distinct retarding action, but, owing to the yellow colour of the solution, the end point of the titration was distinguished with difficulty.
W. P. S.

Volumetric Estimation of Iron in Ferric Compounds. M. M. PATTISON MUIR (*Chem. News*, 1908, 97, 50).—The process is based on the fact that addition of mercuric chloride to a mixture of zinc and dilute sulphuric acid stops the evolution of hydrogen.

The iron solution is placed in a flask fitted with a cork carrying a glass tube narrowed at its upper end. Two hundred c.c. of dilute sulphuric acid and 20 grams of iron-free granulated zinc are introduced, the liquid is warmed until there is a brisk evolution of hydrogen, and the flask is shaken from time to time until the reduction is complete. One hundred c.c. of strong mercuric chloride solution are now added, and, after shaking for a few minutes, the contents are cooled rapidly and at once titrated with standard permanganate. L. DE K.

Application of Sodium Hyposulphite in Volumetric Analysis. HERMANN BOLLENBACH (*Chem. Zeitsch.*, 1908, 32, 146—148).—Sodium hyposulphite, now obtainable in a fairly pure solid condition, has already been used in volumetric estimations. The author gives another instance where it may be successfully applied.

Estimation of Ferric Iron.—The dilute iron solution, the temperature of which should not exceed 30°, is acidified with dilute sulphuric acid until the yellow colour has disappeared. After adding a few drops of potassium thiocyanate, the standardised hyposulphite is added until the red colour has nearly vanished. A few drops of indigo solution are then added, and the titration continued until the liquid is colourless. No notice should be taken of the fact that the solution soon turns blue again.

The hyposulphite solution, which may vary in strength from 2.5 to 30 grams per litre, is checked with a solution of ferrous-ammonium sulphate previously oxidised by means of permanganate. During the titration, the nozzle of the burette should dip into the liquid. A burette arrangement is described in which the hyposulphite is kept in a reservoir, in an atmosphere of either hydrogen, coal-gas, or carbon dioxide. L. DE K.

Separation and Estimation of Cobalt and Nickel. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 66—67).—In the method proposed, the nickel is separated as ammonium-nickel molybdate. The solution containing the nickel and cobalt is rendered faintly acid, an excess of saturated ammonium molybdate solution is added, and then a quantity of ammonium chloride. The mixture is heated to a temperature of 80°, next cooled to 0°, and the precipitate, consisting of ammonium-nickel molybdate, is collected on a filter and washed with cold saturated ammonium chloride solution. The double salt is then dissolved in hot water, the solution is boiled, after the addition of sodium hydroxide, to remove the ammonia, and the nickel is precipitated by the addition of bromine. The hydrated nickel sesquioxide obtained may be weighed or dissolved in a suitable acid, and the nickel deposited electrolytically. The cobalt in the filtrate from the double salt is also precipitated by the addition of bromine in the presence of sodium hydroxide. The results obtained by the method are stated to be trustworthy. W. P. S.

Detection and Estimation of Nickel in Presence of Cobalt, Iron, and Manganese. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1907, 145, 1334—1335).—The neutralised solution, freed from

alkaline earths by addition of ammonium sulphate, is mixed with a large excess of ammonium chloride and a saturated solution of ammonium molybdate, which on heating at 80—90° for a few minutes completely precipitates the nickel and practically all the iron as double molybdates, whilst cobalt and manganese are not precipitated.

The precipitate is well washed with saturated ammonium chloride solution, and the filter is then placed in a beaker containing water. This is heated to boiling, and ammonium chloride and ammonia are added. The iron is precipitated, and the nickel is completely dissolved, and may at once be estimated colorimetrically; or the metal may be precipitated by boiling with excess of potassium hydroxide, and then adding bromine. The sesquioxide is then redissolved, and the nickel precipitated by electrolysis.

L. DE K.

Detection of Nickel. HERMAN GROSSMANN and BERNARD SCHÜCK (*Bull. Soc. chim.*, 1908, [iv], 3, 14—15).—The reaction described by Pozzi-Escot (*Abstr.*, 1907, ii, 818) for the detection of nickel in presence of cobalt is not new, since Markwald (*Inaug. Diss. Berlin*) has already observed that nickel molybdate is less soluble than cobalt molybdate, and that the latter is precipitated much more rapidly than the former, especially in presence of excess of ammonium molybdate.

The reaction is, however, unsuitable for the detection of nickel in presence of cobalt, since salts of the latter, when warmed with excess of ammonium molybdate, yield a precipitate of the anhydrous violet molybdate. The reaction is therefore less delicate as a test for nickel than those described by the authors (*Abstr.*, 1906, ii, 903), Tschugaeff (*Abstr.*, 1907, ii, 989), and Brunck (*ibid.*).

T. A. H.

Volumetric Estimation of Nickel. H. CANTONI and M. ROSENSTEIN (*Bull. Soc. chim.*, 1908, [iv], 1, 1163—1169).—Nickel may be conveniently titrated with potassium ferrocyanide or ferricyanide, using ferric chloride (or uranium acetate) or ferrous sulphate as indicator. The end reaction is determined by placing a drop of the solution on a piece of folded filter paper and applying the spot-test on the paper below. The best results are obtained with ferricyanide in solutions faintly acidified with acetic acid.

The ferro- or ferri-cyanide solution should be checked with a known weight of electrolytically-deposited metal, under the same conditions as in the analysis of the sample. Tables are given showing the influence of acetic acid, sodium acetate, ammonium acetate, sodium sulphate, potassium sulphate, and ammonium sulphate.

L. DE K.

New Colour Test for Molybdenum. WILLIAM BETTEL (*Chem. News*, 1908, 97, 40).—The solution to be tested is evaporated nearly to dryness, carefully neutralised with nitric or sulphuric acid, and mixed with hydrogen peroxide solution. If this should give a yellow coloration, a drop of dilute ammonia is added, when should molybdenum be present, a brownish-red colour will appear. The colour, however, is discharged on dilution and by adding excess of alkali. Accurate quantitative colorimetric results cannot be obtained by this process.

L. DE K.

Separation of Tungstic Acid from Phosphoric Acid. GEORG VON KNORRE (*Zeitech. anal. Chem.*, 1908, 47, 37—57).—Tungstic acid may be separated almost quantitatively from phosphoric acid by precipitation with benzidine hydrochloride (compare Abstr., 1905, ii, 286). The solution containing the phosphotungstate is diluted to a volume of about 400 c.c., 3 c.c. of hydrochloric acid, D 1.12, are added, the mixture is boiled, and a sufficient quantity of benzidine hydrochloride is introduced. When cold, the precipitate is collected on a filter, washed with dilute benzidine hydrochloride solution, and then boiled with 200 c.c. of water in order to remove remaining traces of benzidine phosphate. After again cooling, the precipitate is collected, washed as before, ignited in a platinum crucible, and weighed as tungsten trioxide. Benzidine phosphates are not very soluble in water, and for this reason tolidine hydrochloride may be used for the above separation; tolidine phosphates are readily soluble, so that the precipitate of tolidine tungstate does not need to be boiled with water. In other respects, the process is carried out as described for use with benzidine hydrochloride. Should it be desired to remove any traces of phosphate which may remain in the precipitate, the ignited residue is fused with alkali, and the tungsten then re-precipitated with tolidine hydrochloride. W. P. S.

Detection of Ruthenium in Platinum Alloys. N. A. ORLOFF (*Chem. Zeit.*, 1908, 32, 77).—A portion of the alloy is fused with lead, the regulus is extracted with nitric acid, and the residue ignited in contact with the air to remove any osmium. The mass, consisting of platinum, iridium, rhodium, and ruthenium, is fused with potassium hydroxide and nitrate, dissolved in water, and treated with nitric acid in excess. When this operation is carried out in an Erlenmeyer flask, or simply a test-glass, covered with a piece of filter paper, this will gradually (12—24 hours) darken, owing to the formation of RuO_4 vapours. The paper may then be ignited, the ash fused with potassium hydroxide and nitrate, and the orange-coloured ruthenate extracted with water. L. DE K.

Analysis of Natural Mineral Waters. MAX ROLOFF (*Zeitsch. öffentl. Chem.*, 1908, 14, 53—58).—The author protests against the use of an undue number of decimals in recording the results of analyses of mineral waters. He instances a case in which the total amount of mineral matter in a litre of water is given to six decimal places. In the light of modern knowledge, the practice of combining the bases and acids, found on the analysis of a water, to show that certain salts are present in the water is also open to objection. W. P. S.

Improved Method for Estimating the Acidity of Soils. H. SÜCHTING (*Zeitsch. angew. Chem.*, 1908, 21, 151—153).—Ten to fifty grams of the soil are mixed with a little water contained in a flask, an accurately weighed quantity (about 0.4 gram) of calcium carbonate is added, and the carbon dioxide evolved is removed by means of a current of hydrogen with constant stirring of the mass.

The carbon dioxide is absorbed and titrated (Pettenkofer's process), but this may, as a rule, be omitted.

Dilute hydrochloric acid is now added, and the carbon dioxide evolved determined as before. The difference between the result and the figures calculated from the calcium carbonate added equals the carbon dioxide expelled by the acids from the soil.

If the sum of the carbon dioxide found by the two processes exceeds that of the amount added, the excess is due to carbon dioxide formed by decomposition of organic matters. In accurate analysis, this should be allowed for.

L. DE K.

A New Dephlegmator for the Fractionation of Naphtha. V. F. HERR (*Chem. Zeit.*, 1908, 32, 148—149).—The apparatus consists of a tube or column, which may be conveniently made from the outer jacket of a Liebig's condenser (300—1000 mm.) by removing the water-inlet tube; the outlet tube is then connected with a condenser. After placing a disc of wire gauze at the bottom, the column is filled with shot, and a thermometer is fixed in with its bulb just opposite the outlet tube. The whole is held in position by means of a ring lined with asbestos, and a round-bottomed, short-necked distillation flask is attached. The column is isolated by means of cotton-wool, filter paper, and asbestos. If fractions above 130° should have to be collected, the 1000 mm. column should be surrounded by a thin asbestos covering only, and then be placed in a jacket made of strong sheet copper, which is heated by means of four burners to the desired temperature.

L. DE K.

Observations on the Analysis of Lavender Oils. PAUL JEANCARD and CONRAD SATIE (*Bull. Soc. chim.*, 1908, [iv], 3, 155—159).—This work has been in progress since 1900 to ascertain how the percentage of esters in lavender oils is affected by (1) the altitude at which the plants are grown, and (2) the conditions under which the distillation is conducted.

The results confirm the observations recorded previously (Abstr., 1900, i, 510), and show in addition that the most important factors in ascertaining the value and freedom from sophistication of a lavender oil are (a) the acid number, (b) specific gravity (0.880 to 0.890), (c) rotatory power (-6° to -10° in a 100 mm. tube), and (d) saponification number after acetylation (above 160). The addition of spike oil increases the second and diminishes the third and fourth of these constants. The principal constants of lavender oils produced in (1) the higher Alps, and (2) in the Italian Alps in recent years, are tabulated in the original.

T. A. H.

Estimation of Esters in Wine. GÉZA AUSTERWEIL and PAUL PACOTET (*Chem. Zeit.*, 1908, 32, 112—113).—One hundred to two hundred and fifty c.c. of the carefully-neutralised wine are distilled in a special apparatus at the temperature of boiling ether or ethyl bromide under reduced pressure until about one-third of the liquid has passed over. The distillate is then boiled in a reflux apparatus for one hour with 10 c.c. of *N*/10 potassium hydroxide, when the excess of

alkali is titrated with *N*/10 sulphuric acid. The result is expressed in ethyl acetate. One c.c. of *N*/10 alkali = 0.0088 gram of the same.

L. DE K.

Evaluation of Picric Acid. FRANZ UTZ (*Zeitsch. anal. Chem.*, 1908, 47, 140—144).—0.1 Gram of the sample is heated in a flask with 5 c.c. of 30% aqueous sodium hydroxide and 10 c.c. of 3% hydrogen peroxide for twenty to thirty minutes. The water evaporated is replaced from time to time, and a few drops of hydrogen peroxide are also added occasionally. In this manner, the nitrogen is converted into nitrite; 40 c.c. of water and 100 c.c. of 3% hydrogen peroxide are now added, the temperature is raised to 80°, and 40 c.c. of 5% sulphuric acid are introduced by means of a pipette reaching to the bottom of the flask. After heating once more to 80°, 12 c.c. of 10% solution of nitron in 5% acetic acid are added, and on cooling, the nitric acid formed is precipitated as nitron nitrate. After placing the flask for an hour in iced water, the precipitate is collected by aid of a filter pump, washed with 10—12 c.c. of iced water, dried at 105°, and weighed. One gram = 0.037406 gram of nitrogen.

L. DE K.

Estimation of *m*-Cresol in Cresol Mixtures. FRITZ RASCHIG (*Pharm. Zeit.*, 1908, 53, 99—100).—A reply to Herzog, who seems not to have followed the author's directions (*Abstr.*, 1900, ii, 694), and has, in consequence, obtained incorrect results with high-grade cresols.

The process consists in converting the *m*-cresol into insoluble trinitro-*m*-cresol, and oxidising the *o*- and *p*-cresol with formation of oxalic acid and other soluble substances.

L. DE K.

Analysis of Crude Cresols. JOHANNES HERZOG (*Pharm. Zeit.*, 1908, 53, 141).—The method of estimating *m*-cresol in mixtures of cresols described by Raschig (preceding abstract) is not considered by the author to be a suitable one for use by pharmacists. A good fume-cupboard is required in which to carry out the process, and the results obtained do not appear to be always trustworthy.

W. P. S.

Estimation of Cineol (Eucalyptol) in Eucalyptus Oils. OTTO WIEGAND and M. LEHMANN (*Chem. Zeit.*, 1908, 32, 109—110).—The process described previously by the authors is now applied to the fraction passing over between 170—180°. Ten c.c. of the distillate are shaken vigorously, as directed, with excess of 50% resorcinol solution, and the amount of cineol absorbed may thus be read off and calculated on the original quantity taken for analysis.

L. DE K.

Colour Reaction of Cholesterol on Oxidation. ISAAC LIFSCHÜTZ (*Ber.*, 1908, 41, 252—255).—The recognition of oxycholesterol in bone fat, blood (*Abstr.*, 1907, ii, 899), brain, and pancreatic fat has led to the study of its colour reactions. When a few grains of benzoyl peroxide are added to an acetic acid solution of a few mg. of cholesterol, the whole warmed, then cooled, and four drops of sulphuric acid added to the mixture, a beautiful green or violet-red colour, changing to green, is developed. The sensitiveness of this reaction is 1 in 10,000 in layers of 12—15 mm. Although less sensitive than

Liebermann's reaction (Abstr., 1885, 1075), it has the advantage that the absorption bands are situated between the lines *C* and *d*, whereas in the other the bands are situated near *B* and resinification, caused by the acetic anhydride, may mask the colour. The colours are due to oxysterol or the ether (Abstr., 1907, i, 315, and *loc. cit.*); oxysterol is best prepared by using benzoyl peroxide.

A combination of the above test for oxysterol and Liebermann's test for cholesterol is made by first adding sulphuric acid to an acetic acid solution; the green colour produced by oxysterol is destroyed by acetic anhydride, and if cholesterol is present the characteristic colour due to this substance is developed.

W. R.

Titration of Formaldehyde in Highly-Coloured Solutions. SÖREN P. L. SÖRENSEN and H. JESSEN-HANSEN (*Biochem. Zeitsch.*, 1908, 7, 407—420).—Formaldehyde may be titrated with alkali and phenolphthalein as indicator even if the liquid should be coloured yellow or yellowish-brown, but in such case it is advisable to make a check experiment using water judiciously coloured with tropæolin and Bismarck-brown (*ibid.*, 1907, 64). But even this device fails when the solution is too dark coloured, as in the case of protein decomposition products. In this case, the authors operate as follows: 20 c.c. of the solution are acidified with, say, 5 c.c. of *N*/2 hydrochloric acid (if there is already excess of acid it may be advisable to add *N*/2 sodium hydroxide instead), 4 c.c. of 2*N* barium chloride are added, and then, with constant shaking, 20 c.c. of *N*/3 silver nitrate; the silver chloride formed precipitates most of the colouring matter. After making up the volume to 50 c.c. and adding four drops more water, the liquid is filtered and an aliquot part is used for the usual titration, allowance being made for acid or alkali added.

L. DE K.

Testing the Purity of Salicylaldehyde. HANS KREIS (*Chem. Zeit.*, 1908, 32, 149).—When applying Komarowsky's test for amyl alcohol in spirits, it is necessary to make sure as to the purity of the salicylaldehyde employed. If alcohol free from fusel oil is available, it is easy to make a practical test, but if not, the following test is recommended: three drops of the sample are mixed with ten drops of sulphuric acid. Pure salicylaldehyde turns a clear, orange-red, whilst unsuitable preparations give more or less dark brownish-red colorations. If now 5 c.c. of 95% alcohol are added, the pure substance gives a colourless solution, whilst the impure samples give red solutions of varying intensity.

L. DE K.

Use of *p*-Nitrophenylhydrazine in the Identification of Aliphatic Ketones and Aldehydes. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 235—238).—In the identification of small quantities of simple aldehydes and ketones, *p*-nitrophenylhydrazine is of great service; it gives compounds which are insoluble in water and easily crystallisable. The melting points of the phenylhydrazones of the following substances are given thus: formaldehyde, 181—182°; acetaldehyde, 128—128.5°; propaldehyde, 123—124°; *n*-butaldehyde, 91—92°; isobutaldehyde, 131.5—132°; isovaleraldehyde, 109—110°; glyoxylic acid, about 200°;

acetone, 149°; methyl ethyl ketone, 128—129°; methyl isopropyl ketone, 108—109°; methyl *n*-nonyl ketone, 90—91°. W. D. H.

Estimation of Acetone. GUNNAR HEIKEL (*Chem. Zeit.*, 1908, 32, 75—76).—Both Messinger's process (titration with iodine in alkaline solution) and Denigès's mercuric sulphate method give concordant results. Should a serious difference be noticed, the acetone contains substances which interfere with the tests. In the case of almost pure acetone, the mercury precipitate is yellowish-white, but with inferior samples, it is yellowish-brown, or nearly brown. L. DE K.

Normal Tubes for Saccharimeters. HENRI PELLET (*Ann. Chim. anal.*, 1908, 13, 56—57).—The author thinks that the use of the special tubes recommended by Rousset (this vol., ii, 73) would tend to lead to confusion and require alterations in some of the instruments now employed. W. P. S.

Estimation of Pentoses in Urine. ADOLF JOLLES (*Zeitsch. anal. Chem.*, 1907, 46, 764—771).—The urine is freed from interfering volatile substances by boiling with a few drops of acetic acid and if necessary concentrated. One hundred c.c. of the sample are mixed with 150 c.c. of hydrochloric acid, D 1.06, and distilled in a current of steam until the distillate measures, say, 1 litre. One hundred c.c. of the distillate are then over neutralised with 20% sodium hydroxide solution, using methyl-orange as indicator, and *N*/2 hydrochloric acid is again added until the red colour is permanent.

The furfuraldehyde which represents the pentose is then estimated in the usual way by titration with sodium hydrogen sulphite and standard iodine solution. L. DE K.

Barfoed's Acid Cupric Acetate Solution as a Means of Distinguishing Dextrose from Maltose, Lactose, and Sucrose. F. C. HINKEL and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1907, 29, 1744—1747).—Barfoed's copper solution is made by dissolving 45 grams of crystallised copper acetate in 900 c.c. of water, 1.2 c.c. of 50% acetic acid is added, and the whole is diluted to a litre. Five c.c. of the reagent are then placed in a test-tube, 5 c.c. of the sugar solution are added, and the tube is placed in boiling water for ten minutes. Any reduction is due to dextrose only. The author has investigated this method, but states that in order to get trustworthy results the amount of dextrose should not exceed 2 mg., as otherwise the reduction is incomplete. The filtrate may then be tested for the other sugars. L. DE K.

Estimation of Sugar in Blood. IVAR BANG (*Biochem. Zeitsch.*, 1908, 7, 327—328).—Blood is received from the animal into excess of alcohol; the coagulum is broken up, and then separated by repeated centrifugalisation with alcohol. The alcoholic extracts are mixed, concentrated, shaken with a little kaolin, and filtered. The sugar is estimated in the clear filtrate (compare Rona and Michaelis, this vol., ii, 117). W. D. H.

Estimation of Lactose in Milk. CYRILLE CARREZ (*Ann. Chim. anal.*, 1908, 13, 17—22).—When using the author's process, it is not necessary to know the volume occupied by the coagulum. Fifty c.c. of milk are mixed with 5 c.c. of potassium ferrocyanide solution (150 grams per litre) and then with 5 c.c. of zinc acetate solution (300 grams per litre), and the clear filtrate is then examined polarimetrically. The operation is repeated three times, addition of 10, 25, and 50 c.c. respectively of water being made to the milk. Formulæ are given explaining the calculation of the % of lactose. L. DE K.

The Polarimetric Determination of Sucrose. The Effect of Clarification with Basic Lead Acetate on the Optical Activity and Copper Reducing Power of Sugar Solutions. FRANCIS WATTS and HAROLD A. TEMpany (*J. Soc. Chem. Ind.*, 1908, 27, 53—57).—The authors find that the use of excessive amounts of basic lead acetate has an appreciable effect on the optical activity and reducing power of solutions of invert-sugar. When such an excess is avoided, clarification by means of dry anhydrous basic lead acetate involves no such error (compare Abstr., 1907, ii, 656). In the case of low grade products, such as molasses, trustworthy results are obtained by clarification with dry anhydrous basic lead acetate, followed by treatment with sulphur dioxide; this especially applies to estimations by Fehling's method. The authors consider that it appears to be unnecessary to search for more complicated methods of clarification, since the use of dry anhydrous basic lead acetate gives results which are well within the limits of accuracy of ordinary methods of analysis.

W. P. S.

Detection of Rice Starch in Wheat Flour. PELTRISOT (*Ann. Chim. anal.*, 1908, 13, 50—53).—The method described by Gastine (Abstr., 1907, ii, 137) is considered to be of value in the detection of rice starch in wheat flour; the appearance of the hilum of the starch grain is characteristic. As, however, a few other starch grains, notably those of darnel, may be mistaken for rice, care should be taken to avoid an error of judgment. Whenever possible, the character of the pericarp should be taken into consideration.

W. P. S.

Estimation of Crude Fibre and Separation of Cellulose, Lignin, and Cutin. JOSEF KÖNIG (*Ber.*, 1908, 41, 46—49. Compare Abstr., 1906, ii, 905).—Polemical. A reply to Matthes and Streitberger (Abstr., 1907, ii, 991).

W. H. G.

Estimation of Crude Cacao Fibre. HERMANN MATTHES (*Ber.*, 1908, 41, 400—403. Compare Matthes and Streitberger, Abstr., 1907, ii, 991).—Polemical. A reply to König (preceding abstract).

G. Y.

Solubility of Stearic Acid in Ethyl Alcohol at 0°. WILLIAM H. EMERSON (*J. Amer. Chem. Soc.*, 1907, 29, 1750—1756).—In carrying out some estimations of stearic acid by Hohner and Mitchell's method (Abstr., 1897, ii, 289), difficulty was experienced in obtaining a definite saturated solution of the acid, and a study has therefore

been made of its solubility in alcohol at 0°. It has been found that the solubility is practically constant when not less than 0.7 gram is used with 100 c.c. of alcohol or not less than 0.5 gram with 50 c.c., but that, if smaller quantities of the acid are employed, highly supersaturated solutions are produced. The solubility at 0° of the acid in 100 c.c. has been found to be 0.1246 gram in alcohol of 95.7% strength, 0.1223 gram in 95.5% alcohol, 0.1139 in 95.1%, 0.1035 in 94.5%, and 0.0996 in 94.3% alcohol. When an alcoholic solution of stearic acid is evaporated on the water-bath, small quantities of ethyl stearate are produced, and the solubility of the acid therefore appears greater than it actually is. Thus, on evaporating a solution in 99% alcohol, 1.26% of the acid was converted into the stearate. F. G.

Detection of Glyoxylic Acid in Urine. F. GRANSTRÖM (*Beitr. chem. Physiol. Path.*, 1908, 11, 132—142).—See this vol., ii, 122.

Detection of Tartaric Acid in Cider. G. A. LE ROY (*Compt. rend.*, 1907, 145, 1285; *Ann. Chim. anal.*, 1908, 13, 16—17).—An intense violet coloration is produced when tartaric acid or a tartrate is heated with from 10 to 20 times its weight of a 10% solution of resorcinol or pyrogallol in concentrated sulphuric acid. Under the same conditions, citric acid does not give a coloration, and malic and lactic acids yield yellow colorations. For the detection of tartaric acid or its salts in cider, the test is applied as follows: the cider is neutralised and treated with an excess of basic lead acetate solution, the precipitate is collected on a filter, washed with cold water, and then decomposed with hydrogen sulphide. The lead sulphide is separated by filtration, the filtrate is heated to expel the hydrogen sulphide, an excess of sodium hydrogen carbonate is then added, and the solution is evaporated to dryness. The resulting residue is dissolved in a quantity of the resorcinol or pyrogallol solution and the mixture is heated. If tartaric acid is present, a violet coloration will be produced. W. P. S.

Goldenberg Method for the Estimation of Tartaric Acid in Wine Dregs, Tartar, and other Crude Materials. CHEMISCHE FABRIK. VORM. GOLDENBERG, GEROMONT & Co. (*Zeitsch. anal. Chem.*, 1908, 47, 57—59).—The following manner of carrying out this process is given: Six grams of the sample containing more than 45% of total tartaric acid, or 12 grams if the tartaric acid content is less than 45%, are digested for ten minutes with 18 c.c. of hydrochloric acid, D 1.10. The mixture is then diluted with water to a volume of 200 c.c., mixed, and the solution is passed through a dry filter. One hundred c.c. of the filtrate are transferred to a beaker of 300 c.c. capacity, in which have been placed previously 10 c.c. of 66% potassium carbonate solution, and the solution is boiled for twenty minutes. The solution together with the precipitated calcium carbonate is then rinsed into a 200 c.c. flask, diluted with water to the mark, mixed, and filtered through a dry filter. One hundred c.c. of the filtrate are evaporated in a porcelain basin on the water-bath to a volume of 15 c.c., 3.5 c.c. of glacial acetic acid are now added, and the mixture is stirred for five minutes. After ten minutes, 100 c.c. of 95% alcohol are added, the

stirring is continued for five minutes, and at the end of a further ten minutes the precipitate is collected on a filter and washed with alcohol. The filter and precipitate are next placed in a basin, treated with 200 c.c. of hot water, and the solution is titrated with $N/5$ sodium hydroxide solution, using litmus paper as indicator. The sodium hydroxide solution is standardised with pure potassium hydrogen tartrate. A correction is made for the volume of the insoluble constituents of the crude material; in the case of samples containing less than 45% of tartaric acid, 0.80% is subtracted from the result obtained; for samples containing from 45—60%, the correction is 0.30% and 0.20% for those with from 60—70%. No correction need be applied to the results obtained with samples containing more than 70% of tartaric acid.

W. P. S.

Estimation of Non-volatile Organic Acids in Tobacco. JULES TÓTH (*Rev. intern. Falsif.*, 1907, 20, 165—166).—Further results are given of the estimation of oxalic, malic, and citric acids in tobacco (*Abstr.*, 1907, ii, 513). The quantities found were: oxalic acid, from 0.42 to 2.57%; citric acid, from 0.92 to 4.56%; malic acid, from 1.56 to 7.81%. It is found that by estimating the acids separately and calculating the results into oxalic acid, a value was obtained which was sometimes more and sometimes less than the value obtained by estimating the acids directly by titration, and expressing the result as oxalic acid. The differences were probably due to the influence of the volatile acids present in the tobacco.

W. P. S.

Estimation of Fat in Milk. D. SIDERSKY (*Ann. Chim. anal.*, 1908, 13, 22—24).—The author recommends the process of Soxhlet as modified by Timpe. To 100 c.c. of milk are added, slowly and with gentle shaking, 50 c.c. of sulphuric acid; 50 c.c. of water are then added, and, when cooled to 15°, 60 c.c. of ether are introduced and the whole is well shaken to extract the butter fat. The ether, before use, is well shaken with dilute sulphuric acid (1 : 3).

The percentage of fat is now found by taking the sp. gr. of the ethereal solution and reference to a table.

L. DE K.

Estimation of Fat. ELLY A. BOGDANOFF (*J. Landw.*, 1908, 56, 53—87).—See this vol., ii, 206.

Estimation of the Caprylic [Octoic] Acid Value of Butter-Fat. R. K. DONS (*Zeitsch. Nahr. Genussm.*, 1908, 15, 75—79).—The process is a modification of that described previously by the author (*Abstr.*, 1907, ii, 824). Five grams of the butter fat are saponified in the usual way, the soap is dissolved in 100 c.c. of hot water, and the fatty acids are liberated by the addition of 50 c.c. of dilute sulphuric acid. After cooling, the aqueous portion is removed, and the solid cake of fatty acids is extracted twice with 150 c.c. of hot water. After this treatment, the cake of fatty acids is placed in a flask, 20 grams of glycerol, 5 grams of sodium sulphate, and a few pieces of pumice stone are added, and the mixture is distilled until 110 c.c. of distillate have been collected. One hundred c.c. of this

distillate are neutralised, as in the usual Reichert-Meissl process. The acidity of the distillate is due almost entirely to caprylic [octoic] acid, and this is precipitated by the addition of $N/10$ silver nitrate solution. The quantity of the latter required, expressed as c.c. of $N/10$ solution, multiplied by 1.1, gives the "caprylic acid" value of the fat. A correction is applied for the solubility of the silver salt in the volume of solution and that of the water used for washing the precipitate (20 c.c.); this correction is 0.4 c.c., which is added to the result obtained. Pure butter-fat gives a value of from 1.6 to 2.0; butter containing 10% of cocoanut oil, from 2.7 to 3.0, and pure cocoanut oil, 5.3.

W. P. S.

Blackberry-seed Oil. RICHARD KRZIZAN (*Chem. Rev. Fett-Harz-Ind.*, 1908, 15, 7—9, 29—30).—Blackberry seeds yield about 12.6% of a drying oil having the following chemical and physical constants: D^{25} 0.9256; saponification number, 189.5; iodine number, 147.8; acid number, 2.03; insoluble fatty acids, 96.3%. The liquid fatty acids contain about 80% of linolic acid, 17% of oleic acid, and 3% of linolenic and isolinolenic acids, and amount to about 91%, reckoned on the oil, whilst the solid acids, chiefly palmitic acid, are about 4.7%. Volatile acids are not present in the oil. The unsaponifiable portion of the oil contains 0.6% of phytosterol. The drying properties of the oil are somewhat inferior to those of raspberry-seed oil (*Abstr.*, 1907, i, 821).

W. P. S.

Staněk's Method for Estimating Choline. VLADIMIR STANĚK (*Zeitsch. physiol. Chem.*, 1908, 54, 354).—In reply to Kiesel (*Abstr.*, 1907, ii, 994), it is pointed out that most of his observations have been made previously by the author.

J. J. S.

Indicators in the Titration of Cinchona Bases. ERWIN RUPP and K. SEEGER (*Chem. Zentr.*, 1907, ii, 1363; from *Apoth. Zeit.*, 1907, 22, 743—750).—Hæmatoxylin may be advantageously replaced as an indicator for cinchona alkaloids by dinitrophenolphthalein, or better still by *p*-nitrophenol, in all cases where the solution is colourless or nearly so. In cases of strongly-coloured liquids, tetrachlorotetrabromophenolphthalein may render good service. The indicators are used in the form of 1% alcoholic solutions, ten to twenty drops of the first, or twenty to thirty drops of the latter, solution. The liquids must be diluted with sufficient alcohol to prevent separation of free alkaloid. Both indicators turn yellow in presence of alkali, and the cinchona alkaloids behave towards them as monobasic compounds.

L. DE K.

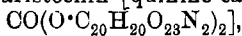
Estimation of Ecgonine in Java Coca. ANNE W. K. DE JONG (*Pharm. Weekblad*, 1908, 45, 42—43. Compare *Abstr.*, 1905, ii, 778).—A criticism of Greshoff's process (*Abstr.*, 1907, ii, 914). The ecgonine hydrochloride obtained is not always pure, but may be contaminated with sodium and, sometimes, ammonium chloride. To prevent this, the "acid-alkaloid" is dissolved in ether and shaken a few times with water, the ether is removed by distillation, and the residue treated

according to Greshoff's method. The aqueous solution may still retain some ecgonine; it is therefore boiled, if necessary, with a slight excess of sodium hydroxide to expel the ammonia. It is then acidified with hydrochloric acid, and evaporated to dryness; the result, after allowing for sodium chloride, represents ecgonine hydrochloride.

The composition of the "acid-alkaloid" cannot be calculated, as stated by Greshoff, from the ecgonine hydrochloride, as it is in reality composed of three alkaloids, namely, cocaine, cinnamylcocaine, and isatropylcocaine.

L. DE K.

Control and Estimation of Atomic Complexes in Drugs. PIO LAMI (*Boll. chim. farm.*, 1907, 46, 826—833).—Methods are given for the examination of protargol, heroine (diacetylmorphine), mesotan (acetylmethyl salicylate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{COMe}$), aspirin (*o*-acetoxybenzoic acid), aristochin [quinine carbonate,



and aristol (iodothyml).

T. H. P.

Estimation of Tannins in White Wines. MAX KOEBNER (*Chem. Zeit.*, 1908, 32, 77).—Ten c.c. of wine are placed in a stoppered cylinder, 10 c.c. of tartaric acid solution (1:10) are added, then three drops of ferric chloride (1:10), ammonia in excess, and water up to 50 c.c. A clear solution is obtained which owes its dark colour to a certain amount of iron tannate. The solution is then compared with one made in a similar manner, using a solution of 1 gram of tannin and 50 c.c. of hydrochloric acid made up to 1 litre as a standard comparison fluid.

L. DE K.

The Polariscope Method for the Estimation of Gliadin. G. W. SHAW (*J. Amer. Chem. Soc.*, 1907, 29, 1747—1750).—Snyder's process (*Abstr.*, 1904, ii, 524) is recommended. If care is taken to make two polarimetric determinations, the first in the original solution, and the second after precipitating the protein with mercuric nitrate, the results compare favourably with the usual chemical methods.

L. DE K.

The Aloin Test for Hæmoglobin. A. BOLLAND (*Bull. Acad. Sci. Cracow*, 1907, 441—448. Compare Schaer, *Abstr.*, 1903, ii, 344).—The blood stain is extracted for twenty-four hours with 1 c.c. of concentrated ammonia, the ammonia is allowed to evaporate, and the residue is dissolved in 3—4 c.c. of water. After concentration and acidification with 2.6 c.c. of a 0.06% solution of citric acid, 1 c.c. of a 0.1% aloin solution and 1 c.c. of oil of turpentine are added. If hæmoglobin is present, a red coloration is produced in ten to fifteen seconds. As in the case of the analogous guaiacum test, citric acid should be added to exclude ferrous compounds, which may produce a coloration similar to that given by hæmoglobin.

G. B.

General and Physical Chemistry.

Index of Refraction of Mixtures of Alcohol and Water.

A. G. DOROSCHEWSKY and S. V. DVORSCHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 101—125).—The experiments were carried out in a similar manner to those of Wagner and Schultze (*Abstr.*, 1907, ii, 821), although quite independently, and it is pointed out that the results of these investigators are vitiated by the employment of an inaccurate method of reading the temperature. Tables and curves are given showing (1) the change in refractive index for 1° rise in temperature for various compositions. (2) The change in this quantity with change in composition. (3) The refractive index of various mixtures at certain temperatures as observed, and also as calculated from the results of experiment. Employing the values of the refractive indices obtained by experiment, the composition of the mixtures is calculated by the formulæ $(n-1)/d$, $(n^2-1)/d$, $(n^2-1)/(n^2+2)/d$; the first formula gives the best results, but all three yield fairly satisfactory results for weak solutions of alcohol in water or vice versa, but not for solutions of medium strength. Contrary to Kiegler's statement (*Abstr.*, 1896, ii, 224), it is shown that the addition of water to a concentrated solution of alcohol at first greatly raises the index of refraction, and then the effect diminishes, until at the composition 50% water it is zero, and further addition lowers the index; it is also shown that C in Pulfrich's formula (*Zeitsch. physikal. Chem.*, 1889, 3, 561) $(D-D^1)/D = C.(N^1-N)/N$ is not a constant.

The refractive index method cannot be employed for the accurate determination of the constitution of concentrated solutions of alcohol in water, but for dilute solutions it yields very satisfactory results.

Z. K.

The Swan Spectrum. KARL VON WESENDONK (*Physikal. Zeitsch.*,

1908, 9, 151—154).—The flame of a hydrocarbon burning in an atmosphere of chlorine shows the Swan spectrum, which would indicate that the latter is due to carbon and not to carbon monoxide.

T. E.

Some Infra-red Spectra. W. J. H. MOLL (*Arch. Néerland.*,

1908, [ii], 13, 100—134).—An automatic spectrometer was employed having silvered concave mirrors in place of lenses. The radiation was measured by Rubens' method, using an iron-constantan couple, and an automatic arrangement was employed for making the photographic record of the galvanometer readings. The rotation of the prism being intermittent, the curve on the drum was traced as a series of separate points.

The arc spectra of sodium, potassium, rubidium, and caesium are tabulated and illustrated by curves, the wave-lengths studied being from 0.55μ to 4μ . The spectrum of mercury was examined as far as 10μ , but beyond 1.7μ emission could not be detected. The absorption

bands of atmospheric air were measured by examining the spectrum of a Nernst lamp.
C. H. D.

Ultra-red Emission Spectra of the Alkali [Metals]. A. BERGMANN (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, **6**, 113—130).—By a combination of the phosphorographic and photographic methods, the author has examined the ultra-red emission spectra of the alkali metals. Phosphorescent screens were prepared from zinc sulphide, obtained by dissolving zinc chloride in water, adding excess of ammonia, precipitating with hydrogen sulphide, and heating the dried product to a moderate white heat. The phosphorescent plates were rendered active by exposing them for one or two minutes to an arc light placed on the further side of a cupriammonium sulphate solution or by exposing them for a few seconds to diffused daylight. They were then subjected to the action of the ultra-red radiation for a few minutes, and then immediately brought into contact with photographic plates. After an exposure of about two hours, the plates were developed.

As source of light, an arc lamp was used, the carbons being axially perforated and filled with the anhydrous chlorides of the alkali metals. The objectives of the collimator and of the camera were specially designed to enable measurements of wave-lengths up to $2000\mu\mu$ to be effected.

Spectral lines in the ultra-red region were obtained as follows, the numbers representing wave-lengths in terms of $\mu\mu$: sodium, 1144.4; potassium, 1177.6 and 1249.4; rubidium, 1322.9, 1344.2, and 1366.8; caesium, 1359.0
H. M. D.

Spectrum of Magnesium and of the so-called Magnesium Hydride, as Obtained by Spark Discharges under Reduced Pressure. E. E. BROOKS (*Proc. Roy. Soc.*, 1908, **80**, *A*, 218—228).—The spark spectrum of magnesium in hydrogen shows among other features a complex system of bands and flutings extending over a considerable part of the visible spectrum (compare Liveing and Dewar, *Abstr.*, 1881, 957; 1882, 254, 255; 1883, 2; 1889, 89), and these lines and flutings have been provisionally ascribed to the presence of magnesium hydride. The author has investigated the spectra obtained with magnesium electrodes in hydrogen and other gases under reduced pressure, but has not succeeded in elucidating the origin of the so-called hydride spectrum.

Discharges of high frequency (with Leyden jars) and of low frequency with alternating currents have been used, and the results are described in detail. In certain circumstances, with the high frequency discharge, the tube is filled with a green flame, the so-called high frequency flame, the current being then carried by magnesium ions. The hydride spectrum appears always to be obtained with the high frequency flame in hydrogen, even when the gas is dried with phosphoric oxide, but is not obtained with other gases in the absence of water vapour. In the low frequency flame, however, the hydride spectrum is not obtained in perfectly dry hydrogen, although under

the same conditions, in the presence of water vapour, it shows distinctly.

The spark spectrum of magnesium in air, nitrogen, and other gases has also been investigated.

In a note appended to the paper, it is mentioned that Fowler has recently observed the "hydride" bands and flutings in the spectra of sun-spots.
G. S.

Zeeman Effect for the Helium Linés. WILHELM LOHMANN (*Physikal. Zeitsch.*, 1908, 9, 145—148. Compare this vol., ii, 152).—All the lines of the helium spectrum are converted into triplets when the glowing gas is placed in a magnetic field and examined at right angles to the lines of force. The distance between the side lines divided by the wave-length squared is the same for all the lines. This is the simplest case foreseen by Lorenz's theory, and it has not been observed in any other substance; it indicates a very simple structure for the helium atom.
T. E.

The Arc Spectrum of Cerium. ARTUR BAKOWSKI (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 73—100).—Five cerium preparations, purified by different methods, were found to give identical spectra. A complete table of the lines in the arc spectrum of cerium from λ 2576 to λ 5003 is given, together with identifications of a large number of lines with lines in the solar spectrum.
C. H. D.

Some Phosphorescent Spectra. HENRI BECQUEREL (*Compt. rend.*, 1908, 146, 440—446).—A comparison of the phosphorescent spectra of two specimens of fluorspar (chlorophane and a fluorspar from Titlis) shows that, whilst the two spectra have bands in common, these are not the most characteristic bands in either spectra, but the flame spectrum of fluorspar from any source is always the same. In view of these facts, the author is of opinion that the bands cannot be wholly attributed to the presence of rare earths as stated by Urbain (Abstr., 1907, ii, 3). The phosphorescent spectra of apatite and scheelite are almost identical, and it would appear, therefore, that neither the phosphorus in the one nor the tungsten in the other mineral plays any part in the phosphorescent phenomenon, which is due to the constituents common to the two minerals, namely, the calcium and the rare earths.
M. A. W.

Absorption Spectra of the Vapours of Benzene and its Homologues at Different Temperatures and Pressures, and also of Solutions of Benzene. W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1908, 80, A, 162—165. Compare Friederichs, Abstr., 1905, ii, 782).—Variations in the vapour-spectra of benzene at different temperatures and pressures are due to the fact that there are two kinds of absorption: (a) general absorption (due to encounters between the molecules), which is broadened and extended towards the less refrangible rays by rise of temperature; (b) selective absorption (due to atomic vibrations), which includes all the individual bands and groups of bands which are not widened or displaced by rise of temperature. The selective absorption can be studied most advantageously by raising the general absorption

to a maximum (at 100°) and studying the spectra produced by reduction of pressure.

The bands of the benzene spectrum between 12.7° and 25° may be resolved into four spectra which partially overlap; two are composed of strong bands, of which there are 54 (27 in each spectrum), and the other two of about 30 weak bands. The intensities of the bands are much the same at 100° and at lower temperatures. The similar groups of bands in the spectra of benzene and its homologues show that the mode of vibration within the nucleus is not greatly affected by the side-chain substitution. The influence of the position of the substituted hydrogens on the number and position of the bands in the spectra of its homologues is clearly shown.

The relationships between vapour-spectra and solution-spectra are discussed. It is shown that up to nine bands may be recognised in the solution spectra of benzene, six of which are similarly constituted, and four of these are almost exactly similar in all respects. These four correspond with the four groups of vapour-bands already mentioned, and occur where these bands overlap to the greatest extent. The view of Baly and Collie (*Trans.*, 1905, 87, 1332) that benzene has seven and no more than seven solution-bands is shown to be incompatible with the facts.
G. S.

Absorption Spectra of Collidine and Nonachlorocollidine. JOHN E. PURVIS and W. H. FOSTER (*Proc. Camb. Phil. Soc.*, 1908, 14, 381—384).—The character of the absorption band of collidine is similar to that of pyridine (Hartley, *Trans.*, 1885, 47, 685) and of lutidine (Baker and Baly, *Trans.*, 1907, 91, 1122), except that it is moved a little more towards the red end of the spectrum. In the case of nonachlorocollidine, there is a much greater shift towards the red end, and also a slight decrease in the persistence of the band. From this the conclusion is drawn that the nine chlorine atoms have replaced the nine atoms of hydrogen in the methyl groups, and have not entered the nucleus.
P. H.

Anomalous Magnetic Rotary Dispersion of Neodymium. ROBERT W. WOOD (*Physikal. Zeitsch.*, 1908, 9, 148—151).—In general, the magnetic rotation of the plane of polarisation is greater for short wave-lengths than for longer ones. For neodymium nitrate, however, the rotation is smallest in the blue, it increases gradually in the green, and then very rapidly as the absorption band in the yellow is approached. No marked increase or decrease on the red side of the band could be observed. The anomaly is thus the same as that observed at the *D* lines in sodium vapour.
T. E.

Does Beer's Law Hold for Colloidal Solutions? OSCARRE SCARPA (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, Supt. II, 50—52).—The dependence of the absorption of light on the concentration and the thickness of the solution has been examined in the case of colloidal solutions of platinum, silver, nickel, cobalt, and copper prepared by the electrical method. Deviations from Beer's law amounting to 10% were observed.

With increasing dilution, the absorption in the violet region diminishes in all cases, whereas in some cases the effect of dilution is to increase the absorption at the red end of the spectrum. Chemically-prepared colloidal solutions of ferric hydroxide, basic ferric acetate, arsenious sulphide and silver, obtained according to Schneider's method by reduction of silver nitrate, also exhibited deviations from the requirements of Beer's law, accompanied by increased absorption in the violet region as the dilution of the solutions was increased.

H. M. D.

The Reduction [of the Photographic Image] with Persulphate and according to Farmer. JOHANNES PINNOW (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 130—135).—The mode of action of ammonium persulphate as a photographic reducing [weakening] agent has been examined. The change of colour from black to a brownish-black, which is sometimes observed on treatment with ammonium persulphate, is evidence of the formation of a new solid substance. This is shown to contain sulphuric acid, and the author supposes that the substance is either silver sulphate or a compound of this with gelatin. The reducing action of persulphate is accelerated by silver salts, a fact which is utilised to explain the mode of action of the persulphate. Two different views are suggested. According to the first, reaction takes place between the finely-divided silver and the persulphate, as represented by the equations: $(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{Ag} = \text{Ag}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$; $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Ag}_2\text{SO}_4 + 2\text{H}_2\text{O} = 2\text{AgO} + (\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$. The silver peroxide then reacts with a further quantity of silver and sulphuric acid to give silver sulphate, which decomposes further persulphate according to the second equation.

According to the second view, the small amounts of Caro's acid which are present in the persulphate are supposed to play a part. The liberation of ozone from Caro's acid takes place very rapidly in presence of silver salts which act catalytically. The formation of silver sulphate, according to the first equation, furnishes the requisite catalytic agent, and the ozone liberated reacts with silver to form peroxide, which, with the finely-divided silver and sulphuric acid, yields a further quantity of the sulphate, and thus the reaction progresses with gradually increasing velocity. The catalytic activity of the silver salts explains the difficulty of obtaining good results when ordinary tap-water is used in reducing by means of persulphate. The formation of silver salts must be prevented by using chlorine-free distilled water.

H. M. D.

What is Radium? The Composition of Metals Calculated and Established. R. FAUST (*Chem. Zentr.*, 1907, ii, 1963; from a pamphlet, *Dresden*, 1907, 1—15).—A theoretical paper, in which the conclusions of Ramsay (*Trans.*, 1907, 91, 1593) are criticised, and the suggestion put forward that the alkali metals are composed of a metal with radium emanation, the latter having a negative atomic weight (-88.5). An example given is $(\frac{1}{2}\text{Cu})_4\text{Ra} = \text{K} = 39$.

J. V. E.

Phosphorescence Produced by Canal Rays. JOHN TROWBRIDGE (*Amer. J. Sci.*, 1908, 25, 141—142).—When canal rays fall on lithium chloride, a red phosphorescence is produced, whereas cathode rays usually give a faint blue colour. The author shows that this difference is due to the greater energy contained in the canal rays, for a cathode stream, if sufficiently intense, induces the red phosphorescence. In order to obtain this result, the cathode stream is concentrated to a focus on the lithium chloride by passing it through the longitudinal magnetic field produced by a solenoid. R. J. C.

The Radioactivity of Sea-Water. JOHN JOLY (*Phil. Mag.*, 1908, [vi], 15, 385—393. Compare Strutt, *Abstr.*, 1906, ii, 716).—The author has measured the radioactivity of sea-water taken from different parts of the Atlantic and also from the Arabian Sea. The emanation was usually distilled off and estimated by the electroscopic method. It was found that trustworthy results could be obtained when the water was acidified with a few c.c. of purified hydrochloric acid per litre in order to liberate the emanation from suspended particles and to prevent the formation of a precipitate during boiling.

The average activity of four samples collected off the West of Ireland and one from the Isle of Man was equivalent to 0.0344×10^{-12} grams of radium per gram of water. A sample from the Arabian Sea gave 0.0278×10^{-12} , and five samples collected between Madeira and the Bay of Biscay gave the value 0.0172×10^{-12} grams radium per gram, whereas Eve (*Phil. Mag.*, 1907, [vi], 13, 248) obtained only 0.0003×10^{-12} grams of radium per gram of water from mid-Atlantic.

These figures point to an increase in radioactive material near the land. The author supposes that much of the radioactive matter reaches the sea in very fine suspension, and ultimately finds its way into the sediments everywhere collecting. R. J. C.

The Lithium in Radioactive Minerals. Mlle. ELLEN GLEDITSCH (*Compt. rend.*, 1908, 146, 331—333).—In continuation of her investigation of radioactive minerals for the presence of copper and lithium (this vol., ii, 9), the author has estimated the copper (as cuprous sulphide) and the lithium (by spectroscopic comparison of the residues remaining after the elimination of all the other metals, except those of the alkalis, with artificial mixtures of sodium and lithium chloride) in some radioactive minerals, and has obtained the following results:

	Copper.	Lithium.	Radioactivity compared with uranium.
Joachimsthal pitchblende	1.2%	0.00017%	1.5
Colorado pitchblende	0.15%	0.00034%	1.75
Carnotite	0.15%	0.030%	0.52
Chalcolite (from Cornwall)	6.54%	0.00011%	2.0
Autunite	0	0.00083%	1.48
Thorite	trace	0.0033%	0.59

The gangue accompanying the chalcolite contained 0.012%, and that with the autunite, 0.0033%, of lithium. It is to be noted that carnotite contains much lithium with but little copper, whilst the reverse is the

case in thorite. Autunite, like gummite (McCoy, *Nature*, Nov. 28th, 1907), contains lithium, but no copper. In the latter cases, the copper may have been transformed into lithium, but this is not very probable, since chalcolite contains so much copper and very little lithium. Owing to the sensitiveness of the spectroscopic reaction of lithium, it is difficult in some cases to determine whether this metal is present in the mineral itself or in the accompanying gangue. The results, whilst not invalidating Ramsay's theory (*Trans.*, 1907, 91, 1593), are not favourable to it; they prove that no simple relation exists between the copper and lithium in radioactive minerals. E. H.

Lithium in Radioactive Minerals. SIR WILLIAM RAMSAY and ALEXANDER CAMERON (*Compt. rend.*, 1908, 146, 456—457).—The detection of lithium in certain radioactive minerals has not the exclusive significance attributed to it by McCoy (*Nature*, Nov. 28th, 1907) and by Mlle. Gleditsch (this vol., ii, 9, and preceding abstract). The authors have shown (*Trans.*, 1907, 91, 1593) that lithium is one of the products of the action of radium emanation on copper salts, but it is probable that other alkali metals are also produced, as the alkali residue obtained from the salt after treatment with radium emanation was greater than before, and a spectroscopic examination showed the presence of both sodium and potassium; experiments now in progress involving the use of silica vessels will decide whether the presence of these metals in the residue is due to the use of glass vessels.

The proportions of the degradation products appear to depend on conditions at present unknown, for, whilst helium is the ordinary degradation product of radium emanation, neon is formed in the presence of water, and argon in the presence of a copper salt.

M. A. W.

Scattering of β -Rays from Uranium by Matter. J. ARNOLD CROWTHER (*Proc. Roy. Soc.*, 1908, 80, A, 186—206).—The scattering of the β -rays from uranium by matter has been investigated by comparing the intensity of a parallel pencil of the radiation traversing a fixed cross-section when a thin plate is interposed between the source and the cross-section at some distance from the latter with that in the absence of the plate. Very thin plates of mica, aluminium, copper, silver, and gold were used. As the source of the rays, uranium-X was employed.

β -Rays are completely scattered in a thickness of material much less than that required to absorb them; scattering is complete after they have traversed a thickness of material varying from 0.015 cm. for aluminium to 0.0002 cm. for gold. The scattering, after correcting for absorption, may be represented by an equation of the form $I/I_0 = e^{-\sigma d}$, where d is the thickness of material traversed, σ is the coefficient of scattering, and I_0 and I are the respective intensities of the radiation passing the cross-section referred to above, in the absence and presence of the thin plate.

The ratio of the coefficient of scattering to the coefficient of absorption (*Abstr.*, 1906, ii, 720) is approximately constant for all the substances examined, its average value being about 13. G. S.

Presence of Thorium in the Soil at Rome. GIAN A. BLANC (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 101—106).—By collecting, on a negatively charged metallic wire, the whole of the thorium products A, B, and C resulting from the thorium emanation liberated from a definite area of the soil at Rome under normal conditions and determining the rate of discharge of a sensitive electroscope under the influence of the wire, the author finds that the soil contains a quantity of thorium capable of generating the same emanation as it would do if it contained 0.00166% of thorium hydroxide. If the thorium is present in the soil in a form other than hydroxide, the proportion of thorium compound must be considerably greater than that given above. T. H. P.

Wehnelt Cathode in High Vacuum. J. E. LILIENFELD (*Physikal. Zeitsch.*, 1908, 9, 193).—The author takes exception to the opinion of Soddy (this vol., ii, 81) that the Wehnelt cathode ceases to be active at very high degrees of exhaustion. The phenomena observed in highly exhausted discharge tubes are due to the large increase in the fall of potential of the positive column, which is independent of the nature of the electrodes, as the author has shown in experiments published previously. H. M. D.

Aluminium in the Potential Series. JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1908, 5, 124—127).—Polemical. A reply to van Deventer and van Lummel (this vol., ii, 12). A. J. W.

Electro-chemistry of Lead. ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1907, 2, 199—213).—The object of the research is to determine the affinity of the change $\text{Pb}^{++++} \rightleftharpoons \text{Pb}^{++} + 2F$, which (at 25°) is expressed in volts by $e = P + 0.0591/n \log_{10} [\text{Pb}^{++++}]/[\text{Pb}^{++}]$, where P is a constant which is characteristic of the reaction, and the bracketed quantities are the concentrations of the quadri- and bi-valent lead ions in a solution. Suitable solutions were made by saturating nitric acid with lead peroxide. The solubility of lead peroxide in nitric acid (in milligram-molecules per litre) is 5.3*N* acid, 0.104; 7.5*N* acid, 0.415; 9.2*N* acid, 0.8, and 11.5*N* acid, 1.54. The effect of the concentration of the acid on the solubility is given by the expression $[\text{Pb}^{++++}]/[\text{H}^+]^4[\text{H}_2\text{O}]^2 = \text{constant}$, and the values found agree with this; it is therefore probable that the lead dissolves as quadrivalent ions. The potentials of platinum electrodes coated with lead peroxide in nitric acid solutions of quadri- and bi-valent lead ions were measured against a calomel electrode, the diffusion potential being eliminated by means of a strong solution of ammonium nitrate. The mean value of P (referred to the hydrogen electrode) found is 1.83 volts, assuming in the calculation that the ionic concentrations vary in the same way as those of the total lead salts dissolved. Measurements of concentration cells containing lead electrodes in solutions of lead nitrate in nitric acid show that this assumption is not true for the bivalent ions, especially in the more concentrated acids.

The solubility of lead nitrate in nitric acid at 25° is found to be

(gram-mols. per litre) in water, 1.62; in 2.02*N* acid, 0.536; in 4.64*N* acid, 0.185; in 8.77*N* acid, 0.042, and in 14.35*N* acid, 0.0017.

The effect on the ionisation of a 0.1 molar solution of lead nitrate of the addition of alkali nitrates was investigated by means of concentration cells. Equal quantities of sodium, potassium, and ammonium nitrates diminish the ionisation to very different extents. Lead nitrate is less soluble in nitric acid or sodium nitrate than it is in water, but more soluble in potassium nitrate, showing that complex ions are formed; hence no information about the dissociation in nitric acid can be obtained from experiments with alkali nitrates.

A few measurements of the concentration of plumbous ions in alkaline solution were made, and the solubility of lead monoxide in water was found to be 3.8×10^{-6} gram-mols. per litre. T. E

Measurement of Electrode Potentials. WLADIMIR KISTIAKOWSKY (*Zeitsch. Elektrochem.*, 1908, 14, 113—121).—The potential difference between a metal and a solution is affected by the quantity of oxygen dissolved in the latter. The author has observed as much as 0.2 volt difference between a copper electrode touching the surface of a solution of potassium cyanide and one dipping under the surface; hence it is better to eliminate oxygen by working in a closed apparatus. The effect of local galvanic actions between different parts of the electrode surface is avoided by polishing the surface and examining it microscopically for inequalities, and by rotating the electrode rapidly and measuring the *E.M.F.* during and after the rotation; the two measurements should give the same result. A number of examples are given in which electrodes of zinc and magnesium are used.

T. E.

Anomalous Anodic Polarisation by Nitric Acid. H. W. HUGO SCHELLHAASS (*Zeitsch. Elektrochem.*, 1908, 14, 121—127).—The anode potential at a platinum anode and the yield of active oxygen are measured in mixtures of sulphuric and nitric acids. The anode potential is a maximum in a mixture of 70 mols. sulphuric acid and 30 mols. nitric acid of normal strength; in 4*N* acid the maximum is at 90 mols. H_2SO_4 , and in 10*N* acid at about 98 mols. H_2SO_4 . These results are true for a current density of 0.05 ampere per sq. cm.; at higher current densities the maximum is much closer to the sulphuric acid end of the curve. The quantity of oxygen fixed at the anode rises and falls with the anode potential. Even in pure nitric acid some oxygen is fixed, which may be due to the formation of a pernitric acid.

T. E.

Thermodynamics of Cells with Solid Substances. RICHARD LORENZ and M. KATAYAMA (*Zeitsch. physikal. Chem.*, 1908, 62, 119—128).—A theoretical supplement to Katayama's experimental work (this vol., ii, 145). It is shown that the Gibbs-Helmholtz formula is applicable to the cells which were investigated. J. C. P.

Alkali Double Salts of Cadmium Chloride. EUGEN VON BIRON and B. P. APHANASSIEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 70—78).—With the view of determining whether the rôle of the alkali halides in the formation of double salts is merely the furnishing of

halogen ions by their dissociation, concentration cells of the type $\text{Ag}|\text{AgCl}|N/1\text{MCl}|\text{sat. MCl}|N/1\text{MCdCl}_3|\text{AgCl}|\text{Ag}$ have been investigated (where M equals an alkali metal).

The concentration of Cl' ions is the same for potassium and ammonium, since the degree of dissociation of potassium and ammonium chloride is the same at both concentrations, $N/1$ and $N/2$, but the lowering of concentration of Cl' , taking place partly owing to the formation of CdCl_3' , is greater for KCdCl_3 than for NH_4CdCl_3 ; it is thus evident that the elementary dissociation of the alkali salts is not the only cause of the formation of double salts in solution, the process being probably far more complex.

If $\delta_1\delta_2$ = lowering of concentration of Cl' for solutions $N/1\text{MCl} + N/1\text{CdCl}_2$ and $N/1\text{MCl} + N/2\text{CdCl}_2$ respectively, then for potassium and ammonium $\delta_2 > \delta_1/2$, but for lithium and sodium, which form most probably the salts M_2CdCl_4 or $\text{M}_3\text{Cd}_2\text{Cl}_7$, $\delta_2 < \delta_1/2$. Z. K.

Concentration Cells. II. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 79—92. Compare this vol., ii, 145).—When working with cadmium electrodes, a white or grey deposit is always obtained, which, on examination, proves to be an oxychloride of cadmium mixed with a little metallic cadmium. The formation of this layer can only be avoided when the air is wholly removed from the reacting solution and vessel, but in that case there seems to occur a slight distillation of the cadmium, which appears as thin layers here and there on the surface of the cathode.

Experiments were made with electrodes which had been (1) untreated, (2) polished, (3) polished more thoroughly, with the following results. (a) Electrodes of equal surface display a greater difference when they have been variously treated than when they have undergone the same treatment. (b) In $N/1$ or more concentrated solutions, the more highly polished electrode always forms the + pole of the element. (c) With removal of air, the difference between the electrodes diminishes, but the more polished electrode becomes the cathode even in very dilute solutions. (d) The difference in potential diminishes with time, and the more rapidly the more thoroughly evacuated the solution. In any case, this difference is more marked for dilute than for concentrated solutions, and cannot be overcome even by vigorous stirring.

From these and other experiments in a specially constructed vacuum apparatus, the conclusion is drawn that cadmium forms good electrodes only in a vacuum, that the electrodes should always undergo the same treatment, and that all the anomalies observed by various investigators when working with cadmium electrodes are due to the formation of cadmium oxychloride by the interaction of the enclosed air and the cadmium chloride solution. Z. K.

A Silver Micro-voltameter. EMIL BOSE and F. CONRAT (*Zeitsch. Elektrochem.*, 1908, 14, 86—88).—The silver nitrate solution is contained in a U-tube, one limb of which contains the anode, consisting of a small piece of silver fused to the end of a platinum wire, and the other limb the cathode, This is a piece of platinum wire 0.05 to

0.1 mm. diameter and 1.5 to 2.5 cm long, which is hung on a platinum hook so that it dips into the solution about 1 cm. It is weighed on a Nernst micro-balance. The currents used varied from about 0.003 to 0.1 milliampere, and the quantities of silver deposited from 0.5 to 2 mg., the accuracy being 0.25 to 0.5%.

Experiments in which the electrolyte was a solution of silver nitrate, treated with excess of metallic silver at 95°, gave deposits about 2% heavier than those obtained from a cold solution with the same current. This result is attributed to the presence of Ag_2^+ ions, which would also explain the irregularities of the silver voltameter. T. E.

Electrical Conductivity and Internal Friction. N. LEMCKE (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1134—1138).—In order to determine whether the regularities regarding the internal friction of sodium chloride solutions were also applicable to other salts, glycerol and aqueous solutions of potassium chloride and bromide were examined by the method employed previously (Pissarjewsky and Lemcke, *Abstr.*, 1905, ii, 684), with the following results: (1) the degree of dissociation of potassium chloride is greater in a mixture of glycerol and water than in pure water. (2) $k = \mu_\infty \cdot \eta_\infty$ = about 151 both for potassium chloride and bromide, and is independent of the solvent. (3) As in the case of sodium chloride so with potassium chloride, the internal friction changes periodically with the increase in volume of the solvent. Z. K.

Electrical Conductivity in Mixtures of Acid or Base and Water. G. BOIZARD (*Ann. Chim. Phys.*, 1908, [viii], 13, 289—361. Compare *Abstr.*, 1906, ii, 419).—The paper commences with a résumé of the work done on this subject during the past twenty years. This is followed by a detailed description of the two methods of measurement employed; (1) Lippmann's (*Compt. rend.*, 1876, 83), modified by Bouty (*Ann. Chim. Phys.*, 1884, [vi], 3), and (2) Kohlrausch's, in which the solution and the solvent to be compared form two arms of the Wheatstone bridge, and by a discussion of their causes of error. The work described in the present paper relates only to sulphuric acid as a solvent and ammonium, sodium, potassium, and potassium hydrogen sulphates, acetic acid, and potassium acetate as solutes. The sulphuric acid is used in concentrations of 0.25%, 0.5%, 1%, 2%, 3%, 5%, 10%, 15%, 20%, 30%, 45%, 60%, 73%, 84.5%, 88%, 92%, 97.5%, and 100%. The ratios (l) of the differences between the conductivities of solutions of the above salts at varying concentrations in these solvents and the conductivities of the solvents, compared with the latter are given in tabular form, and also plotted against the concentrations in gram-molecules per litre (m) of solution, in the form of curves. The latter are shown to be of five distinct types. The results show that for all the above salts there are two concentrations of sulphuric acid, one very high and the other very low, between which addition of the salt lowers the conductivity of the acid. At concentrations of sulphuric acid above the higher and below the lesser of these limits, addition of solute has the normal effect of increasing the conductivity. The curves show that in 0.25%, 0.5%, and 1% acids, Bouty's law (compare *Abstr.*, 1884,

881, 1241; 1886, 653, 839; 1887, 758, 877, 882) holds for ammonium and potassium sulphates at concentrations up to half a gram-molecule per litre, and, if allowance is made for the water set free by secondary changes of other salts, the conclusion is drawn that the law holds generally for sulphuric acid as a solvent, considering always the acid of minimum conductivity. In many cases, it is observed that the solutions in acid are better conductors than the aqueous solutions of the same salts, showing that sulphuric acid is a more highly dissociating solvent than water. The conductivity of 20% acid is not altered by addition of potassium hydrogen sulphate at concentrations up to a half gram-molecule per litre; the same phenomenon is observed with the sodium salt in 15% acid. In acids of concentrations from 20 to 90%, the molecular variation of the conductivity of ammonium sulphate remains constant at concentrations up to 1 gram-molecule per litre. Determinations of the solubility of this salt in sulphuric acid of varying strengths show that 60% acid has the least dissolving power. Similarly, sodium and potassium sulphate have a minimum solubility in 60% acid. The ratio l varies slightly with the temperature according to the equation $l_t = l_{18}[1 + k(t - 18)]$, k being positive or negative, and generally independent of the concentration. A table of the observed values of k for different salts is given.

In the case of solutions, which according to their concentration are at first less and then more highly conducting than the solvent, in the neighbourhood of the concentration of equal conductivity, the temperature effect is to change the sign of the variation of conductivity. But at very high or very low concentrations, rise in temperature produces an increase in the variation. In the case of the acid sulphates and acetic acid, k is negative for all the solvents studied. At high temperatures, the temperature effect for ammonium sulphate tends towards zero.

The author finds that an acid more nearly 100% than that indicated either by Kohlrausch (Abstr., 1883, 413, 769) or by Knietsch has the minimum conductivity 70.6×10^{-4} , instead of the value 80×10^{-4} given by Kohlrausch.

E. H.

Electrolysis of Solutions of Pure Hydrogen Chloride. EMMANUEL DOUMER (*Compt. rend.*, 1908, 146, 329—331).—During the electrolysis of hydrochloric acid, pure hydrogen is collected at the cathode, but the chlorine collected simultaneously at the anode is never pure, being always mixed with varying quantities of oxygen. The volume of oxygen evolved varies with the strength of the solution, increasing considerably as the concentration of hydrogen chloride diminishes. In a series of experiments in which solutions of hydrogen chloride, containing 14.5—0.72 grams per litre, were electrolysed between platinum wires 0.5 mm. thick and 6 cm. long by currents of about the same intensity in each case, the ratio (v/V) of the volume of oxygen (v) to that of the hydrogen (V) evolved, increased from 0.034 to 0.212. To determine whether the oxygen is formed by the action of the nascent chlorine on the water, or from actual electrolysis of the water, an experiment was made, using a silver anode to combine with the chlorine set free. In this case, a larger volume of oxygen was

produced, from which it is deduced that the latter explanation is correct. The deficit of oxygen with the platinum anode is probably due to the formation of oxides of chlorine. If all the oxygen evolved could be measured, the ratio of the number of ions produced from the water to the total number of ions could be determined. The conclusion is drawn that, in the electrolysis of hydrochloric acid, part of the current is used in decomposing the water, and it is therefore necessary to take this into account when determining the transport numbers of H^+ and Cl^- , or the conductivity of hydrogen chloride solutions. E. H.

Strong Electrolytes. ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1907, 2, 213—221).—In order to eliminate the potential difference at the contact of two dissimilar solutions, a strong solution of potassium chloride has been interposed between the solutions. The author studies the effect of solutions of potassium and ammonium nitrates. A 10*N* solution of the latter salt completely eliminates the diffusion potential between solutions of hydrochloric acid and of lithium chloride. A saturated solution of potassium nitrate is not sufficiently concentrated to do so. Solutions of salts the ions of which have very different mobilities are quite ineffective, as the theory requires.

The above result was applied to the measurement of the *E.M.F.*'s of cells containing silver electrodes in solutions of silver nitrate directly connected or separated by a 10*N* solution of ammonium nitrate. Using *N*/10 and *N*/100 silver nitrate directly connected, the *E.M.F.* is 0.0590 volt, whilst when connected through ammonium nitrate it is 0.0556; the difference between these numbers is the eliminated diffusion potential, which is calculated from Nernst's formula to be 0.0033 volt, in close agreement with the experimental result. The *E.M.F.* of the concentration cell, apart from the diffusion potential, may be calculated from the ratio of the concentrations of the silver ions in the two solutions; taking the conductivities as a measure of these concentrations, the *E.M.F.* comes out at 0.0557 volt. In a similar way, the author finds for 0.01*N* and 0.001*N* solutions the *E.M.F.* to be 0.0579 volt (0.0580 calculated), and for 0.1*N* and 0.5*N* solutions 0.029 volt (0.0292 calculated). He considers that conductivity is a true measure of ionisation. T. E.

Decomposition Curves of Lithium Chloride in Pyridine and in Acetone. The Effect of Water. HARRISON E. PATTEN and WILLIAM R. MOTT (*J. Physical Chem.*, 1908, 12, 49—74. Compare *Abstr.*, 1904, ii, 379).—Lithium can be deposited on a smooth platinum cathode at 25° from an anhydrous saturated solution of its chloride in pyridine or in acetone at a current density of 0.001 amp./cm². The cathode polarisation due to deposited lithium is +2.60 volts both in pyridine and in acetone, as compared with about 2.45 volts for water ("absolute" potentials according to Ostwald), although the heats of solution of the chloride in the respective solvents are very different, being equivalent to 0.254, 0.371, and 0.613 volt in acetone, water,

and pyridine respectively. The total polarisation of the cell is about 4 volts in pyridine and 4.15 volts in acetone.

When a little water is added to the solution of lithium chloride in pyridine, the current rapidly diminishes almost to zero, owing to the formation of an insulating film on the cathode.

The effect on the conductivity of the gradual addition of water and lithium chloride respectively to pyridine has been determined. For solutions containing more than 0.5% of lithium chloride, the increase of specific conductivity with further increase in the proportion of salt is very slow. The conductivity of a pyridine solution of lithium chloride is greatly increased at first by adding a little water, 0.5% of the latter doubling the conductivity of a $N/3$ solution of the chloride; the effect of adding water to the acetone solution is much less.

The current efficiency (estimated by measuring the gas liberated at the cathode) for the deposition of lithium from a pyridine solution at a current density of 0.1 amp./cm.² is 23.3%; from an acetone solution at a current density of 0.001 amp./cm.², 38.5%, and from an amyl alcohol solution at a current density of 0.0012 amp./cm.², 44.8%. G. S.

Validity of Faraday's Law in the Electrolysis of Hot Porcelain. FRITZ HABER [with A. RIEFF and P. VOGT] (*Zeitsch. anorg. Chem.*, 1908, 57, 154—173. Compare Abstr., 1907, ii, 6, 66 67).—As electrolyte, unglazed porcelain (a Rose's crucible) was used. The current was conveyed by graphite rods dipping in melted tin, the latter making contact both outside and inside with the crucible, the tin inside the crucible forming the cathode. The *E.M.F.* was so adjusted that 3—4.5 milliamperes per sq. cm. passed from the anode to the cathode tin through the crucible at the lower temperatures, and the current was measured with a silver voltmeter. The whole arrangement was kept at an approximately constant temperature (at intervals between 800° and 1250°) in an electric furnace, access of oxygen to the cathode compartment being carefully prevented. After the electrolysis, the amounts of different metals which had passed into the cathode tin were determined by analysis. Porcelain is a conductor from 300° upwards.

The cathode compartment was found to contain aluminium (very little at lower temperatures), iron, calcium, magnesium, potassium, and sodium. There is reason to suppose that the conductivity at the lower temperatures is mainly due to alkalis, and that aluminium silicate, the chief constituent of porcelain, becomes to some extent a conductor at higher temperatures. On this view, the relatively large proportions of magnesium and calcium in the cathode liquid are a little surprising, and some evidence has been obtained that the liberated alkali metals react in a secondary manner with the porcelain, liberating magnesium and calcium. The results were checked by analysis of the porcelain before and after electrolysis.

Comparison of the quantity of electricity which passes with the amounts of the different metals liberated in the electrolysis show that, within the limits of experimental error (which is naturally somewhat large), Faraday's law is valid for porcelain as electrolyte.

G. S.

Thermo-electric Power of Lithium and Sodium. ARCIERO BERNINI (*Nuovo Cim.*, 1908, [v], 15, 29—42. Compare Matthiessen, *Ann. Phys. Chem.*, 1858, 103; Naccari and Bellati, *Nuovo Cim.*, 1876).—The author has investigated the thermo-electric properties of lithium and sodium at various temperatures, lead being used as the second metal of the couples used.

In the case of lithium, the constants b and c of Avenarius's formula $e = (t_1 - t)[b + c(t_1 + t)]$ are found to have the mean values 0.00001281 and 0.00000001905 respectively for the temperature interval 10—173°. The temperature of inversion, given by the quotient $-b/c$, is -674.2° , and the neutral point -332.1° . These results, which were obtained by means of a Latimer Clark potentiometer, were very nearly confirmed by measurements made with a Dolezalek electrometer.

Sodium differs from lithium in being negatively thermo-electric towards lead. The values of b and c for sodium are 0.000004339 and 0.0000000113 respectively, these holding, with close approximation, up to temperatures higher than the melting point of sodium; the neutral point is here -192° . Naccari and Bellati (*loc. cit.*) were led to the conclusion that, in the neighbourhood of the melting point of sodium, the course of the curve connecting the *E.M.F.* of the sodium-lead couple with the temperature cannot be well represented by a parabola of the second degree, but the author finds no such irregularity.

Taking the thermo-electric power P as being $b + 2ct$, and $\theta = 273 + t$, the following equations are obtained: $P = 1.26 + 0.04\theta$ for lithium, and $P = -1.63 + 0.028\theta$ for sodium, the results being in microvolts.

T. H. P.

Quantitative Investigations on the Electrical Synthesis of Colloids. II. THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, Supt. II, 39—44).—The influence of changes in the arrangement of the electrical circuit on the production of a colloidal solution of cadmium in ethyl ether has been studied. The extent to which the electrodes are disintegrated and the medium decomposed is the same whether the induction coil is connected directly with the condenser or with the electrodes. The yield of colloid is unchanged whether a mercury or a Wehnelt alternator is used. By altering the constants of the discharge circuit within wide limits, the effect of varying the unsymmetrical distribution of potential was studied, and under all conditions the loss of weight of the two electrodes was found to be the same.

H. M. D.

Relation between the Ignition Temperature and the Vapour Pressure of Inflammable Liquids of Low Boiling Point. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 138—140).—Various fractions of naphtha and of light petroleum have been investigated, and the close dependence of the ignition temperature on the boiling point and vapour pressure of the substance is shown in tabular form.

Z. K.

Modified Bomb Calorimeter. ÉTIENNE RENGADE (*Bull. Soc. chim.*, 1908, [iv], 3, 188—190).—A modified form of Mahler's bomb

calorimeter is described and figured, which is suitable for investigating the heat relations of such actions as the solution of the alkali metals in water.

The wiring arrangement for electric firing of the bomb is done away with, and is replaced by a steel piston passing through a pressure-stopper in the cover of the bomb and terminating (1) outside, in a pulley by means of which the bomb can be rotated in alternate directions, and (2) inside, in a disc, which can be used to break a fragile vessel containing a weighed quantity of the alkali metal. A stoppered outlet in the cover of the bomb is provided for the escape of gases at the end of the operation. A glass rod is placed diagonally inside, so that when the bomb is rotated the liquid is mechanically stirred by the rod. The precautions necessary in using the bomb and the corrections, which must be applied to results obtained by its use, are given.

T. A. H.

The Neutral Alkali and Alkali-earth Carbonates. ROBERT DE FORCRAND (*Compt. rend.*, 1908, 146, 511—515)—The whole of the thermochemical data necessary for comparison with experiments on the decomposition by heat of the alkali and alkali-earth carbonates has not hitherto been known. The thermochemical cycles concerned are: $M_2O(\text{solid}) + CO_2(\text{gas}) = M_2CO_3(\text{solid}) + x$; $M_2CO_3(\text{solid}) + Aq = A$; $M_2O(\text{solid}) + Aq = B$; $CO_2(\text{gas}) + Aq = 5.60 \text{ Cal.}$; $M_2O(\text{diss.}) + CO_2(\text{diss.}) = M_2CO_3(\text{diss.}) + C$ (in all of which M_2 represents two atoms of an alkali, or one atom of an alkali-earth metal). The values of A for sodium and potassium carbonates, of B for lime, and of C for sodium, potassium, calcium, strontium, and barium oxides have long been known. The values of A for calcium, strontium, and barium carbonates are zero; for lithium, rubidium, and caesium carbonates at 15° , the author finds $+3.06$, $+8.75$, and $+11.84 \text{ Cal.}$ respectively. Rengade (*Abstr.*, 1907, ii, 737; this vol., ii, 155) has determined the heats of dissolution (B) of sodium, potassium, rubidium, and caesium oxides; for lithium, strontium, and barium oxides, the author has obtained the values $+31.2$, $+30.8$, and $+35.64 \text{ Cal.}$ respectively, whilst for the heats of neutralisation (by dissolved carbon dioxide) of lithia, rubidium, and caesia, he finds the values $+20.57$, $+20.57$, and $+20.49 \text{ Cal.}$ From these data are calculated the heats of combination of the solid oxides with gaseous carbon dioxide: $(Na_2O, CO_2) + 76.88 \text{ Cal.}$, $(K_2O, CO_2) + 94.26 \text{ Cal.}$, $(Rb_2O, CO_2) + 97.42 \text{ Cal.}$, $(Cs_2O, CO_2) + 97.53 \text{ Cal.}$, $(CaO, CO_2) + 43.3 \text{ Cal.}$ (amorphous) $+ 42.0 \text{ Cal.}$ (calc. spar.) $+ 42.6 \text{ Cal.}$ (aragonite), $(Li_2O, CO_2) + 54.23 \text{ Cal.}$, $(SrO, CO_2) + 57.3 \text{ Cal.}$ (orthorhombic), $(BaO, CO_2) + 63.44 \text{ Cal.}$ The first numbers in the series are not in accordance with Lebeau's results (*Abstr.*, 1903, ii, 477; 1904, ii, 121), according to which caesium carbonate would be more easily dissociated than rubidium carbonate, and the latter more so than potassium carbonate. From the author's general relation $Q/T = 30$, the temperatures of dissociation are calculated to be calcium carbonate (aragonite) $+1160^\circ$, lithium carbonate, 1535° , strontium carbonate (orthorhombic), 1637° , and barium carbonate, 1842° , although the relation is not rigorously applicable, since the carbonates fuse below these temperatures. Experimentally, it is known that lithium carbonate loses all its carbon dioxide at 800°

in a current of hydrogen; Zavrieff (Abstr., 1907, ii, 768) has found the temperature 910° for the dissociation of calcium carbonate, and Herzfeld and Stiepel have found 1250° for strontium carbonate and 1450° (approx.) for barium carbonate. The author considers that the discrepancies between the calculated temperatures are explained by a decrease in the heats of formation of the carbonates at high temperatures. In support of this, a concordant series of numbers having the mean $+34.76$ Cal. is calculated by application of Clapeyron's formula to Zavrieff's curve between 800° and 900° . With this value for calcium carbonate, and values for lithium, strontium, and barium carbonates, obtained by applying similar reductions to those at the ordinary temperature, the temperatures 886° , 1200° , 1284° , and 1450° are obtained for the dissociation of the several carbonates. These (except that for lithium carbonate) agree with the observed values. E. H.

Heat of Formation of Antimony Hydride. ALFRED STOCK and FRANZ WREDE (*Ber.*, 1908, 41, 540—543).—The earlier determinations of Berthelot and Petit (Abstr., 1889, 666) by decomposing antimony hydride by bromine according to the equation $\text{SbH}_3 + 4\text{Br}_2 = \text{SbBr}_5 + 3\text{HBr}$ cannot be accurate. The gas used contained only a small percentage of the hydride, and the greater portion of the antimony existed as tribromide, so that, in addition to the large amount of gas required, the method involved the knowledge of the heats of formation of hydrogen bromide and antimony tri- and pentabromides, as well as the heat of solution of bromine in potassium bromide. A simpler method was therefore desirable, and this was carried out by decomposing antimony hydride quantitatively into its elements by the electric spark in a stout cylindrical glass vessel of 300 c.c. capacity provided with a capillary tube, in which a small bulb was blown, fitted with platinum wires, and closed with a glass rod. At the other end of the cylinder a bent capillary tube was fused for the admission of the gas. The quantity of gas introduced was 0.8 gram, and a correction was made for the departure from the gas laws (compare Abstr., 1907, ii, 180). The calorimeter contained 4 litres of water, and the temperature was measured by a platinum resistance thermometer. The mean of three determinations gave $\text{Sb}(\text{metal}) + 3\text{H} = \text{SbH}_3 - 33.98$ Cal. at constant pressure and -34.27 Cal. at constant volume. The earlier determinations gave -86.8 Cal., and a comparison of Berthelot's determinations of the heats of formation of the hydrides of phosphorus and arsenic with that of antimony renders their re-investigation a necessity. W. R.

Heat of Vaporisation of Propionic Acid. A. FAUCON (*Compt. rend.*, 1908, 146, 470—473).—Preliminary to the determination of the heat of vaporisation of propionic acid by Berthelot's method, the author has redetermined the corresponding constant in the cases of benzene and formic and acetic acids, with the following results: For benzene, $L = 93.62$ Cal. [Schiiff found 93.40 Cal. (Abstr., 1887, 9); Luginin, 92.97 Cal. (Abstr., 1899, ii, 269); Miss Marshall, 94.4 Cal. (Abstr., 1896, ii, 349)]; for formic acid, $L = 121.03$ Cal. [Favre and

Silbermann, 120·7 Cal.; Miss Marshall, 120·36 Cal. (Abstr., 1896, ii, 589); Raoult, 120·9 Cal.]; and for acetic acid, $L = 97·37$ Cal. [Miss Marshall found 97 Cal. (Abstr., 1896, ii, 349); Raoult, 97·4 Cal.; Favre and Silbermann, 101·9 Cal., and Berthelot, 120·8 Cal.]. The propionic acid employed was purified by repeated crystallisations, and had b. p. $139·8^\circ/761·2$ mm. and m. p. $-19·3^\circ$; the value of df/dt , using Schiff's number, 0·536, for the specific heat (*loc. cit.*), was found to be 23·61 mm., and the heat of vaporisation 90·43 Cal. In common with acetic and formic acids, propionic acid does not obey Trouton's law, the value of MS/T being 16·20 instead of 20·21. M. A. W.

Application of Low Temperatures to Some Chemical Problems: (1) Use of Charcoal in Vapour Density Determinations; (2) Rotatory Power of Organic Substances. SIR JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1908, 80, 4, 229—238).—Barkla and Sadler (Abstr., 1907, ii, 731), on the basis of certain experiments depending on the use of Röntgen rays, have recently suggested that the accepted atomic weight of nickel is much too low. To test this point, the authors have redetermined the density of nickel carbonyl at 0° and low pressures by a method depending on the use of low temperatures and condensation with charcoal.

A vessel, measuring over two litres and surrounded by melting ice, was connected to a manometer and to an absorption tube containing charcoal, which could be detached and weighed. The apparatus was first exhausted by a Fleuss pump, and finally by subsidiary tubes containing charcoal and immersed in liquid air; the vessel was then filled with nickel carbonyl at a definite pressure, and, after equilibrium was attained, the carbonyl was absorbed in the tube for that purpose, immersed in liquid air, the tube being finally removed and weighed. It is shown that the method is fairly accurate.

The density of nickel carbonyl at 0° and 16—47 mm. pressure is 84·67—84·79, in satisfactory accordance with the accepted atomic weight.

The optical rotatory power of certain organic compounds, dissolved in alcohol and in light petroleum, has been measured at very low temperatures in a jacketed metal polarimeter with ends of thick glass, the cooling agent being poured into the space between the tube proper and the outer jacket.

The negative rotation of nicotine in alcohol diminishes regularly with temperature down to -120° , just as it does at temperatures above 0° , and that of bitter orange oil increases regularly down to -95° , also in accordance with its behaviour at higher temperatures. In both cases, the curve showing the relation between rotation and temperature is approximately a straight line, and extrapolation indicates that the rotation in both cases would be considerable at the absolute zero. G. S.

Anomalous Viscosity at the Clearing Point of so-called Crystalline Liquids. EMIL BOSE and F. CONRAT (*Physikal. Zeitsch.*, 1908, 9, 169—173).—The viscosity of anisaldazine is measured

between 170° and 190° . The sample used changed from a turbid to a clear liquid at 182.8° . The viscosity of the turbid liquid diminishes as the temperature rises up to 180° ; it then begins to increase rapidly, reaching a maximum at the clearing temperature; above this temperature the viscosity of the clear liquid diminishes again in the usual way. The change of viscosity in passing from the turbid to the clear liquid is thus not isothermal, but is spread over an interval of two to three degrees. T. E.

Conductivity and Viscosity of Solutions of Certain Salts in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Binary Mixtures of these Solvents. VII. HARRY C. JONES and W. R. VEAZEY (*Zeitsch. physikal. Chem.*, 1908, **61**, 641—697).—The conductivity of cupric chloride in water, methyl alcohol, ethyl alcohol, and in binary mixtures of these solvents has been determined, as also the conductivity of potassium thiocyanate in all the four solvents mentioned in the title and their binary mixtures. The viscosities of these solvents, of their mixtures, and of the potassium thiocyanate solutions have been measured.

In some cases, a minimum of conductivity has been observed; even where a real minimum does not occur, the values found for the conductivity in the mixed solvent are in many cases considerably below the values calculated by the mixture rule. To these cases of virtual minima, as well as to the cases of actual minima, the theory of Jones and Lindsay (see Abstr., 1902, ii, 55; also Jones and Murray, Abstr., 1902, ii, 637; Jones and Veazey, Abstr., 1907, ii, 438) is applied.

A conductivity maximum has been observed for solutions of potassium thiocyanate in mixtures of acetone with methyl and ethyl alcohols, and it is shown that the fluidity also of the mixed solvent is at a maximum at the same composition. The explanation of such conductivity maxima adopted by Jones and Bingham (Abstr., 1906, ii, 66) is extended, and the phenomenon is referred ultimately to an aggregation of the two kinds of solvent molecules.

Whereas the conductivity of cupric chloride is greater than that of potassium thiocyanate at a corresponding concentration in water, the reverse is the case when the solvent is methyl alcohol, ethyl alcohol, or acetone. It is suggested that ternary electrolytes, although yielding three ions in water, dissociate into only two ions in organic solvents.

The temperature-coefficient of conductivity is found to be greatest for those mixtures of water and organic solvent which contain 25% of the latter. It is accordingly supposed that in these mixtures more complex aggregates between the solute and solvent are formed than in any other mixture of the same two liquids.

The conductivity of potassium thiocyanate is higher in acetone than in water; this is shown to be due to the greater fluidity of acetone, and the consequent higher speed of the ions; further, as shown by the difference between the temperature-coefficients of conductivity in the two solvents, the aggregates present in the water solution are much more complex than those in the acetone solution. J. C. P.

Conductivity and Viscosity of Tetraethylammonium Iodide in Water, Methyl Alcohol, Ethyl Alcohol, Nitrobenzene, and Binary Mixtures of these Solvents. VIII. HARRY C. JONES and W. R. VEAZEY (*Zeitsch. physikal. Chem.*, 1908, **62**, 44—58. Compare preceding abstract).—The conductivity of tetraethylammonium iodide in water and methyl alcohol exhibits a minimum for the 50% mixture both at 0° and 25°. A minimum conductivity, not so well marked, is observed also in water and ethyl alcohol. In mixtures of the two alcohols, and in mixtures of nitrobenzene and methyl alcohol, no minimum conductivity is observed, only a slight falling below the values calculated by the mixture rule. Both at 0° and 25°, the conductivity of tetraethylammonium iodide in mixtures of ethyl alcohol and nitrobenzene exhibits a slightly marked maximum, noticeable for all dilutions. A mixture of these two solvents, containing 25% of nitrobenzene, has, both at 0° and 25°, a greater fluidity than either of the constituents.

The various observations recorded in this paper are interpreted on the lines already described (*loc. cit.*).

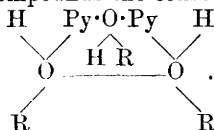
In connexion with viscosity, the authors consider that the very marked influence of slight impurities accounts for the different values found by various observers for the viscosity of a given liquid. J. C. P.

Viscosities of Binary Mixtures of Organic Compounds. Formation of Molecular Compounds in the Liquid State. I. Mixtures of (a) Acetone and Chloroform, and (b) *m*-Cresol with (1) Aniline and (2) *o*-Toluidine. II. Mixtures of Pyridine with (1) Acetic Acid and (2) Butyric Acid. D. E. TSAKALOTOS (*Bull. Soc. chim.*, 1908, [iv], **3**, 234—242, 242—247).—The previous work of Poiseuille (*Ann. Chim. Phys.*, 1843, **50**; 1847, **76**), Graham (*Phil. Trans.*, 1861, **373**), Thorpe and Rodger (*Trans.*, 1897, **71**, **360**), Varenne and Godefroy (*Abstr.*, 1904, **i**, **2**), and Dunstan (*Trans.*, 1907, **91**, **83**, 1728) has shown that viscosity curves of liquid binary mixtures may be (1) *normal* (equal or only slightly below those calculated from the viscosities of the two components), (2) *negative* [much below the calculated, due according to Dunstan (*loc. cit.*) to breaking down of associated molecules of the components], (3) *positive* (much above the calculated) and showing one or more maxima, probably corresponding with the formation of molecular compounds. The object of the present investigation is to use viscosity determinations as a method of investigating the formation of such molecular compounds between liquids.

All the mixtures studied gave positive curves. The figures quoted are molecular concentrations per cent. For the two systems *m*-cresol and aniline and *m*-cresol and *o*-toluidine (at 25°), a maximum occurs at *m*-cresol, 65, and not 50 as might be expected. The deviation is probably due to partial decomposition of the molecular compound in each case. With chloroform and acetone, the curve for "time of flow" at 0° shows a maximum at chloroform, 50, but the maxima of the viscosity curves at 0, 20, and 40 for this mixture are displaced beyond that point. The viscosity curves of mixtures of (1) pyridine

and acetic acid and (2) pyridine and butyric acid show well-marked maxima at acetic acid, 77.9, and butyric acid, 74.4, respectively.

The conclusion is drawn that in the first three mixtures, the compounds formed contain 1 mol. of each component, and in the last two, 2 mols. of pyridine combined with 3 mols. of the acid. The acetone-chloroform compound may have the constitution $\text{CMe}_2\text{:O:CHCl}_3$, and the pyridine-fatty acid compounds the constitution



T. A. H.

Simple Apparatus for Demonstrating the Dissociation Pressure of Solid and Liquid Substances. JAN VON ZAWIDZKI (*Chem. Zeit.*, 1908, 32, 186—187).—A glass tube, 15—18 cm. long and 10 mm. external diameter, closed at one end, is filled to about 1/8 to 1/4 of its length with a substance which readily dissociates, such as $2\text{AgCl}, 3\text{NH}_3$, $\text{CaCl}_2, 4\text{NH}_3$, or $\text{ZnCl}_2, 4\text{NH}_3$; a plug of glass wool is then inserted, and the open end drawn out and fused on to a capillary tube, *b*, 60—70 cm. long and about 2 mm. internal diameter. By means of a very fine, thin-walled capillary tube, a thread of mercury about 1 cm. long is introduced into the capillary tube *b* some 10 cm. from the junction with the large tube, after which the end of the tube *b* is sealed off. The length of the tube between the mercury and the sealed end is divided into divisions, representing pressures of 1, 2, 3, 4, &c., atmospheres in the large tube, by means of small indiarubber rings.

By preparing several tubes containing varying quantities of the same or different substances, it is possible by placing the tubes in an oil-bath to show that the pressure is (1) independent of the quantity of substance taken, and (2) varies with different substances.

W. H. G.

Adsorption Compounds. GUNNER JÖRGENSEN (*Zeitsch. anorg. Chem.*, 1908, 57, 353—358. Compare *Abstr.*, 1902, ii, 26).—The absorptive power of metastannic acid for nitric acid has been investigated by extraction of mixtures of the two acids with successive quantities of water for three or four months at room temperature and at 36°, the removal of the nitric acid been then practically complete. The ratios of the distribution of the nitric acid between the water and metastannic acid are tabulated. Similar experiments have been made with hydrochloric acid.

G. S.

Fibre-like Developed Alumina (Fibre-alumina) and its Surface Actions (Adsorption). HANS WISLICENUS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, Supt. II, 11—20).—In contact with mercury and moist air, aluminium oxidises with the formation of aluminium hydroxide of fibrous character. This resembles in many respects the natural fibres of plants and animals. It is doubly refracting, and, when examined through a plate of gypsum, it shows exactly the same colour distribution as the eccentric portion of a starch granule. The

cause of the double refracting power is to be found in the lamellar structure; the double refraction disappears when the aluminium hydroxide is immersed in water or in xylene. The micro-structure and the optical properties remain unchanged when the hydroxide is converted into oxide by heating.

The fibrous aluminium hydroxide has very strongly developed adsorptive properties. The adsorptive power apparently increases when the hydroxide is converted into oxide, but, if equal molecular quantities are compared, the adsorptive powers are about the same. The adsorptive properties have been studied in detail by experiments with aqueous solutions of a large number of different substances, and comparative measurements have also been made on tannin solutions with other adsorbing materials. From these, it is evident that the adsorptive power of fibrous alumina is approximately equal to that of hide powder, and is much greater than that of other adsorbents, such as kieselguhr, meerschäum, and animal, bone, and wood charcoal.

The removal of substances from solution is shown to be due chiefly to surface action, and not to the formation of chemical compounds; in general, the quantities taken up from concentrated solutions are relatively smaller than the quantities removed from dilute solutions of the adsorbed substance.

An apparatus is described for "adsorption analysis," in which fibrous alumina is used as the active adsorbing material. This may be applied in the examination of all kinds of colloidal extracts, including tannin, plant-, colour-, and drug-extracts. H. M. D.

Changes in Tanning [Processes]. REGINALD O. HERZOG and J. ADLER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, Supt. II, 3—11).—The adsorption of various substances from aqueous solution by lightly chromated hide powder has been investigated. The experiments were made at 25°, 5 grams of hide powder being shaken up with 100 c.c. of the solution for four hours, when the adsorption was found to be complete.

Phenol, catechol, resorcinol, and pyrogallol solutions of various concentrations were used, and for comparison the adsorption of the two first substances by animal charcoal was examined.

The experimental data are discussed in reference to the equation $c = K \cdot a^m$, in which c denotes the concentration of the aqueous solution, a the quantity of substance adsorbed by the hide powder, and K and m are constants. When $\log a$ is plotted as a junction of $\log c$, the experimental data should be represented by a straight line if the above equation is satisfied. This is the case for the adsorption of phenol and catechol by animal charcoal, and of resorcinol and pyrogallol by hide powder, but the data for phenol and catechol adsorbed by hide powder correspond with curves which are convex to the $\log c$ axis.

A study of the influence exerted by mineral substances in $N/10$ solutions on the adsorption of phenol has shown that this is diminished by hydrochloric acid and still more by potassium hydroxide. A smaller, but similar, effect is produced by ammonium chloride, whereas salts of the alkaline-earth metals are without influence, and salts of the alkali metals slightly increase the adsorption.

Measurements of the adsorption of a number of acids, mineral salts, sugars, carbamide, acetone, colloidal substances, and colouring matters are also recorded. In general, the adsorption cannot be at all accurately represented by the equation $c = K.a^m$.

Attempts were made to measure the rate of adsorption of phenol, but the process was found to be too rapid both at 25° and at 0°. The fact, that the adsorption from a 0.025*N* phenol solution was the same as that from a 0.05*N* solution after the hide powder in the second case had been treated with an equal volume of water, is considered to be evidence in favour of a reversible process in the adsorption phenomena.

H. M. D.

Time-law of the Capillary Rise of Liquids and the Relation-ship of Velocity to the Chemical Constitution. WOLFGANG OSTWALD and F. GOPPELSROEDER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, Supt. II, 20—39).—The author finds that the experimental data obtained by F. Goppelsroeder (*Verh. der Naturforsch. Ges. Basel*, 1907, 19) in his investigations of the rate of rise of liquids in filter paper can be represented by the exponential equation $s = K.t^m$, in which s denotes the distance through which the liquid rises in time, t , and K and m are constants depending on the nature of the liquid, the fibrous character of the filter paper, the temperature, and other factors which in comparative experiments may readily be kept constant. The constant K varies from 2.21 to 15.10, and m from 0.04 to 0.49.

The view is put forward that the rate of rise of a liquid is determined by the magnitude of the capillary forces and the viscosity of the liquid. The fact that the values of the maximum capillary rise of different liquids in filter paper are not all proportional to the values obtained in glass tubes, is attributed to differences in the "wetting power" of the various liquids for filter paper, on the one hand, and glass, on the other. In the comparable series of monohydric fatty alcohols, the velocity constants, K , are shown to be related to the viscosity values. Examples of stoichiometric relationships between the values of m and the chemical nature of the various liquids are also quoted.

H. M. D.

The Crystalline State as a General Property of Matter. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 27—64. Compare this vol., ii, 90).—A theoretical résumé is given of the experimental work performed by the author and other investigators on the crystalline and colloidal states of matter.

It is claimed that the conclusions arrived at regarding the discontinuity and crystalline structure of all forms of matter, whether liquid, solid, or gaseous, and the non-existence of amorphous substances, are based on purely experimental evidence.

It is incorrect to say that, since chemically-pure colloids are unknown, therefore they are complexes of the suspended substance with the solvent, for any inorganic colloid can be obtained in a pure state by recrystallisation from a solvent which dissolves it appreciably; on the other hand, any crystalline substance can be obtained in such

minute crystals as to render it difficult to free it from the remnants of water or other matter absorbed by it. Z. K.

Physico-chemical Investigations on Soaps Considered as Colloids. ANDRÉ MAYER, GEORGES SCHAEFFER, and E. F. TERROINE (*Compt. rend.*, 1908, 146, 484—487).—An examination of the optical properties of solutions of soaps of the fatty acid series shows that the acetate, propionate, butyrate, and valerate form homogeneous solutions in acid, alkaline, or neutral aqueous, or in alcoholic alkaline solution; the hexoate, octoate, laurate, palmitate, oleate, and stearate yield colloidal solutions or jellies, according to the complexity of the molecule and the nature of the medium. These colloidal solutions are caused by the hydrolysis of the salts and partial or complete precipitation of the fatty acid.

The viscosity of solutions of the lower members of the series is only slightly altered by the addition of acids, but increased by the addition of bases; but in the case of the hexoate and the higher members of the series, the viscosity of the solution is increased either by the addition of an acid or a base, and the minimum point on the viscosity curve is a critical point coinciding with the first appearance of ultra-microscopical granules in the solution. M. A. W.

The Process of Gelatinisation. IV. S. A. LEVITES (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 237—241; see this vol., ii, 161).—A solution of gelatin in dilute formaldehyde gelatinises, owing to the conversion of the gelatin into an insoluble substance. The change is very slow at low temperatures. Salts of univalent ions and non-electrolytes retard the change about equally; salts of bivalent ions have a greater effect. Hydrogen ions retard the change very much, and hydroxyl ions accelerate it enormously. By prolonged boiling with water, gluten, sodium α -thymus-nucleates, and agar-agar are converted into substances which do not set. The change is accompanied by a diminution of the viscosity of the solution, which is measured and reproduced in curves. T. E.

The Equilibrium $2\text{Au}(\text{metal}) + \text{Au}^{+++} \rightleftharpoons 3\text{Au}^+$. EMIL BOSE (*Zeitsch. Elektrochem.*, 1908, 14, 85—86).—By means of the apparatus described previously (Abstr., 1907, ii, 735), it is shown that the equilibrium in question exists (this had already been proved by Wohlwill, Abstr., 1899, ii, 105), and that it is displaced in the direction of aurous ions by rise of temperature. T. E.

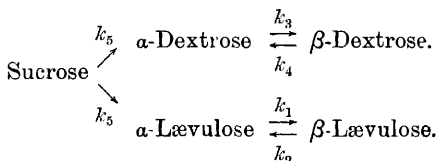
Temperature-coefficients of Ionic Mobilities in Water as a Function of the Mobilities. FRIEDRICH KOHLRAUSCH (*Zeitsch. Elektrochem.*, 1908, 14, 129—133).—The formula proposed by Rasch and Hinrichsen (this vol., ii, 148, 149), $\alpha = A/\log l$, where α is the temperature-coefficient and l the mobility, requires another constant, owing to the fact that l is really the product of a number and the dimensions of the unit of conductivity. If l is expressed in C.G.S. units, the original formula gives impossible results.

By plotting all known temperature-coefficients against the corre-

sponding mobilities, it is seen that the ions formed of univalent elements lie on a smooth curve, whilst univalent compound ions (except OH and NH_4) lie below the curve and bivalent ions lie above it. For the univalent elementary ions, four formulæ are tried: (1) $\alpha = 0.0136 + 0.67/(18.5 + l)$; (2) $\alpha = 0.01341 + 0.640/l - 6.94/l^2$; (3) $\alpha = 0.03481/\log l - 0.207$; (4) $\alpha = 0.0394/\log l$. The first three agree with the experimental results within the limits of error, and the fourth gives a systematic deviation. The first formula (which was used by the author in 1901) is the only one which gives probable values for α when l becomes very large or very small. The ions probably carry with them an envelope of water molecules, the size of which depends on the nature of the ion; the arguments for this view are summarised. T. E.

Reactivity of Undissociated Electrolytes. RUDOLF WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1908, 14, 133).—Referring to Meyer and Trutzer's work on the decomposition of ammonium nitrite (this vol., ii, 181), the author points out that it is impossible to decide from measurements of the velocity of reaction whether undissociated molecules or ions react, the result being the same so long as the two are in equilibrium. The same applies to the change of trichloroacetic acid into chloroform and carbon dioxide studied by Timoféeff and Koboseff (*Abstr.*, 1904, i, 470). T. E.

Theory of the Inversion of Sucrose. JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1908, 62, 59—88).—In view of the birotation of dextrose and lævulose, the inversion of sucrose by dilute acids cannot be a simple unimolecular reaction; it is to be regarded as a reaction completed in several stages, which may be represented by the scheme:



On this basis, a general formula is deduced which permits the calculation of the angle of rotation of a solution at any moment from the reaction constants and the specific rotatory powers of the components, and which gives also the concentration of each constituent at any given time.

In order to study the various separate changes involved in the inversion of sucrose, the author has investigated the mutarotation of dextrose at 18° and 25° in water and in dilute hydrochloric acid solution. For α -dextrose, the mean value of $[\alpha]_D$ is 109.575° ; for β -dextrose, 20.460° , and for the equilibrium mixture, 52.335° . The value of $k_3 + k_4$ has been determined experimentally, and the separate values of k_3 and k_4 which follow from these data are given below:

Temperature.	k_3 .	k_4 .	
18°	0.00747	0.00415	} in water
25	0.01513	0.00844	
18	0.01147	0.00638	} in 0.02N HCl
25	0.02609	0.01452	

The equilibrium between α - and β -dextrose is not noticeably displaced either by the presence of acid or by rise of temperature.

In the case of α - and β -lævulose, the sum ($k_1 + k_2$) only of the velocity coefficients of the opposing reactions has been determined. On rise of temperature, the equilibrium is shifted in the direction of β -lævulose.

In its very earliest stages, as careful experiments have shown, the inversion of sucrose is not a simple unimolecular reaction; the velocity coefficient, calculated on the supposition that it is such a reaction, diminishes as inversion proceeds. Only after inversion has taken place to the extent of 4—5% does its course correspond with that required for a unimolecular reaction. When the curve obtained by plotting the inversion coefficient against time is extrapolated to zero time, an approximate value is obtained for k_5 , the true inversion constant. When this value of k_5 is inserted in the general formula already mentioned, the latter can be considerably simplified, and ultimately reduced to the unimolecular form. For the inversion of an 8% sucrose solution by 0.02*N* HCl, the value of k_5 is found to be 0.000050 at 18°, and 0.000150 at 25°. The temperature-coefficient is 4.5 for an interval of 10°.

A formula representing the change of rotation of a solution containing dextrose and lævulose is deduced and tested by experiment with satisfactory results.

J. C. P.

A New Method for Studying Intramolecular Change.

THOMAS S. PATTERSON and ANDREW McMILLAN (*Ber.*, 1907, 40, 2564—2573).—In continuation of work previously published (*Trans.*, 1907, 91, 504), the authors have determined the rate of change of anis-*syn*-aldoxime into the *anti*-isomeride, when dissolved in various esters, by observing the change in the rotatory power of the ester. The following values have been obtained for 1000*k*: in methyl tartrate, 3.0; ethyl tartrate, 1.8; *n*-propyl tartrate, 1.0; methyl malate, 5.0; ethyl malate, 6.7; *n*-propyl malate, 8.4. The value for *k* diminishes with increasing mol. weight of the tartrate, but increases with increasing mol. weight of the malate. The high value, 1000*k* = 3.9, previously observed for anis-*syn*-aldoxime in ethyl tartrate solution (*loc. cit.*) is ascribed to the use of an impure oxime.

The rotatory power of a solution of *m*-nitrobenz-*syn*-aldoxime in *n*-propyl tartrate, containing 5.05% of the aldoxime, changes from α_D^{20} (100 mm.) + 18.14° to α_D^{20} (100 mm.) + 14.68°; 1000*k* = 0.5. An ethyl tartrate solution containing 5.04% of *m*-nitrobenz-*anti*-aldoxime has $\alpha_D^{19.8}$ (100 mm.) + 14.68° (compare Ciamician and Silber, *Abstr.*, 1904, i, 161; Goldschmidt, *Abstr.*, 1904, i, 250; Ciusa, *Abstr.*, 1907, i, 137).

G. Y.

Catalytic Reactions at High Temperatures and Pressures.

XVI. Function of Oxides in Catalysis. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1—27. Compare *Abstr.*, 1907, i, 5, 6, 457, 827, 828).—To determine the rôle of the catalyst nickel oxide in hydration and dehydration processes, it is necessary in the first place to study its behaviour on reduction at ordinary and at

high pressures. The conclusions arrived at by Moissan regarding the reduction of this oxide (Abstr., 1881, 77) are mostly inaccurate, owing to the fact that he did not analyse the original material.

Pure commercial nickel oxide contains far more nickel than that necessary for the formula Ni_2O_3 , is not always of constant composition, and contains about 6% water, which it commences to lose at 120° , but loses the last traces only above 300° . It is probable that the main constituent is really the lower oxide NiO . The best reagent for detecting even very minute quantities of nickel produced by the reduction of the oxides is nitric acid, D 1.38—1.40, which, whilst producing no effect on the oxides, evolves oxides of nitrogen in the presence of nickel, and it is even possible to estimate the latter by the appearance of the reacting mixture.

At the ordinary pressure, nickelic oxide is reduced by hydrogen at 170 — 190° , forming metallic nickel and lower oxides, mostly NiO , but it is improbable that the oxide Ni_3O_4 is formed. Nickelous oxide, NiO , only commences to be reduced above 200° , and cannot be oxidised either with dry or moist oxygen even at 480° . At high pressures, nickelic oxide is reduced at 180° , and at 210° pure nickel is produced; nickelous oxide under the same conditions yields almost pure nickel at 172° .

In all cases, the reduction of the oxides is either prevented or greatly retarded when any water is removed by previous heating. The temperature of reoxidation of the reduced nickel depends on the temperature at which it was produced, and is lower when moist oxygen or air is employed; in any case only nickelous oxide is formed.

When the reduction of benzene is performed at high pressures in the presence of nickelic oxide, both the organic substance and the oxide are only very slowly reduced unless precautions are taken not to wet the oxide with the liquid. Employing nickelous oxide, both the benzene and the oxide are readily reduced at 172° , but not if the oxide has been previously well dried.

Comparing the velocity of reduction of benzene in the presence of nickelic oxide, nickelous oxide, and reduced nickel, $(\delta p/\delta t)_{\text{max.}}$ is found to be greatest for the first and least for the last. It is thus evident that the oxides form the most important part of the catalyst in these reactions, the traces of water always present in the oxides employed being as important in these cases as they are in catalytic processes of oxidation. Thus, in presence of reduced nickel, which always contains the oxides and water, hydrogen under pressure reduces the oxide, forming the metal and water, which in their nascent state react on one another, reproducing the oxide and nascent hydrogen, which hydrogenates rapidly the organic compound.

The current ideas regarding catalytic reactions require modification in the light of the facts disclosed by the study of heterogeneous catalysis at high temperatures and pressures. Thus it is probably not true that a catalyst merely increases the speed of a reaction which otherwise proceeds at a slow rate; firstly, the catalyst often alters the limits of a reaction, and, secondly, it seems more probable that it acts as a transformer of heat into chemical energy.

To understand the different catalytic actions displayed by various

metals, it is necessary to study their chemical properties and also those of their oxides. Z. K.

Kinetics of the Elimination of Carbon Dioxide from Camphorcarboxylic Acid. GEORG BREDIG and R. W. BALCOM (*Ber.*, 1908, 41, 740—751).—In aqueous solution, the decomposition of *d*-camphorcarboxylic acid when heated follows a mass action law of the first order. Substitution of dilute hydrochloric acid for water led to no increase in the rate of change. The sodium salt decomposes very much less rapidly than the free acid, and the rate of change of the salt is only slightly depressed by excess of alkaline hydroxide. The temperature-coefficient is large, being 3.15 for 10°. In benzene solution it is 3.0.

The decomposition obeys a similar mass action law in benzene, aniline, alcohol, phenetole or ether; in heptane and acetone solution this is not the case, and the velocity constant increases as the reaction proceeds. In ethyl alcohol, a simultaneous esterification and elimination of carbon dioxide takes place. The influence of the solvent on the rate of change is very large, the change being particularly rapid in aniline and alcohol.

The decompositions of both *d*- and *l*-camphorcarboxylic acids in *d*- and *l*-limonene solutions do not follow mass action laws of the first or second order, but the four reaction curves, when plotted, appear to be identical within the limits of error. This is not apparently a suitable case for the detection of stereochemical differences in the catalytic action of the solvent (see following abstract). E. F. A.

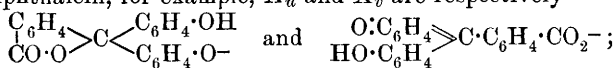
Stereochemistry of Catalysis. GEORG BREDIG and K. FAJANS (*Ber.*, 1908, 41, 752—763).—The decomposition of the optically active camphorcarboxylic acids is studied, not in an indifferent optically active medium as formerly (see preceding abstract), but in presence of an optically active pronounced base, such as nicotine, used either alone as solvent or diluted with an indifferent substance. Under these conditions, the elimination of carbon dioxide follows a unimolecular reaction of the first order. In nicotine solution, the *d*-acid decomposes about 13% more quickly than the *l*-acid; in nitrobenzene solution, containing 5% of nicotine, the *d*-acid is decomposed 8% more rapidly than its isomeride, and nine times as quickly as when no nicotine is present, showing the powerful catalytic activity of the base. In acetophenone solution containing 10% of nicotine, the *d*-acid is attacked 17% more quickly than the *l*-acid.

The stereochemical conditions of the catalysis of optically active substances by optically active catalysts are thus very similar to those in the case of enzyme action, and, adopting the analogy from enzymes, it is considered that there is an intermediate temporary formation of an additive compound between catalyst and substrate. The results are parallel to Dakin's (*Abstr.*, 1904, i, 1071; 1905, i, 556) observations on the hydrolysis of mandelic acid esters by lipase. E. F. A.

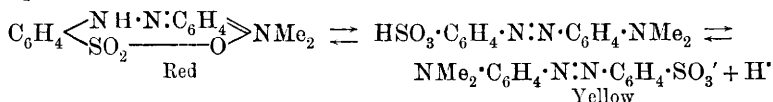
The Relationship between the Strength of Acids and their Capacity to Preserve Neutrality. LAWRENCE J. HENDERSON (*Amer. J. Physiol.*, 1908, 21, 173—179).—Acids the ionisation

constant of which is nearly equal to the hydrogen ionisation at neutrality, possess with the help of their salts a great capacity for preserving neutrality in simple solution, whilst other acids in like concentration have relatively little effect in this direction. W. D. H.

Constitution of Indicators used in Acidimetry. JOHN T. HEWITT (*Analyst*, 1908, 33, 85—89. Compare Hewitt and Mitchell, *Trans.*, 1937, 91, 1251).—In order that a substance may act as an indicator, it must be a weak acid or a weak base, and the complex ion which it forms must have a different constitution to the parent substance. Weakly acidic indicators are present in solution in a state of equilibrium represented thus: $X_uH \rightleftharpoons X_vH \rightleftharpoons X_v' + H'$, where X_u and X_v are isomeric complex radicles. In the case of phenolphthalein, for example, X_u and X_v are respectively



since X_u is the stable configuration and the substance is a very weak acid, X_vH and its ions are only present to an exceedingly small extent in neutral solution, and the absorption due to X_u is observed (with phenolphthalein this is in the ultra-violet and the substance is colourless). Addition of bases removes the hydrogen ions, the equilibrium is disturbed towards the right, and the colour due to X_v makes its appearance. In the case of methyl-orange, the aqueous solution will contain the internal salt, the real dimethylaminoazobenzenesulphonic acid, and the ions of the latter in a state of equilibrium, thus :

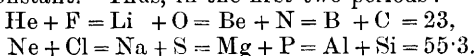


Addition of a weak base results in the removal of hydrogen ions, and the solution becomes yellow.

It is stated in conclusion that extremely sharp results are obtained by using 1-nitro-2-sulphobenzene-4-azo- α -naphthol as an indicator. The acid and its monobasic salts are yellow; addition of excess of alkali turns the yellow solution sharply to a purple; the purple colour is not discharged by an excess of alkali, hot or cold, neither is it affected by alcohol even in strongly alkaline solutions.

W. H. G.

Symmetry in the Law of Atomic Weights. N. DELAUNAY (*Chem. News*, 1908, 97, 99. Compare Abstr., 1908, ii, 97).—The elements are arranged on a set of curves with the numbers 0, 1, 2, 3; 3, 2, 1, 0 successively as ordinates, and the atomic weights commencing with helium as abscissæ. The curve obtained for each period of eight elements is completely symmetrical; in other words, the elements of each period fall into pairs the sum of the atomic weights of which is constant. Thus, in the first two periods :



R. J. C.

Demonstration of the Formation of Ammonium Amalgam by Electrolysis of Ammonium Chloride. JOHANNES SCHROEDER (*J. pr. Chem.*, 1908, [ii], 77, 271—272).—The author describes and figures two simple pieces of apparatus designed to enable a large audience to observe the formation of ammonium amalgam by electrolysis of ammonium chloride with a mercury cathode. G. Y.

Three Lecture Experiments. EDMUND KNECHT (*Ber.*, 1908, 41, 498—499).—1. *Synthesis of Calcium Carbide.*—Small quantities of calcium carbide are readily prepared by igniting a piece of calcium, about the size of a pea, placed on wood-charcoal, by means of a small blowpipe flame; the metal burns for a moment with an intense orange-yellow flame, and then sinks into the charcoal. The calcium carbide formed is readily obtained by breaking the piece of charcoal.

2. *A Visible Autoxidation.*—An approximately $N/10$ potassium permanganate solution acidified with sulphuric acid is divided into two portions. One portion is kept for comparison; small quantities of titanous sulphate are added from time to time to the other portion, the blood-red colour of which gradually changes through scarlet to orange-yellow. Excess of the salt decolorises the solution.

3. *Precipitation of Metallic Copper by Titanous Sulphate.*—About 1 c.c. of a 10% copper sulphate solution is added to a 1—2 litre glass cylinder nearly full of water; about 5 c.c. of a solution of titanous sulphate is then stirred into the solution from which metallic copper separates in a few minutes. The precipitate is so fine that most of it passes through a filter paper, and the solution which appears copper-coloured by reflected light is blue by transmitted light. The reaction may be employed as a test for copper, since it is visible in the presence of 1 part of copper per 1,000,000 parts of solution.

W. H. G.

New Pressure Cylinder. BALTHASAR PFYL and BR. LINNE (*Chem. Zeit.*, 1908, 32, 205).—The pressure cylinder, previously described by the authors (*Abstr.*, 1905, ii, 770), has been in use for more than two years, and continues to act in a satisfactory manner. T. H. P.

Gas Current Pressure Regulator. FREDERICH M. G. JOHNSON and K. BUCH (*Ber.*, 1908, 41, 640—641).—An apparatus to regulate the pressure of a gas current has been designed on the principle of the electromagnetic thermo-regulator, and is here described and figured.

G. Y.

A Laboratory Pump. ROBERT LUTHER (*Chem. Zeit.*, 1908, 32, 267—268).—The pump, which is driven by an electro-motor, is designed for driving a continuous stream of water through thermostats or condensers. It consists of four tubes arranged in the form of a cross, which rotates about a vertical axis in a metal box. The water enters the cross from below by a pipe at the centre of the cross and passing through the bottom of the metal box, the rotation of the cross draws the water up and forces it out into the metal box, from which it passes out by a side tube.

P. H.

Inorganic Chemistry.

Purification of Hydrogen from Arsenic. HANS RECKLEBEN and GEORG LOCKEMANN (*Zeitsch. angew. Chem.*, 1908, 21, 433—436).—The absorption of arsine, when mixed with hydrogen, has been studied previously (this vol., ii, 176, 224) by shaking the mixed gases with various reagents. An account is now given of the results obtained on passing the mixed gases through most of the reagents previously employed, and, in addition, mercuric chloride and silver nitrate solutions, and a mixture of cupric and cuprous oxides (Lionet, *Abstr.*, 1880, 2). For the purification of hydrogen in the laboratory, it is recommended to pass the gas through a saturated solution of potassium permanganate, and, finally, to test the purity of the gas, through a 5—10% solution of silver nitrate, when the presence of traces of arsenic is shown by the formation of a precipitate. Mercuric chloride solution can be employed only so long as the precipitate formed is yellowish-white. Copper oxide forms the best solid absorbent; iodine may be used if the hydrogen is afterwards passed through a wash-liquid to retain hydrogen iodide and traces of iodine vapour. Only potassium hypochlorite solution, dropped on to pumice stone or bleaching powder kept thoroughly moistened with water, is suitable for use on the technical scale. It is recommended to employ bromine when traces of arsine have to be removed from large volumes of hydrogen. G. Y.

Decomposition of Hydrogen Peroxide in the Presence of Various Substances. EDUARDO FILIPPI (*Chem. Zentr.*, 1907, ii, 1890; from *Arch. Farm. speriment.*, 1907, 6, 363—395).—The author finds that all inert powders decompose hydrogen peroxide, the velocity of decomposition being proportional to the exposed surface of the added powder and independent of the concentration of the hydrogen peroxide. Various ferment-containing organic substances which give the guaiacum reaction, and also ferment-free organic substances which cannot give this reaction, decompose hydrogen peroxide. Therefore the conclusion is drawn that these tests are insufficient to establish the nature of the ferment present in a substance. J. V. E.

Atomic Weights of Nitrogen, Oxygen, and Carbon. ANATOLE LEDUC (*Compt. rend.*, 1908, 146, 399—400).—The value $N=14.01$ adopted by the International Committee on Atomic Weights, and based on Guye's recent determinations, is greater than the value $N=14.005$ obtained by the author (*Abstr.*, 1897, ii, 549). Using the value $N=14.01$ and the ratio of the densities of carbon monoxide and nitrogen determined by Lord Rayleigh (*Abstr.*, 1895, ii, 444; 1898, ii, 290) and the author (*Abstr.*, 1893, ii, 165; 1897, ii, 140), the atomic weight of carbon lies between 12.011 and 12.16; whilst taking $C=12.000$, the atomic weight of nitrogen lies between 14.002 and 14.004. M. A. W.

Formation of Oxides of Nitrogen in the Ozone Generator. WILHELM MANCHOT (*Ber.*, 1908, 41, 471—472).—In connexion with the study of the action of ozone on alkalis (Manchot and Kampschulte, this vol., ii, 101), it has been observed that on prolonged exposure to a current of ozone, prepared from 98% oxygen, the coloured compounds at first formed with alkalis are decolorised and converted into nitrates (Warburg and Leithäuser, *Abstr.*, 1906, ii, 743). The presence of nitric oxide in ozone prepared from 99.3% oxygen has been determined in the same manner. On passing 10% ozone slowly through 15% potassium hydroxide, the concentration falls to 4%; the resulting gas, which is free from nitric oxide, has not an acid reaction, and does not increase the conductivity of water, but behaves towards organic and inorganic bases as described previously (*loc. cit.*). Hence, contrary to Baeyer and Villiger's view (*Abstr.*, 1902, ii, 650), ozone is not an acid anhydride. G. Y.

Irregularities in the Combination of Nitric Oxide and Oxygen. ALFRED MANDL and FRANZ RUSS (*Zeitsch. angew. Chem.*, 1908, 21, 486—491).—It is usually assumed that nitric oxide and oxygen, when mixed in the proportion of 2 vols. to 1 vol., undergo complete combination. This is found to be not always the case, the reaction often coming to an end whilst considerable amounts of nitric oxide and oxygen are still uncombined. The results of experiments quoted show that the extent to which the combination takes place depends on the genesis of the oxygen, about 97% of the nitric oxide combining with oxygen prepared from air by Linde's method, about 95% with oxygen obtained by electrolysis of water and passed over heated palladium asbestos, but only about 40% with oxygen prepared by the action of potassium dichromate and sulphuric acid on barium peroxide. As the reaction takes place also to a much smaller extent with oxygen prepared by electrolysis of water but not passed over palladium asbestos, the retardation might result from the presence of hydrogen peroxide. This could not be tried, but comparative experiments with Linde's oxygen and the same oxygen after ozonisation show that the combination is markedly retarded by the presence of ozone. This retardation may be a direct action of the ozone, or may result from the destruction by the ozone of some catalyst necessary to the reaction. G. Y.

Nitrogen Sulphide. HANS WÖBLING (*Zeitsch. anorg. Chem.* 1908, 57, 281—289).—Certain compounds of nitrogen sulphide, N_4S_4 , with the higher halogen derivatives of certain elements have been prepared, and a reduction product of nitrogen sulphide has been obtained by the action of stannous chloride in alcoholic solution on the sulphide. Unless otherwise mentioned, the compounds were obtained by interaction of the components dissolved in carbon tetrachloride.

The compound, $N_4S_4 \cdot TiCl_4$, occurs as an amorphous, brownish-red precipitate, insoluble in most solvents; it decomposes in moist air, reacts very vigorously with water and with alkali, and is split up into its components by hydrochloric acid and by alcohol. The compound, $N_4S_4 \cdot SbCl_5$, occurs as a scarlet, amorphous powder, which is very stable,

not being attacked by water, by hydrochloric or by nitric acid in the cold; it yields ammonia on heating with potassium hydroxide. The *compound*, $2\text{N}_4\text{S}_4\cdot\text{SnCl}_4$, occurs as an amorphous, insoluble, Bordeaux-red powder, which behaves towards reagents like the antimony compound; it decomposes when heated above 160° .

The *compound*, $\text{N}_3\text{S}_4\text{Cl}$ (compare Muthmann and Seither, Abstr., 1897, ii, 255), can be prepared conveniently by heating nitrogen sulphide with the theoretical amount of sulphur dichloride, S_2Cl_2 , in carbon tetrachloride solution for two hours in a reflux apparatus. The corresponding *bromide*, $\text{N}_3\text{S}_4\text{Br}$, appears to be obtained by interaction of nitrogen sulphide and sulphur dibromide, S_2Br_2 , dissolved in carbon tetrachloride, but in carbon disulphide solution only the *compound*, $\text{N}_4\text{S}_5\text{Br}$, was obtained. Nitrogen sulphide and selenium dichloride, Se_2Cl_2 , react in boiling carbon tetrachloride to form a green, insoluble, amorphous *compound*, probably $\text{N}_4\text{S}_4\cdot\text{Se}_2\text{Cl}_2$, which has not been obtained pure. This compound is not affected by water or hydrochloric acid, but is decomposed immediately by nitric acid and by potassium hydroxide.

By the action of hydrogen sulphide on nitrogen sulphide dissolved in benzene and in alcohol, precipitates of ammonium polysulphides and of ammonium thiosulphate respectively were obtained.

Stannous chloride does not combine directly with nitrogen sulphide, but in warm benzene solution the latter compound is reduced, and a compound of the empirical formula NSH separates in yellow, lustrous leaflets, which, after recrystallisation from pyridine, have m. p. (decomp.) 152° . The new compound is not combustible or explosive, is not acted on by cold potassium hydroxide, but gives off ammonia when heated; with hydrochloric acid, sulphur dioxide is given off, and it reacts vigorously with nitric acid. Its constitution has not yet been determined.

G. S.

The Essentially Chemical Causes of the Allotropic Transformation of Phosphorus Dissolved in Oil of Turpentine. ALBERT COLSON (*Compt. rend.*, 1908, 146, 401—403).—The gradual and irreversible change to the red modification that phosphorus dissolved in oil of turpentine undergoes at 250° (this vol., ii, 35, 176) is due to the formation of small quantities of hydrogen phosphide and its subsequent decomposition into red phosphorus and hydrogen, the latter reacting with the dissolved phosphorus to form a further quantity of hydrogen phosphide. A 2% solution of phosphorus in oil of turpentine was sealed in a tube with hydrogen phosphide and enclosed in a tube containing a further quantity of the solution. After heating at 240° for four hours, the inner tube contained a copious deposit of red phosphorus, whilst the contents of the outer tube remained clear even after twelve hours at 250° . The red phosphorus formed under these conditions has D 2.095, and contains small quantities of the phosphides of hydrogen, which are eliminated on distillation in a vacuum.

Phosphorus dissolved in an oxygenated solvent, such as ethyl benzoate, does not undergo any allotropic transformation even when the solution is heated at $305\text{--}310^\circ$ for twenty-five hours. M. A. W.

Hittorf's Phosphorus. ALFRED STOCK (*Ber.*, 1908, 41, 764).—The crystallographic determinations cited in the previous communication (this vol., ii, 176) were made by F. von Wolff. E. F. A.

Phosphoryl Bromide. ERNEST BERGER (*Compt. rend.*, 1908, 146, 400—401).—A convenient method of preparing phosphoryl bromide consists in gently heating a mixture of phosphorus pentabromide and phosphoric oxide until traces of bromine vapour appear; after four to five hours, the liquid product is distilled over a little phosphoric oxide; the reaction is represented by the equation $3\text{PBr}_5 + \text{P}_2\text{O}_5 = 5\text{POBr}_3$, and the yield amounts to 85% of that theoretically possible. Phosphoryl bromide forms colourless crystals, m. p. 55—56°, b. p. 189.5°/774 mm., and the heat of formation as determined by decomposing the compound with water is 75900 cal. (compare Ogier, *Abstr.*, 1881, 218). M. A. W.

Sulphides of Phosphorus. II. Phosphorus Pentasulphide. ALFRED STOCK and WILHELM SCHARFENBERG (*Ber.*, 1908, 41, 558—564. Compare *Abstr.*, 1905, ii, 703).—By the distillation of phosphorus pentasulphide in a high vacuum, Stock and Thiel (*Abstr.*, 1905, ii, 703) observed the formation of another substance in addition to pure phosphorus pentasulphide, m. p. 276°. A special apparatus is now described in detail which enabled the distillation of larger quantities in a high vacuum and rapid cooling of the vapour. This had, in particular, the advantage that the phosphorus pentasulphide distilled at a much lower temperature than formerly, and the distillate contained but little else than pentasulphide. When superheated even in a high vacuum, phosphorus pentasulphide decomposes; the density is normal at 630°, but rapidly becomes less above this temperature. Phosphorus pentasulphide when distilled or sublimed decomposes somewhat at atmospheric pressure, decomposes more in a high vacuum or in a stream of carbon dioxide, and still more when the vapours are superheated. E. F. A.

Sulphides of Phosphorus. III. Vapour Densities of the Compounds P_4S_3 , P_4S_7 , and P_2S_5 . ALFRED STOCK and HEINRICH VON BEZOLD (*Ber.*, 1908, 41, 657—660. Compare *Abstr.*, 1905, ii, 703; this vol., ii, 176).—The existence of only three, P_4S_3 , P_4S_7 , and P_2S_5 , of the numerous compounds of phosphorus and sulphur described in the literature can be considered as established. The vapour density determinations made with these three substances by various authors have given normal results, but in no case is the temperature of the determination recorded. The present authors have therefore determined the vapour densities of the three compounds at temperatures up to 1000°. A Victor Meyer's apparatus, made of glazed porcelain, filled with nitrogen, and heated in a Heräus's resistance-oven was employed. The temperatures were recorded by means of a thermoelement. The results are tabulated and expressed in the form of curves. All three compounds decompose at a red heat; the compound P_2S_5 commences to decompose immediately above its b. p., whereas P_4S_3 and P_4S_7 give normal results at temperatures considerably above

their b.p.'s. Hence these two compounds can be distilled under the ordinary pressure, only P_4S_3 undergoing slight decomposition (Mai and Schaffer, *Abstr.*, 1903, ii, 363). Remarkable is the rapid fall in the vapour density of P_4S_7 between 750° and 800° . G. Y.

Yellow Arsenic. HUGO ERDMANN (*Ber.*, 1908, 41, 521—523).—Many of the results published by Linck in his paper on the polymorphous modifications of the phosphorus-arsenic group (this vol., ii, 176) were communicated to him by the author and Reppert, who intend to publish their own work, the more so as Linck's statements as to it are frequently incorrect. C. S.

Solubility of Graphite in Iron. CARL BENEDICKS (*Metallurgie*, 1908, 5, 41—45).—A sample of iron containing 3.9% carbon and 0.75% silicon was repeatedly heated rapidly to 800° , and then slowly cooled. By this treatment, the whole of the carbide was decomposed, the mass consisting only of ferrite and graphite. This iron was then heated for two hours at 940° and quenched. The microscopic examination then showed the presence of martensite, troostite, sorbite, and perlite. This indicates a considerable solubility of graphite in iron at 940° , amounting to about 1%, a fact in accordance with the older views as to the stable iron-carbon system, and not with the theories of Heyn and Ruer. C. H. D.

Conversion of Diamond into Coke in High Vacuum by Cathode Rays. CHARLES A. PARSONS and A. A. CAMPBELL SWINTON (*Proc. Roy. Soc.*, 1908, 80, A, 184—185).—The vacuum tube employed was provided with two concave aluminium electrodes, so arranged as to focus the rays on the diamond, which rested on an iridium support. Two diamonds, each about 0.2 in. in diameter, were employed, and an alternating current was used. With an *E.M.F.* of 8000 volts and a current of 44 milliamperes, the diamond began to throw off small sparks; at 9600 volts and 45.5 milliamperes it commenced to blacken, and at 11,200 volts and 48 milliamperes appeared to be converted completely into coke. The temperature at which disintegration took place, as measured by an optical pyrometer, was 1890° .

It was not found possible to determine whether the gas pumped off from the tube during the experiment originated from the diamond or from the rest of the apparatus, neither could a marked difference be detected in specimens of gas removed from the vacuum tube just before and just after conversion. G. S.

Action of Alkali Salts of a Fixed Base on the Combustion of Gases and Combustible Powders. DAUTRICHE (*Compt. rend.*, 1908, 146, 535—538).—The author has detonated cartridges, made of explosives, either alone or mixed with small proportions of certain salts, in a large vessel full of air, and determined the proportion of the evolved gases (hydrogen and carbon monoxide) burnt by measurement of the heat developed. A decanitrated cotton developed less than half as much heat when mixed with 3% of potassium sulphate as when detonated alone. One to two per cent. of sodium hydrogen carbonate, or 2% of potassium nitrate, effects a slightly less reduction in the amount

of heat developed, whilst calcium and magnesium carbonates and lead nitrate have only about one-half the effect. With a nonanitrated cotton, the heat developed is reduced about 60% by addition of 10% of sodium hydrogen carbonate. Trinitrotoluene when mixed with 5% of potassium nitrate develops only one-fourth as much heat as when detonated alone; the effect of barium nitrate is only one-third as great. These results show that the combustion of the products of detonation of explosives can be prevented by addition of small amounts of sodium or potassium salts, and that such an addition should be made to explosives used in mines containing fire-damp. It is shown that addition of 3% of sodium hydrogen carbonate to a mixture of a decanitrated cotton (30%) with ammonium nitrate (70%) prevents inflammation when detonated. Potassium nitrate has a similar effect on a mixture of trinitrotoluene and ammonium nitrate. The conclusion is drawn that a cloud formed of the powder of any sodium or potassium salt whatever tends to prevent the combustion of gases and combustible powders, whilst salts of the alkaline-earth metals have only a secondary action.

E. H.

Combustion without Flame and the Inflammation of Gases at the End of a Metallic Rod. JEAN MEUNIER (*Compt. rend.*, 1908, 146, 539—540).—An interesting experiment with an alcohol-fed incandescent burner is described. The burner has the form of an æolipile supported on four tubes through which cotton wicks pass supplying the alcohol. The æolipile has an annular form, the flame rising from a central cylinder which is covered with a convex disc, perforated with closely occurring holes. An iron stem 8 cm. long, supporting the mantle, rises from the centre of the disc. It is observed that after continued use the light becomes less bright, and that the darkening of the mantle commences at the moment that the disk reddens. After removal of the mantle, the author succeeded in getting the disk to redden without production of a flame. Once the disk is red hot, its incandescence increases with the supply of alcohol vapour. It is impossible to ignite either a pad moistened with alcohol, a wick soaked in light petroleum, or a wooden match by bringing them near the hot disc, although the wood of the match is charred. This flameless combustion occurring on the surface of the disk is to be explained by the retention of either the combustible gas or the oxygen on this surface, as suggested by Couriot and Meunier (this vol, ii, 11) in the case of the non-explosion of an explosive mixture by an incandescent filament. Application of a lighted match to the upper end of the metallic stem results in the production of a flame at this point, which continues to burn so long as it is protected from draughts, showing that the oxygen is retained by the disk, and that the excess of combustible gas rises around the stem without mixing with the surrounding air and without igniting, although the stem is at a fairly high temperature. The shape of the flame is altered by varying the form of the upper extremity of the metallic rod.

The experiment, besides its important bearing on the mechanism of combustion by incandescence, seems to show that gases have a certain amount of cohesion.

E. H.

[Preparation of Silicon Monoxide.] HENRY N. POTTER (D.R.-P. 189833).—When silica is heated electrically in an inert atmosphere with sufficient reducing agent (carbon or silicon carbide) to remove half its oxygen, it is converted into a very voluminous, brown powder, which contains 91.28% of *silicon monoxide*, SiO . This oxide, which has $D\ 2.24$, is much less soluble than silica in hydrofluoric acid, but dissolves more readily in aqueous alkali hydroxides; it is a bad conductor of heat or electricity. The monoxide exists in the vitreous condition. G. T. M.

Tschermak's Method of Preparing Silicic Acids from Natural Silicates. OTTO MÜGGE (*Centr. Min.*, 1908, 129—134. Compare Abstr., 1906, ii, 771; Ann. Rep., 2, 273; 3, 303).—Tschermak's method is criticised, and the determinations are repeated for natrolite. The position of the break in the drying curve is found to vary greatly with the temperature at which the silica jelly dries: at 9° , corresponding with 33.5—46% H_2O , and at 33.3° with 20% H_2O . Further, the break in the curve is never very sharply defined, and its position cannot be accurately estimated to within 1 or 2 per cent., and some of the complex silicic acids assumed by Tschermak do not differ from one another by more than this amount. L. J. S.

Rare Gases of Thermal Waters. Gaseous Outputs of Some Springs. CHARLES MOUREU and ROBERT BIQUARD (*Compt. rend.*, 1908, 146, 435—437. Compare Moureu, Abstr., 1896, ii, 298; 1903, ii, 222; 1905, ii, 5; 1906, ii, 126, 442; Moureu and Biquard, Abstr., 1906, ii, 685).—The authors have conducted a series of experiments on the gases evolved from thermal springs, and from the results have calculated the total gaseous output of the spring, and the percentage of rare gases and of helium. The volume of gas evolved varies from 4891 to 560,640 litres per annum.; the proportion of rare gases varies from 1.24 to 6.39 per cent., and of helium, from 0.097 to 5.34 per cent.; the Bourbon-Lancy spring evolves annually 16,644 litres of rare gases, of which 10,074 litres are helium.

In conclusion, the authors draw attention to the close connexion existing between the results obtained by them on the rare gases from thermal waters, all more or less radioactive, and those obtained by Sir W. Ramsay and Cameron (*Trans.*, 1907, 91, 1266) on the chemical properties of radium emanation. M. A. W.

Solubility of Potassium Chloride in Aqueous Pyridine at 10° . JOHANNES SCHROEDER (*J. pr. Chem.*, 1908, [ii], 77, 267—268. Compare Abstr., 1905, ii, 306).—Potassium chloride is not appreciably soluble in anhydrous pyridine, but dissolves in aqueous pyridine, the solubility increasing with the proportion of the water. The results of two series of determinations are given in tables. More complicated phenomena are observed at higher temperatures and with other salts; two layers are formed the composition of which is readily affected by changes of temperature. G. Y.

Electrochemical Behaviour of Silver and its Oxides. ROBERT LUTHER and F. POKORNÝ (*Zeitsch. anorg. Chem.*, 1908, 57, 290—310).—When silver is oxidised at the anode in alkaline solution (normal

sodium hydroxide) with small current-density, silver oxide, Ag_2O , is at first formed quantitatively and reversibly; on further oxidation, it is changed quantitatively and reversibly to a higher oxide, AgO . The change $\text{Ag} \rightarrow \text{Ag}_2\text{O}$ takes place at +1.172 volts (taking the hydrogen electrode as zero), the change $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ at +1.40 volts, both at 25° , and no higher peroxide could be obtained in alkaline solution.

Wöhler (1868) has described the preparation of a silver peroxide by electrolytic oxidation of a silver anode in sulphuric acid, and Mulder (Abstr., 1897, ii, 551, &c) has described a "peroxynitrate" and other salts of silver prepared by electrolysis of neutral solutions of silver salts. By electrolytic reduction experiments, the authors now show that Wöhler's peroxide and Mulder's salts consist essentially of the peroxide, Ag_2O_3 (in the latter case with occluded or adsorbed silver salts); in alkaline solution, the change $\text{Ag}_2\text{O}_3 \rightarrow \text{AgO}$ takes place at +1.57 volts.

In acid solution, the compound Ag_2O_3 is decomposed directly into silver on electrolytic reduction, and, conversely, silver can be oxidised directly to Ag_2O_3 .

From the potential of the electrode $\text{Ag}/\text{Ag}_2\text{O}$ in sodium hydroxide (1.172 volts), the *E.M.F.* of the hydrogen-oxygen cell is calculated at 1.221 volts, in fair agreement with the value, 1.217 volts, recently obtained by Lewis (Abstr., 1906, ii, 262) by a less direct method.

G. S.

Alloys of Calcium with Zinc, Cadmium, Aluminium, Thallium, Lead, Tin, Bismuth, Antimony, and Copper. L. DOŃSKI (*Zeitsch. anorg. Chem.*, 1908, 57, 185—219).—From an investigation of these alloys by Tammann's method of thermal analysis, controlled by microscopic observations, evidence has been obtained of the existence of the following compounds: CaZn_{10} , CaZn_4 , Ca_2Zn_3 , $\text{CaZn}(\text{?})$, Ca_4Zn ; CaCd_3 , CaCd , $\text{Ca}_3\text{Cd}_2(\text{?})$; CaAl_3 ; CaTl_3 , $\text{CaTl}(\text{?})$; CaPb_3 , CaSn_3 . In only two cases does the composition correspond with the ordinary salt valencies, and the frequent occurrence of the formula CaM_3 is remarkable.

The experiments were greatly interfered with by oxidation of the calcium, and in many cases it was not found possible to investigate alloys rich in the latter metal.

Zinc-Calcium Alloys.—The freezing-point curve shows two maxima at 717° and 5.7% calcium and 688° and 29% of calcium, corresponding with the compounds CaZn_{10} and Ca_2Zn_3 respectively, a break at 680° and 12.8% calcium, corresponding with the compound CaZn_4 , which possibly melts without decomposition, and two eutectic points at 635° and 17% and 410° and 57% of calcium respectively. Between 29% and 56% of calcium, the compound Ca_2Zn_3 reacts with the fused mass at 431° to form a fourth compound, the composition of which could not be accurately determined, but may be CaZn . At 385° , between 52% and 84% of calcium, a fifth compound, Ca_4Zn , is produced by reaction of the compound of unknown composition with calcium.

Alloys containing up to 6% of calcium are rather harder than zinc, and are fairly stable in air and towards water, but with increasing

proportion of calcium they darken in the air and act more vigorously on water. The brittleness increases up to 30% of calcium, and then diminishes.

Cadmium-Calcium Alloys.—The freezing-point curve of these metals does not show any maxima, but there are two eutectic points at 319° and 1% of calcium (components calcium and CaCd_3) and 415° and 71% calcium (components CaCd_3 and mixed crystals rich in calcium). Between 12% and 64% of calcium, the alloy forms two layers which react at 685° with formation of the compound CaCd ; the latter has a transition point at 635° . At 615° , the compound CaCd reacts with the fused mass rich in cadmium to form a second compound, CaCd_3 . A further break in the cooling curve at 510° appears to indicate a reaction between CaCd and the fused mass to form a third compound, the formula of which may be Ca_2Cd_3 .

Alloys containing up to 10% of calcium are stable in the air, and scarcely act on water; beyond that point, the action on water increases with increase in the proportion of calcium. The brittleness increases rapidly between 10% and 40% of calcium, and beyond that point diminishes.

Aluminium-Calcium Alloys.—In this case, special precautions, which are described in detail, had to be employed to diminish oxidation. The freezing-point curve shows two eutectic points at 610° and 8.1% (components aluminium and CaAl_3) and 550° and 75% (components calcium and CaAl_3) of calcium respectively. Between 16% and 43% of calcium, the alloys separate into two liquid layers, which react at 692° to form the compound CaAl_3 .

Alloys containing 0–8% of calcium are the colour of aluminium, and somewhat harder than that metal. Those containing a moderate amount of calcium are brittle and porous, and those rich in the latter metal are less brittle and are unstable in the air.

Thallium-Calcium Alloys.—Only alloys containing up to 15% of calcium could be investigated. The eutectic temperature lies about 6° higher than the melting point of thallium, from which the conclusion is drawn that mixed crystals rich in calcium are present; at the eutectic temperature, these are in equilibrium with the compound CaTl_3 and the fused mass. Between 6% and 16% of calcium, the compound CaTl (needles) separates; at 524° this compound reacts with the fused mass to form CaTl_3 (bluish crystals), which separate primarily from about 0.5–6% of calcium.

The alloys are harder than thallium, brittle, and oxidise rapidly in the air. Those containing more than 6% of calcium do not decompose water at the ordinary temperature.

Lead-Calcium Alloys.—Only alloys up to 12% of calcium were examined. The freezing-point curve rises steeply from the melting point of lead to a maximum at 648° and 6% of calcium, corresponding with the compound CaPb_3 , and then falls to a eutectic point at 625° and 9.7% of calcium.

Alloys containing up to 4% of calcium are harder than lead and not brittle; those containing a higher proportion of calcium are brittle. Alloys containing up to 6% of calcium are not markedly decomposed even by hot water.

Tin-Calcium Alloys.—Only alloys up to 18% of calcium were examined. The freezing-point curve rises steeply from the melting point of tin to a maximum at 623° and 10.1% of calcium, corresponding with the compound CaSn_3 , and then falls to a eutectic point at 603° and 14.9% of calcium.

Alloys containing up to 4% of calcium are harder than tin and fairly tough; with further increase of calcium they become brittle. Those containing 2% of calcium are acted on by cold water.

Calcium-Bismuth Alloys.—Only alloys up to 10% of calcium could be investigated. The freezing point of bismuth is lowered about 5° by the addition of calcium; the eutectic mixture contains much less than 1% of the latter metal. From the eutectic point, the freezing-point curve rises to 500° and 4.5% of calcium, and then runs horizontally as far as it could be followed. The metals form a compound (needles) the formula of which could not be determined; it decomposes rapidly in moist air, and even in a vacuum over sulphuric acid.

Antimony-Calcium Alloys.—Only alloys up to 9% of calcium were investigated. The freezing point of antimony is lowered to 585° by the addition of calcium, the eutectic mixture containing 8% of the latter metal.

The alloys containing a small proportion of calcium are less brittle than antimony; the alloy containing 9% of calcium is brittle and porous. Those containing up to 6% of calcium are not acted on even by hot water.

Copper-Calcium Alloys.—On account of the high melting point of copper, these alloys could not be investigated satisfactorily. The melting point of copper is lowered 74° by the addition of 5% of calcium.

The alloy containing 1% of calcium is acted on by cold water.

G. S.

Preparation of Dry Calcium Hypochlorite. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 188524).—Calcium hypochlorite in a dry, stable condition can be obtained by saturating milk of lime with chlorine, filtering the solution of hypochlorite, and evaporating this down as rapidly as possible under reduced pressure.

Crystalline calcium hypochlorite is precipitated in the concentrated solution, and thus freed from calcium chloride. As the instability of the crystalline salt is due to the presence of water, this is removed by drying the compound in a vacuum until all the moisture and a portion of the water of crystallisation has been removed. The final product does not deliquesce in air, owing to its freedom from calcium chloride; it dissolves in water to a clear solution, and on treatment with hydrochloric acid evolves 80% to 90% of its weight of chlorine. G. T. M.

Monoxides and Monosulphides of the Elements of the Second Group of the Periodic System. JAKOB BECKENKAMP (*Zeitsch. Kryst. Min.*, 1908, 44, 239—263).—A discussion of the dimorphic relations and the crystalline structure of the oxides and sulphides of glucinum, magnesium, calcium, zinc, &c., many of which crystallise in both the cubic and the rhombohedral systems with very nearly the same angles.

L. J. S.

Mixtures of Zinc Sulphide with Other Sulphides. K. FRIEDRICH [with P. SCHOEN] (*Metallurgie*, 1908, 5, 114—128).—Mixtures of zinc sulphide with other metallic sulphides were submitted to thermal and microscopic examination.

Pure zinc sulphide appears to melt at about 1660° . Mixtures with lead sulphide show a eutectic point at 1045° and 6% ZnS; there is no indication of the formation of a double sulphide or of mixed crystals. The eutectic structure is well marked in the solidified mixtures. Mixtures of cuprous sulphide with zinc sulphide, on the other hand, do not show any eutectic structure, and only a single branch of the freezing-point curve could be observed, the eutectic point, if present, lying close to the freezing point of cuprous sulphide.

Mixtures of the sulphides of silver and zinc form a eutectic containing 3% ZnS and solidifying at 800° . Zinc sulphide and ferrous sulphide also form an eutectic containing 5% ZnS and solidifying at about 1175° .

Zinc sulphide is somewhat volatile at high temperatures.

C. H. D.

Atomic Weight of Lead. I. Analysis of Lead Chloride. GREGORY P. BAXTER and JOHN HUNT WILSON (*Zeitsch. anorg. Chem.*, 1908, 57, 174—184; *J. Amer. Chem. Soc.*, 1908, 30, 187—195).—The amount of silver (in the form of nitrate) required for the complete precipitation of a known weight of lead chloride was determined, and the weight of silver chloride produced was also estimated.

Two samples of the chloride were prepared by different methods and crystallised several times in platinum vessels. When, however, the samples were finally heated in a current of hydrogen chloride, they darkened a little, and, on dissolving in water, left a dark residue, showing that some impurity was present. This difficulty is ascribed to a reaction between the salt and filter paper. A sample which remained colourless on heating and formed a clear solution with water was finally obtained by repeated crystallisation in platinum from solutions containing excess of hydrochloric acid. The pure chloride was melted in a stream of dry hydrogen chloride in a platinum vessel before weighing; the precautions taken are fully described.

The determination of the ratios $\text{PbCl}_2 : 2\text{Ag}$ (with the help of the nephelometer) and $\text{PbCl}_2 : 2\text{AgCl}$ were carried out as described in previous papers. As a mean of nine concordant experiments from the ratio $\text{PbCl}_2 : 2\text{Ag}$, the value $\text{Pb} = 207.188$ was obtained, and from six determinations of the ratio $\text{PbCl}_2 : 2\text{AgCl}$ the value 207.193. The most probable value is the mean of the two series, $\text{Pb} = 207.190$ [$\text{Ag} = 107.93$; $\text{Cl} = 35.473$].

G. S.

The Sulphides of Lead, Copper, Silver, and Iron. K. FRIEDRICH [with P. SCHOEN] (*Metallurgie*, 1908, 5, 23—27, 50—58. Compare Abstr., 1907, ii, 687, 951).—The experimental difficulties encountered in determining the freezing point of metallic sulphides and mixtures of sulphides are discussed. By examining mixtures containing both more and less sulphur than is required to form the pure sulphide, fairly accurate values for the freezing point of the latter may be obtained.

The most probable values are : PbS , 1120° ; Cu_2S , 1135° ; As_2S_3 , 812° ; FeS , 1171° ; in each case with an accuracy of $\pm 10^\circ$ only.

Solidification takes place in all these cases over an interval of temperature, which, however, is possibly due merely to the low conductivity of the mass for heat and to the low velocity of crystallisation.

When a further quantity of sulphur is added, the freezing point of lead, silver, and iron sulphides is raised, and that of cuprous sulphide is depressed.

C. H. D.

Electrolytic Extraction of Copper from its Ores. LUCIEN JUMAN (D.R.-P. 189643 and 189974).—The roasted copper ores, when treated with an ammoniacal solution of ammonium sulphite or sulphate, furnish a solution containing 7% of the metal; this solution, when freed from uncombined ammonia by evaporation, is treated with sulphur dioxide, whereby a precipitate of cuprosocupric sulphite ($\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$) is obtained, which is dissolved in an ammoniacal solution of ammonium sulphite or sulphate, and the metal precipitated by electrolysis with 0.5 ampere per sq. decimetre and 0.3 to 0.4 volt. The ammonia and ammonium salts can be again utilised in subsequent extractions of the roasted ore. By treating ammoniacal solutions of copper with sulphurous acid, or a normal or hydrogen sulphite, a precipitate of cuprous sulphite, cuprosocupric sulphite, or copper ammonium sulphite, or a mixture of these three salts is obtained. The solution is used for the extraction of more copper ores, and the precipitate is treated with an acid, such as sulphuric acid, which only gives rise to a cupric salt, so that a portion of the copper is precipitated, $\text{Cu}_2\text{SO}_3 + \text{H}_2\text{SO}_4 = \text{Cu} + \text{CuSO}_4 + \text{SO}_2 + \text{H}_2\text{O}$, and then subjected to electrolytic refining.

G. T. M.

Conditions of Formation of Natural Copper Carbonates. FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1907, [v], 17, i, 82—85. Compare *Rend. Accad. Lincei*, 1906, [v], 15, ii, 732).—From the results of experiments in which carbon dioxide was passed through copper sulphate solution placed in a tall cylinder and containing powdered marble in suspension, the author draws the following conclusions: (1) The necessary condition for the formation of the less basic of the two natural copper carbonates, namely, azurite, is the presence of calcium carbonate in large excess compared with the copper sulphate. (2) The presence of carbon dioxide, which dissolves the calcium carbonate, accelerates the formation of both malachite and azurite, and is possibly indispensable for the formation of the latter mineral, since only by its aid can a sufficiently large amount of calcium carbonate be brought into solution.

T. H. P.

Determination of Atomic Weight of Europium. GUSTAV JANTSCH (*Compt. rend.*, 1908, 146, 473—475).—Owing to the discrepancies existing between the values for the atomic weight of europium (Demarçay, $\text{Eu} = 151$, Abstr., 1900, ii, 481; Urbain and Lacombe, $\text{Eu} = 151.99$, Abstr., 1904, ii, 340, and Feit and Przibylla, $\text{Eu} = 152.57$, Abstr., 1906, ii, 745), the author has, at Urbain's

suggestion, undertaken a redetermination of the constant. The method employed was the one used by Urbain and Lacombe (*loc. cit.*), and consisted in preparing the octahydrated sulphate from a nitric acid solution of the pure oxide, and weighing the anhydrous sulphate and the oxide obtained on ignition of the same. The purity of the oxide used was tested by photographing its spectrum, obtained by the electric arc (Griner and Urbain, this vol., ii, 108), on the same plate as the similarly obtained spectra of gadolinium and samarium; the only lines common to the three spectra were those of iron, silicon, and magnesium, due to traces of these elements as impurities in the carbon electrodes. The mean value of four determinations gives $\text{Eu} = 152.03$ with an error of ± 0.02 when $\text{O} = 16$, $\text{H} = 1.008$, $\text{S} = 32.06$.

M. A. W.

Fluorides of Gadolinium, Neodymium, and Praseodymium.

JOAN POPOVICI (*Ber.*, 1908, 41, 634—635).—*Gadolinium fluoride*, GdF_3 , is obtained as a white, gelatinous precipitate when a solution of the sulphate is mixed with concentrated hydrofluoric acid. The precipitate becomes granular when heated on the water-bath; it is insoluble in water, but somewhat soluble in hot hydrofluoric acid. Gelatinous precipitates of the fluorides of neodymium, NdF_3 , and praseodymium are formed when concentrated hydrofluoric acid is added to solutions of the nitrates. When warmed, the neodymium precipitate forms a pale lilac-coloured, crystalline powder, and the praseodymium fluoride a mass of yellow, glistening crystals.

J. J. S.

Lutecium and Neoytterbium. GEORGES URBAIN (*Compt. rend.*, 1908, 146, 406—408).—In a previous communication (*Abstr.*, 1907, ii, 956), the author has described the resolution of Marignac's ytterbium into the two elements lutecium and neoytterbium, which were characterised by their spark spectra; in the present paper, the results of the atomic weight determinations are recorded. The crude ytterbium was isolated from the xenotime earths by first eliminating the earths of the cerium, gadolinium, terbium, dysprosium, and holmium group by fractional crystallisation of the ethyl sulphates; the mother liquors, which contained the yttrium, erbium, thulium, and ytterbiums, were then submitted to repeated fractional crystallisations of the nitrates (*Abstr.*, 1907, ii, 956), involving in all 15,000 successive crystallisations. The atomic weight of the ytterbiums, determined by analysis of the octahydrated sulphates of sixteen successive fractions, varied from 170.66 in the first fractions to 174.04 in the latter fractions. From the ytterbium sulphate, corresponding with atomic weight of 173.5, the base was fractionally precipitated by dilute sodium hydroxide, and each fraction converted into the sulphate; the atomic weight of the element yielding the weaker base (lutecium) was found to be 173.82, and that of the stronger (neoytterbium) 171.70.

The magnetic susceptibilities of the oxides of the two elements were determined by means of Curie and Chéneveau's magnetic balance; neoytterbia is much more para-magnetic than lutecia, the ratio between the two values being represented by the fraction 53/13.

In conclusion, the author claims priority against Auer von Welsbach [*Sitzungsber. K. Akad. Wiss. Wien. (Math. Natur. Klasse)*, 1907, 468] on the ground that the two elements *aldebaranium* and *cassiopeium*, isolated by him from ytterbium, are identical with lutecium and neoytterbium respectively. M. A. W.

An Isomeric Modification of Hydrated Hypovanadic Acid. GUSTAVE GAIN (*Compt. rend.*, 1907, 146, 403—405).—Hydrated hypovanadic acid, $V_2O_4 \cdot 2H_2O$ (Abstr., 1907, ii, 32), when kept out of contact with the moisture of the air, loses its red colour and changes into an olive-green isomeric form. Each isomeride loses H_2O at $140\text{--}150^\circ$, forming the bluish-black monohydrate, $V_2O_4 \cdot H_2O$, or when heated in hydrogen at $200\text{--}250^\circ$ is converted into the black tetroxide, V_2O_4 . The red hydrated hypovanadic acid dissolves in sulphuric acid to form an azure-blue solution containing the sulphate, $V_2O_4 \cdot 2SO_3$; the green isomeride, under similar conditions, gives a green solution, the heats of solution in the two cases being 12.62 Cal. and 10.89 Cal. respectively, and each solution, on neutralisation with potassium hydroxide, becomes colourless. The heat of neutralisation of the blue solution is 16.92 Cal., and that of the green solution 18.56 Cal. It follows therefore that the loss of energy involved in the change from the unstable, red modification of hydrated hypovanadic acid to the stable, green isomeride is equivalent to 1.64 Cal. M. A. W.

Hardness of Aluminium Zinc Alloys. A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 95—100. Compare this vol., ii, 294).—Here, as in the case of tin and lead, the close relation existing between the structure and hardness of an alloy is very evident from the resemblance between the curves representing the relation between the composition of an alloy and its solidifying point and hardness respectively. The hardest alloy is one containing 30% zinc, which very much resembles the alloy of composition 72% aluminium, 24% zinc, 4% copper. The alloys containing 20—25% of zinc have a strong tendency to combine with iron, forming probably a definite chemical compound with great development of heat. The composition and limit of elasticity curve does not altogether correspond with the other curves, the variation of elasticity depending chiefly on the formation of solid solutions, but the hardest alloy has also the highest limit of elasticity. Z. K.

Alloys of Aluminium with Copper, Iron, Nickel, Cobalt, Lead, and Cadmium. ALFRED G. C. GWYER (*Zeitsch. anorg. Chem.*, 1908, 57, 113—153).—From an investigation of these alloys by Tammann's method of thermal analysis, controlled by microscopic observations, evidence has been obtained of the existence of the following compounds: $CuAl_2$, $CuAl$, Cu_3Al ; $FeAl_3$; $NiAl_3$, $NiAl_2$, $NiAl$; Co_3Al_{13} , Co_2Al_5 , $CoAl$. Lead and cadmium do not enter into chemical combination with aluminium.

Most of the cooling curves were taken in an atmosphere of nitrogen in order to avoid oxidation.

Copper-Aluminium Alloys. (Compare Campbell, Abstr., 1904, ii, 820; Guillet, Abstr., 1905, ii, 712; Carpenter and Edwards, Eighth

Rep. Alloys Research Committee, 1907).—The freezing-point curve of these alloys shows a maximum at 1050° and 87.6% copper, corresponding with the compound Cu_3Al , two breaks at 625° and 56% and at 590° and 45% of copper respectively, a minimum at 88.5% of copper, and a eutectic point at 545° and 32.5% of copper, the components of the mixture being the compound CuAl_2 and mixed crystals containing 4% of copper. Three series of mixed crystals contain 0–4%, 71–88.5%, and 91.5–100% of copper respectively. From 88.5–91.5% of copper, the alloys consist of the two saturated mixed crystals, but, although the curve shows a minimum at the point, there is no true eutectic. At 625° , the saturated mixed crystal containing 71% of copper reacts with the fused mass to form the compound CuAl ; at 590° , the latter reacts with the fused mass containing 44% of copper to form a third compound, CuAl_2 .

The work of Guillet (*loc. cit.*) is adversely criticised, and the author's results differ from those of Carpenter and Edwards (*loc. cit.*), inasmuch as the latter observers suggest the formation of a compound Cu_4Al , but did not detect the well-defined compound CuAl .

Iron-Aluminium Alloys. (Compare Guillet, *Abstr.*, 1902, ii, 21; Roberts-Austen, *Engineering*, 1895, 59, 744).—The freezing-point curve falls fairly rapidly from 100–50% of iron, shows a distinct break at the latter point, falls slowly from 50–30% of iron, and then rapidly to the melting point of aluminium. Two series of mixed crystals contain 40–48% and 66–100% of iron respectively; the end member of the first series may be the compound FeAl_3 (40.7% of iron). Alloys containing 60–65% of iron show eutectic breaks in the cooling curve at 1087° , but the breaks occur at higher temperatures from 50–57.5% of aluminium; alloys containing 52–65% contain a eutectic of the same structure, but the latter appears to differ in structure from the eutectic in 50% iron. Several points in the behaviour of alloys containing 48–66% iron remain unexplained.

Only alloys containing more than 70% of iron are magnetic, and the temperature at which the magnetic permeability disappears on heating is gradually lowered as the proportion of aluminium increases.

Nickel-Aluminium Alloys.—These metals combine almost explosively when heated at 1300° . The cooling curve was taken in magnesia tubes. The freezing-point curve shows a maximum at 1628° and 68.4% of nickel, corresponding with the compound NiAl , two breaks at 830° and 27% and 1130° and 42% of nickel respectively, a minimum at 87% nickel, and a eutectic point (Al—NiAl_3) at 630° and 6% of nickel. Two series of mixed crystals contain 68.4–81% and 87.5–100% of nickel respectively at 1370° , but the limits of saturation are considerably displaced on change of temperature. For example, the alloy containing 85% of nickel becomes homogeneous on prolonged heating at 1050° . The explanation of the minimum in the curve is the same as in the case of the iron-aluminium alloys, to which these alloys bear a close resemblance. At 1130° , NiAl reacts with the fused mass to form the compound NiAl_2 , and at 830° the latter reacts with the fused mass to form a third compound, NiAl_3 (long needles).

Only alloys containing more than 85% of nickel are magnetic, and the magnetic power falls off rapidly with decrease in the proportion of

nickel. The temperature at which the magnetic permeability disappears is greatly lowered by the presence of aluminium.

Cobalt-Aluminium Alloys.—The freezing-point curve of these alloys shows a maximum of 1628° and 68.5% of cobalt, corresponding with the compound CoAl , two breaks at 1165° and 38% and 940° and 20% of cobalt, and a minimum at 90% of cobalt. Two series of mixed crystals contain 68.5–80% and 90.5–100% of cobalt respectively. Alloys containing 82–90% of cobalt did not become homogeneous on heating for three hours at 1250 – 1270° . At 1165° , the compound CoAl reacts with the fused mass to form the compound Co_2Al_5 ; at 940° , the latter reacts with the fused mass to form a third compound, $\text{Co}_3\text{Al}_{13}$.

Only alloys containing more than 68.5% of cobalt are magnetic, and the temperature at which the magnetic power disappears on heating is progressively lowered by the addition of aluminium.

Aluminium-Lead Alloys. (Compare Heycock and Neville, *Trans.*, 1892, 61, 888).—These metals are not miscible in the fused state. Alloys containing up to 5% of lead solidify without separating into two layers, forming a sort of emulsion.

Aluminium-Cadmium Alloys.—These metals are also not miscible in the fused state. Separation into two layers only takes place when the alloy contains more than 10% of cadmium.

The paper is illustrated by twenty-two photomicrographs. G. S.

Preparation of Hydrosols of Metallic Hydroxides from Hydrogels. ARTHUR MÜLLER (*Zeitsch. anorg. Chem.*, 1908, 57, 311–322).—Colloidal solutions of certain metallic hydroxides have been prepared by dissolving the precipitated washed hydroxides (hydrogels) in dilute mineral acids, or in strongly hydrolysed solutions of the corresponding metallic salts. The hydroxide is shaken up in a flask with water, and the acid or salt solution added in successive portions until a clear solution is obtained, the mixture being well boiled after each addition of electrolyte.

The preparation, by the above method, and the properties of colloidal solutions of the hydroxides of aluminium, thorium, yttrium, cobalt, and iron are described. The solutions show the usual properties of colloidal solutions, the particles being positively charged.

There is no definite relation between the quantity of electrolyte used and the amount of hydroxide brought into solution, the amount of electrolyte required depending on the age and previous treatment of the colloidal hydroxide. G. S.

The Decarburisation of Iron. FRIEDRICH WÜST (*Metallurgie*, 1908, 5, 7–12).—In the conversion of cast-iron into malleable-iron by heating in contact with iron oxide, the removal of carbon only begins after a decomposition of the carbide (cementite) into ferrite and carbon (temper-carbon) has taken place. By experiments with a cast-iron containing 4.15% of carbon, 3.45% of which was in the form of temper-carbon, it was found to be immaterial whether the iron was in contact with the ferric oxide or not. By exhausting the apparatus and analysing the gases formed from time to time, it was found that

the oxidising agent is oxygen, evolved by the ferric oxide at 1000° and upwards. This oxygen diffuses into the iron, forming carbon dioxide, which then diffuses further, being converted into carbon monoxide by the temper-carbon in the interior. This carbon monoxide is reoxidised by the ferric oxide, ferrous oxide and metallic iron being produced. Should the quantity of iron oxide be insufficient, the pressure of carbon dioxide may rise to such an extent that the process is reversed, the outer layers of iron being carburised by the decomposition of the carbon dioxide.

This explanation of the process is confirmed by the microscopic examination of the outer and inner layers of the mass of iron.

C. H. D.

Influence of Phosphorus on the System Iron-Carbon.

FRIEDRICH WÜST (*Metallurgie*, 1908, 5, 73—87).—The temperature at which saturated iron-carbon alloys begin to solidify is lowered by the addition of phosphorus, 1% of phosphorus causing a depression of 27° . When the proportion of phosphorus exceeds 6.7%, the freezing point again rises. The ternary eutectic melts at 950° , and contains 6.7% P, 2.0% C, and 91.3% Fe. The eutectic disappears at a phosphorus content of 15%, corresponding with the phosphide Fe_3P . Alloys containing between 6.7% and 15% of phosphorus show crystals of the phosphide.

The solubility of carbon in iron is reduced by the addition of phosphorus, but the temperature of formation of the eutectoid perlite is not influenced by the presence of the phosphide.

The paper is illustrated with photomicrographs, in some of which the oxidation-tints of the constituents are reproduced by colour-photography.

C. H. D.

Different Colours of Ferric Oxide, an Effect of the Size of the Grains.

LOTHAR WÖHLER and C. CONDREA (*Zeitsch. angew. Chem.*, 1908, 21, 481—486).—A study of the conditions of the formation of differently coloured ferric oxides. The violet substance, formed by heating yellowish-red ferric oxide with sodium chloride in an iron crucible over the blowpipe flame, is pure ferric oxide. It is prepared also by heating yellow ferric oxide with other salts, such as calcium chloride, sodium sulphate, potassium chloride, and borax. The shade varies from brown to violet with the temperature and with the amount and nature of the salt added, the deepest shades being obtained when the added salt is not less than 6% of the weight of the ferric oxide. The amount of salt which must be added diminishes as the temperature is raised; the reaction does not take place below the m. p. of the salt. The rate of cooling is without influence on the shade, at least with small quantities. At low temperatures, the presence of water is found to affect the shade in the same manner as that of salts at high temperatures. These results point to the size of the grains as determining the colour of the ferric oxide. In agreement with this, brown or violet ferric oxide is converted into the yellowish-red variety by alternate grinding and washing.

G. Y.

Ferronitrososulphides. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 202—207. Compare this vol., ii, 41).—The author discusses previous work on the constitution of Roussin's salts, and describes further experiments bearing on this question.

An excess of silver sulphate together with dilute sulphuric acid was treated with potassium ferronitrososulphide in an atmosphere of carbon dioxide. Subsequent titration with permanganate showed that, in this reaction, the iron is reduced quantitatively to the ferrous state. In some cases, when the temperature and acidity are chosen so as to cause the reaction to proceed very rapidly, the iron may undergo only partial reduction, a large proportion of the nitroso-groups not being oxidised, but yielding hyponitrous acid. The reducing action of the nitroso-groups here manifest is demonstrated even more clearly by treating excess of ferric sulphate and silver sulphate in presence of sulphuric acid with potassium ferronitrososulphide; in this reaction, 7 mols. of nitric oxide and 7 atoms of ferrous iron are obtained per mol. of ferronitrososulphide.

The action of potassium ferronitrososulphide on silver sulphate yields silver nitrate and silver hyponitrite, the gas evolved under the action of sulphuric acid consisting of nitric oxide and nitrous oxide; the latter owes its formation to the deficit of ferric iron. The production of 7 mols. of nitric oxide per mol. of ferronitrososulphide is hence necessarily connected with the formation of seven ferrous ions. The reaction in presence of ferric salt may be represented by the equation: $[\text{Fe}_4\text{S}_3(\text{NO})_7] + 3\text{Fe}^{+++} = 7\text{Fe}^{++} + 7\text{NO} + 3\text{S}^0$. Seven mols. of nitric oxide are also liberated from potassium nitrososulphide by the action of copper sulphate, which acts as an oxidising agent, and passes into the cuprous form.

These results lead to the conclusion that Roussin's salts do not contain the residue of hyponitrous acid, $(\text{ON}:\text{NO})^0$. These salts contain a univalent group, NO^0 , capable of acting in two ways: firstly, giving hyponitrous acid, and, secondly, of yielding nitric oxide under the action of various oxidising agents. T. H. P.

Hydrolysis of Ferric Chloride. Effect of the Valency of the Negative Ions. G. MALFITANO and LEOPOLD MICHEL (*Compt. rend.*, 1908, 146, 338—341. Compare this vol., ii, 111).—It is known that the precipitation of ferric colloids by anions diminishes as the valency of the latter increases. It is now shown that the anions act according to the same rule in preventing the formation of colloid. The authors have measured the increase in the conductivity at 50° of $N/150$ solutions of ferric chloride containing nitric, oxalic, hydrochloric, sulphuric, arsenic, and phosphoric acids at concentrations $N/1000$, $N/250$, and $N/100$ as a function of the time, and have illustrated the results by curves.

The activity of the acids in retarding the progress of the irreversible hydrolysis (indicated by the increase in conductivity with the time) is shown to be partly dependent on their degree of ionisation, but the influence of the anion is shown by the difference in activity between equally ionised acids, such as hydrochloric and nitric acids, and particularly by the activity of oxalic acid, which is much higher than

would be expected from its ionisation coefficient. As the concentration of the acids diminishes, the influence of the hydrogen ions becomes negligible, and that of the anions, when multivalent, preponderant, probably through the replacement of chlorine in ferric chloride and formation of less dissociable molecules.

Curves are given showing the increase with time of the conductivity of $N/150$ ferric chloride solutions containing varying quantities of phosphoric acid. The increase is least when the concentration of the acid is $N/250$; at lower concentrations, the hydrolysis and formation of colloid are only slackened, and at higher concentrations the formation of colloid is definitely prevented, the conductivity meanwhile increasing with time. This can only be explained by the quantity of free hydrogen chloride displaced by the phosphoric acid. The phenomenon becomes more evident at 100° ; solutions of ferric chloride containing an equivalent of phosphoric acid, when heated at this temperature, give a white positive colloid containing iron and phosphoric acid, which tends to disappear on cooling the more easily the greater the concentration of the ferric chloride. The formation of the hydroxide colloid is prevented when the ratio Fe/PO_4 reaches the values $1/6000$ at 18° , $1/200$ at 50° , and $1/16$ at 100° , increase in temperature and dilution affecting only the irreversible, not the reversible, hydrolysis. The authors conclude that the ferric ions become less apt to form complex ions, $(\text{Fe}[\text{Fe}(\text{OH})_3]_n)$, as the valency of the accompanying anions increases, and the micro-cells, conceived as complex ions of large dimensions (n being very great), protect the molecules of the hydroxide from the hydrochloric acid. Consequently, if these complex ions cannot be formed, the irreversible hydrolysis is impeded.

E. H.

Thermal Dissociation of the Anhydrous Sulphates of Iron. GUSTAV KEPPELER and JEAN D'ANS (*Zeitsch. physikal. Chem.*, 1908, 62, 89—118).—The authors have studied some problems bearing on the ferric oxide contact process for the manufacture of sulphuric acid (compare Lunge and Pollitt, *Abstr.*, 1903, ii, 70; Lunge and Reinhardt, *Abstr.*, 1904, ii, 724). The anhydrous sulphates investigated were ferric sulphate, basic ferric sulphate, $\text{Fe}_2\text{O}(\text{SO}_4)_2$, and ferrous sulphate; details of the preparation of these substances are given in the paper.

A current of air or nitrogen was passed through a tube containing the anhydrous sulphate and heated to a definite temperature; the proportion of sulphur dioxide and sulphur trioxide in the issuing gas was then determined analytically.

The equilibrium between ferric sulphate and sulphur trioxide is represented as $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$. The change of the SO_3 tension with temperature in this system is given adequately between 500° and 700° by the formula $\log p = 11.8626 - 44720/4.584T$. In the gaseous phase, the equilibrium $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ is established, and the equilibrium constants found for this reaction are in good agreement with the values given by Bodenstein and Pohl (*Abstr.*, 1905, ii, 581).

The tension of sulphur trioxide over basic ferric sulphate is greater than over normal ferric sulphate at the same temperature, and the

former is accordingly regarded as a labile compound. It was observed that in the gaseous phase at the lower temperatures the expected equilibrium was not reached; in all cases too much sulphur dioxide was found.

The behaviour of ferrous sulphate is best represented by the equation $2\text{FeSO}_4 \rightleftharpoons (\text{Fe}_2\text{O}_3, \text{SO}_3) + \text{SO}_2$, the sulphate on the right hand side of this equation being the normal one. In the gaseous phase above ferrous sulphate at a high temperature there is a constant ratio between the partial pressures of sulphur dioxide and sulphur trioxide.

Indications were obtained that at 640° ferric oxide undergoes an allotropic change. It was at this temperature that Lunge and Reinhardt (*loc. cit.*) found a maximum yield of sulphur trioxide from gases containing 2.1% of the dioxide. At this temperature, also, the observed tension of sulphur trioxide is the same as that of ferric sulphate. Above 640° , the velocity of the catalytic combination of sulphur dioxide and oxygen is greater than the velocity of formation of ferric sulphate.

J. C. P.

New Method for Determining the Tension of Sulphates. LOTHAR WÖHLER, W. PLÜDDERMANN, and P. WÖHLER (*Ber.*, 1908, **41**, 703—717).—This investigation was undertaken as the knowledge of the partial pressures of sulphur trioxide from sulphates is necessary for the interpretation of the contact process. The tension of the sulphates was determined by a statical method which had to satisfy the following conditions: (1) sulphur trioxide should not condense, (2) the gas ought not to come in contact with the mercury in the manometer, (3) the equilibrium $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ must be accomplished in the shortest possible time, (4) sufficient substance should be taken in order to carry out a series of determinations, and (5) no india-rubber connexions or greased cocks should be employed.

The apparatus consisted of a porcelain tube which contained the sulphate, placed in a platinum tube, on the top of which a piece of platinum gauze was placed, and then some spongy platinum. The tube, heated in a Heräus vertical tube furnace, is connected to a condenser, heated by steam, by means of a ground-joint smeared with deliquesced phosphoric oxide and sealed with mercury. The manometer is connected to the condenser by a T-piece through a tube containing sodium hydroxide and calcium chloride, the other end of the T-piece being connected to the pump.

The equilibrium pressure was determined by closing the tube, heated to the desired temperature, and allowing air into the evacuated apparatus at a known pressure, opening momentarily the connecting stopcock, and, if the pressure did not change, the equilibrium pressure was reached. With ferric sulphate, for example, at 599° , the pressure observed was 53.0 mm.; at 630° it was 102.5 mm. To ascertain whether ferric sulphate was decomposed direct into oxide and sulphur trioxide, the basic material, $\text{Fe}_2\text{O}_3, \text{SO}_3$, was heated, and the tension found at three different temperatures agreed with those found for $\text{Fe}_2\text{O}_3, 3\text{SO}_3$, thus showing that a basic sulphate of iron is not formed and that there is no evidence for the formation of a solid solution of oxide and

sulphate. In this way, it was found that aluminium and thorium sulphates also decompose directly to oxide. As the normal chromium and titanium sulphates could not be obtained, the water-free basic sulphates, $\text{Cr}_2\text{O}_3, 2\text{SO}_3$, $2\text{Cr}_2\text{O}_3, 3\text{SO}_3$, were prepared the first by heating in a stream of carbon dioxide to 280° , and the second by heating to $450\text{--}460^\circ$ in a crucible. With the latter basic sulphate, the tensions observed are lower than with the more acid sulphate. A material of composition $7\text{Cr}_2\text{O}_3, 2\text{SO}_3$ showed the same tensions as the sulphate $2\text{Cr}_2\text{O}_3, 3\text{SO}_3$. Similar results were obtained with the basic titanium sulphates $\text{TiO}_2, \text{SO}_3$, $2\text{TiO}_2, \text{SO}_3$.

Copper sulphate is shown to form in addition to the normal sulphate, only the basic oxide, $2\text{CuO}, \text{SO}_3$. Cerium sulphate by heating loses oxygen and passes into cerous sulphate.

The method of calculating the partial pressure of sulphur trioxide from the total pressure is given, and the heat of dissociation of $\text{Fe}_2\text{O}_3, 3\text{SO}_3$, $\text{Al}_2\text{O}_3, 3\text{SO}_3$, $\text{Cr}_2\text{O}_3, 2\text{SO}_3$, $\text{ThO}_2, 2\text{SO}_3$, CuO, SO_3 , and ZnO, SO_3 found to be 27, 17, 22, 21, 13, and 36 calories respectively.

A method has been devised for the quantitative separation of iron and zinc by means of their different tensions. At 680° , the tension for ferric sulphate is nearly 1 atmos., whereas for zinc sulphate it is only 6 mm., so that by heating the mixture of sulphates at that temperature until constant in weight, the ferric oxide remains mixed with the unchanged zinc sulphate. Other separations can be effected, but, in general, metals of similar chemical characteristics cannot be separated in this way, for example, iron and aluminium. W. R.

Metallic Silicates. I. Preparation of Metallic Silicates by Wet Methods. EDUARD JORDIS (*J. pr. Chem.*, 1908, [ii], 77, 226—237. Compare this vol., ii, 103).—A discussion of the conditions which must be observed in the study of the formation of silicates of the heavy metals in the wet way, and a criticism of Gröger's investigation of copper carbonate (*Abstr.*, 1900, ii, 542). G. Y.

Metallic Silicates. II. Interactions of Sodium Silicate and Metallic Salt Solutions. EDUARD JORDIS AND W. HENNIS (*J. pr. Chem.*, 1908, [ii], 77, 238—261).—The reactions of copper sulphate, ferrous sulphate, and ferric chloride with sodium silicate in aqueous solution do not take place according to the equations which can be written for them. If the reagents are mixed in equivalent amounts, an acid liquid is obtained which contains silicic acid, in considerable amount from the ferric chloride reaction. The amount of the metal found in the filtrate varies independently of the reaction of the liquid, and is especially large with ferric chloride. In presence of much alkali, the metal dissolves together with silicic acid. If an excess of either reagent is added, the portion which passes into the filtrate increases with the excess from a minimum.

The course of the reaction is especially complicated in the case of ferric chloride. The acid filtrate requires considerable amounts of alkali for neutralisation, and thereafter combines with still larger amounts of alkali before becoming alkaline. This reaction is taken part in, not only by the precipitate, but also by dissolved substances.

The amount of alkali neutralised is approximately proportional to the total amount of silicic acid present. Precipitates of varying composition are obtained from the clear filtrate by addition of hydrochloric acid, by the action of heat, and on neutralisation. Permanent changes are produced by heating. In many cases the reaction, especially between the precipitate and the mother liquor, takes place slowly. The precipitates are soluble in acids only when freshly formed. Clear filtrates are obtained from the turbid reaction mixture only when a colloidal layer has been formed on the surface of the filter. Pure ferrous silicates are bluish-green, and on oxidation become yellow, passing through green or brown intermediate stages.

The copper silicates are blue or, when anhydrous, green; precipitates formed with an excess of copper sulphate are more or less green, in consequence of the formation of crystalline, basic copper sulphate.

The silicate precipitates remain unchanged when boiled with their mother liquors, whereas under the same conditions a partly oxidised ferrous hydroxide becomes black; this blackening, however, does not take place if the precipitate is ground with colloidal silica before being boiled.

Solutions of $\text{Na}_2\text{Si}_2\text{O}_5$ or 2NaHSiO_3 , which analytically are identical, react in the same manner as solutions of Na_2SiO_3 . It is probable that they contain the ion $\text{Si}_2\text{O}_5^{''}$. G. Y.

Freezing-point Curve of the Nickel Sulphides. K. BORNE-MANN (*Metallurgie*, 1908, 5, 13—19).—Mixtures containing from 0% to 31% sulphur were examined, mixtures richer in sulphur being unstable under atmospheric pressure. The components are completely miscible in the liquid state. The equilibrium diagram is complicated, five series of mixed crystals separating from the fused mass. The freezing-point curve, up to 31% sulphur, consists of five branches, with eutectic points at 21.4% and 30.6% sulphur and 644° and 812° respectively. The only compound capable of existence in contact with the melt is Ni_3S_2 , melting at 787° . A number of transformations take place in the solid state, the existence of the compounds NiS , Ni_3S_4 , and NiS_2 being proved by Tammann's method. All these dissociate below the melting point. The compound Ni_2S has no existence, mixtures of that composition having a eutectic structure. The existence of Ni_6S_5 is highly probable, but mixtures of this composition lose sulphur on fusion. The curves representing the thermal transformations in the solid state have been completely studied, there being a well-marked eutectoid point at 29.7% sulphur and 520° .

The results of the thermal analysis are fully confirmed by a comparative study of the density and microscopic structure of mixtures allowed to cool slowly and rapidly quenched. C. H. D.

The Constitution of Nickel Matte. K. BORNE-MANN (*Metallurgie*, 1908, 5, 61—68. Compare preceding abstract).—The thermal and microscopic examination of mixtures of ferrous sulphide with the stable nickel sulphide, Ni_3S_2 , shows the existence of a compound $2\text{FeS}, \text{Ni}_3\text{S}_2$, which melts at 840° and dissociates considerably on

fusion. The compound forms mixed crystals in all proportions with Ni_3S_2 , but ferrous sulphide only dissolves it to a very small extent in the solid state. At lower temperatures, transformations occur which it has not been possible to determine accurately.

When the mixtures are prepared with a nickel sulphide of the composition Ni_2S , a more complicated thermal diagram is obtained. This compound, although incapable of separate existence, forms stable compounds with ferrous sulphide. The only compound which is stable in contact with the fused mass is $2\text{FeS}, \text{Ni}_2\text{S}$, which melts at 886° , but breaks up on cooling to 575° into FeS and $3\text{FeS}, 2\text{Ni}_2\text{S}$. At a still lower temperature this compound combines with FeS to form $4\text{FeS}, \text{Ni}_2\text{S}$, but the change is not accompanied by development of heat, and could only be detected by microscopic examination and by determinations of density.

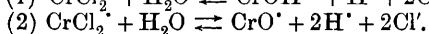
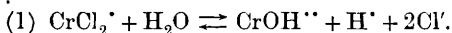
C. H. D.

Molecular Weight of the Greyish-blue Hydrate of Chromic Chloride. I. Neutralisation of the Salt by Sodium Hydroxide. JULIUS SAND and F. GRAMMLING (*Zeitsch. physikal. Chem.*, 1908, 62, 1—27. Compare Werner and Gubser, Abstr., 1901, ii, 453; Bjerrum, Abstr., 1907, ii, 554, 662).—If sodium hydroxide is gradually added to a solution of the greyish-blue chromic chloride, the colour assumes more and more a green tinge, but remains perfectly clear until 1 molecule of sodium hydroxide has been added for every atom of chromium present; further addition of the alkali produces an opalescence, and, finally, when two or more molecules of sodium hydroxide have been added for every atom of chromium, a precipitate is formed.

The gradual neutralisation of the greyish-blue salt by sodium hydroxide in the first stage, and the consequent removal of the hydrogen ions, have been followed by the electrochemical method already employed (Sand and Eisenlohr, Abstr., 1907, ii, 178). Two formulæ showing the relation between the *E.M.F.* of a hydrogen electrode immersed in a partly neutralised solution of the chloride and the amount of sodium hydroxide added are deduced; these are respectively based (1) on the supposition that the chromium ion is Cr^{+++} , and (2) on the supposition that it is Cr_2^{+++} . The experimental figures are in good agreement with the second formulæ, and the greyish-blue salt is accordingly formulated as $\text{Cr}_2(\text{H}_2\text{O})_{12}\text{Cl}_6$, and it is regarded as probable that the two chromium atoms in this compound are connected with each other through an oxygen atom. The reaction which takes place on the first addition of sodium hydroxide is represented by the equation

$\text{Cr}_2(\text{H}_2\text{O})_{12}\text{Cl}_6 + 2\text{NaOH} = 2\text{Cr}[\text{OH}(\text{H}_2\text{O})_x]\text{Cl}_2 + 2\text{NaCl} + (12 - 2x)\text{H}_2\text{O}$.
At this stage of the neutralisation the concentration of the hydrogen ions will be determined by the hydrolytic equilibrium: $\text{Cr}_2^{+++} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CrOH}^{++} + 2\text{H}^+$.

The green chromic chloride, on the basis of similar electrochemical measurements, is found to be unimolecular. The addition of sodium hydroxide to a solution of this salt leads to simultaneous hydrolysis in two directions:



J. C. P.

Molecular Weight of the Greyish-blue Hydrate of Chromic Chloride. II. Hydrolysis of the Salt by Potassium Iodide and Iodate. JULIUS SAND and F. GRAMMLING (*Zeitsch. physikal. Chem.*, 1908, **62**, 28—43. Compare preceding abstract).—The velocity with which solutions of the greyish-blue hydrate of chromic chloride liberate iodine from a mixture of potassium iodide and iodate has been determined, and from these measurements the proportion of hydrogen ions in solutions of the hydrate has been deduced (compare Sand and Eisenlohr, Abstr., 1907, ii, 179).

On the basis of the supposition that the hydrolytic equilibrium involved is $\text{Cr}_2^{+++} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CrOH}^+ + 2\text{H}^+$, formulæ are deduced for the rate of liberation of iodine from the iodide-iodate mixture which are in good agreement with the experimental figures. On the other hand, there is no agreement between the experimental figures and the values of the velocity-coefficient based on the supposition that chromic chloride has the unimolecular formula $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$. The evidence therefore goes to show that this formula must be doubled, and that the molecule of the greyish-blue hydrate contains two chromium atoms linked together. J. C. P.

Chromates. NICOLA PARRAVANO and A. PASTA (*Zeitsch. anorg. Chem.*, 1907, **57**, 240. Compare Abstr., 1907, i, 961).—A claim for priority against Briggs (this vol., ii, 113) with reference to the preparation of compounds of certain dichromates with pyridine.

G. S.

Sulphate of Tervalent Uranium. ARTHUR ROSENHEIM and HEINRICH LOEBEL (*Zeitsch. anorg. Chem.*, 1908, **57**, 234—239).—A solution of uranium trichloride, UCl_3 (Peligot, 1842), in a large excess of hydrochloric acid, was obtained by the electrolytic reduction of the trioxide, UO_3 , dissolved in hydrochloric acid (D 1.12) in a special apparatus, in which a layer of mercury was used as the cathode. To complete the reduction, the solution had to be cooled to 0° towards the end of the experiment. In the presence of traces of dissolved mercury or of platinum, the reduction stops at quadrivalent uranium, probably because these substances facilitate the liberation of hydrogen.

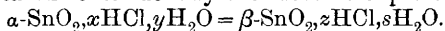
The great majority of reagents, even water, decompose the acid solution of uranium trichloride with formation of quadrivalent uranium compounds, but when the solution is mixed with fairly concentrated sulphuric acid, both previously cooled to 0° , deep brown leaflets of the compound $\text{UH}(\text{SO}_4)_2$ separate. Before analysis, the crystals were washed with anhydrous acetic acid, but, owing to the difficulty of removing all the sulphuric acid, the formula of the compound is not regarded as being conclusively established.

G. S.

Hardness of Tin and Lead Alloys. A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 92—95).—Tin and lead do not form chemical compounds, but solid solutions are formed by tin in lead up to the composition 10—15% tin. As tin is added to lead, the hardness of the alloy increases until 40% tin is present, when it

decreases, but at the composition 66% tin, the hardness attains a maximum. Since this point coincides with the eutectic point of the alloy, it confirms the view previously expressed that the hardness of alloys is very closely related to their structure. Z. K.

Stannichlorides of the Type $M_2'SnCl_6$, $M''SnCl_6$. III. Hydrolysis of Stannic Chloride. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 963—993. Compare Abstr., 1905, ii, 40).—The first products of the hydrolysis of stannic chloride are oxychlorides intermediate in nature between meta- and para-chlorostannic acids, and it is these oxychlorides which yield the colour reaction with stannous chloride before β -stannic acid has been formed either as a hydrosol in solution or as a precipitate. The latter occurs the more rapidly the more dilute the solution; at higher concentrations, however, β -stannic acid is not precipitated, but undergoes condensation, forming oxychlorides with a smaller proportion of chlorine, thus leaving more free hydrochloric acid in solution, and the quantity of the latter determined by measuring the electric conductivity of the solution is taken as a measure of the extent of hydrolysis of the stannic chloride (compare Foster, *Phys. Review*, 1899, 9, 41; Kowalewski, Abstr., 1900, ii, 256; Kohlrausch, Abstr., 1900, ii, 408; Van Bemmelen and Klobbie, Abstr., 1900, ii, 338). The increase in the initial electrical conductivity on dilution proceeds more rapidly than is the case for ordinary electrolytes, and the acidity of the solution, in spite of the fact that $SnCl_4$ itself is not an electrolyte and the analogy of $SnCl_4$ with $TiCl_4$ and $SiCl_4$ leads to the conclusion that it decomposes in water, thus: $SnCl_4 + (n+2)H_2O \rightleftharpoons SnO_2 \cdot nH_2O + 4HCl$, and side by side with this the following reaction probably also occurs: $SnCl_4 + mSnO_2 \cdot nH_2O = SnCl_4 \cdot mSnO_2 \cdot nH_2O$ or $SnCl_4 + mSnO_2 \cdot nH_2O = (m+1)[SnO_2 \cdot xHCl \cdot yH_2O]$, but the main reaction, being instantaneous, is not applicable to the slow hydrolysis of stannic chloride. Although all aqueous solutions of stannic chloride are electrolytes when freshly prepared, only those solutions give the reaction with stannous chloride the electric conductivity of which changes with time. It is thus evident that the change in electric conductivity is a consequence of the formation of the derivatives of β -stannic acid, the β -oxychlorides of tin being formed by the gradual condensation of the stannic acid contained in the indefinite oxychlorides of tin termed α -oxychlorides, the hydrochloride thus disengaged causing a rise in the electric conductivity. The slow hydrolysis of stannic chloride may therefore be expressed thus:



In concentrated solutions, part of the stannic chloride decomposes, forming stannic acid, which with undecomposed chloride forms α -oxychlorides containing a high percentage of chlorine, which prevents the condensation of its constituent stannic acid, thus hindering the occurrence of slow hydrolysis. In such solutions, there is also present undecomposed stannic chloride either in the form of hydrates or as chlorostannic acid. If at the very commencement of a reaction hydrochloric acid is added to a dilute solution undergoing slow hydrolysis, the latter cannot proceed, since the condensation of stannic acid is prevented; when, however, the solution is too dilute, the α -oxy-

chlorides contain too little chlorine, consequently, instead of forming β -oxychlorides, they are converted into β -stannic acid, which is precipitated in a more or less condensed form, depending on the time intervening between the preparation of the solution and the precipitation of the acid. Z. K.

Stannichlorides of the Type $M'SnCl_6$, $M''SnCl_6$. IV. Dissociation of Stannichlorides in Aqueous Solutions. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 994—1036. Compare preceding abstract).—Sodium chloride retards the formation of β -oxychlorides in concentrated solutions of stannic chloride; as the solutions are diluted, this effect becomes less, and in very dilute solutions (0.01 part $SnCl_4$ per litre) it considerably accelerates the separation of stannic acid. Probably in concentrated solutions it is the sodium stannichloride which exerts most influence, whereas in dilute solutions the free sodium chloride affects the rate of the reaction. Investigation of the electrical conductivity of such solutions confirms these results, and shows that, as the concentration of sodium chloride is increased, the change in specific conductivity, $\Delta\kappa$, becomes less, and finally becomes constant. The same is true for magnesium chloride, but the action of cadmium chloride is quite different, its log.time-sp. conductivity curve being very similar to that for pure stannic chloride.

The following reasons lead to the conclusion that the metallic stannichlorides are only partly dissociated in solution: (1) the possibility of crystallising them from solutions containing an excess of tin chloride. (2) $\Delta\kappa$ varies in the same way in experiments with an excess of tin chloride as with an excess of sodium chloride, and, since the latter does not influence $\Delta\kappa$ merely as such, the variation of $\Delta\kappa$ must depend on the formation in the solution of a stannichloride. (3) The influence of sodium chloride on the slow hydrolysis of stannic chloride is 420 times as great as that on tin metachloride. (4) The addition of sodium chloride reduces the electrical conductivity to below that of a solution of sodium chloride, and this can, of course, only be due to the presence of a complex compound. (5) $\Delta\kappa$ continually diminishes with time in the case of pure stannic chloride, whereas in the presence of a metallic chloride it remains constant for considerable intervals, and, although the hydrolysis is of the same character with or without the metallic chloride, the stannichloride formed in the presence of the latter acts as a reserve for the continual supply of more ions for preserving equilibrium. (6) The impossibility of obtaining cadmium stannichloride agrees with its abnormal behaviour mentioned above. A large number of experiments with various stannichlorides (0.5 part per litre) shows that, except for zinc and cadmium, $\Delta\kappa$ is constant for ten days and does not depend on the degree of dissociation of the metallic chloride or on the initial conductivity of the solution, but the latter depends on the mobility of the cation. These and other experiments also point to the fact that $\Delta\kappa$ is a true measure of the degree of dissociation of the given stannichloride. In the case of the alkaline earths, in dilute solutions, $\Delta\kappa$ is practically identical for each, but, as the concentration of the free metallic chloride increases, $\Delta\kappa$ becomes least for calcium and highest for barium, this probably depending on the formation of hydrates of the metallic chlorides.

Thus, whilst the quantity of the chloride is small and the active mass of water large, the formation of these hydrates cannot influence the course of the reaction, and Δx therefore indicates the degree of dissociation of the stannichloride, but, when the concentration of the chloride is high, the formation of hydrates diminishes the active mass of water; Δx therefore diminishes, and the extent of this diminution will depend on the degree of hydration of the chloride. This is also observed, to a less extent, in the case of the other metals. Z. K.

Stannichlorides of the Type $M_2'SnCl_6$, $M''SnCl_6$. V. Partition of Stannic Chloride between Two Metallic Chlorides. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1036—1063. Compare preceding abstract).—The conclusions arrived at in the preceding abstracts are confirmed by a spectrophotometric method. As stannic chloride is added to a solution of cobalt chloride, the absorption region of the latter spreads out towards the red end of the spectrum, and at the same time there is increasing absorption at the violet end. By thus investigating the absorption spectra of solutions of stannic chloride, cobalt chloride, and some other transparent chloride, it is possible to calculate the partition of the stannic chloride between the two metallic chlorides. Stannic chloride itself does not absorb light, and the absorption, which after a certain concentration of stannic chloride becomes constant, must thus be due to the formation in solution of cobalt stannichloride, which has a greater absorption-coefficient than cobalt chloride. The quantity of stannichloride in solutions in which it is appreciably dissociated can be calculated by a series of calculations by means of the formula $a = A(c - x) + A'x$ (c = quantity of $CoCl_2$, x = $CoSnCl_6$ formed, A' = fractional-coefficient of absorption of cobalt stannichloride, and A = similar coefficient for cobalt chloride; the values so obtained agreeing well with the experimental results). The equilibrium constant $k = C_c C_s / C_{cs}$ (C_c = concentration of cobalt chloride, C_s = concentration of tin chloride, and C_{cs} = concentration of cobalt stannichloride). Calculating in this way the values $Co:M$ (M = any metal) in relation to the affinity of their chlorides for stannic chloride, and comparing them with the values $1/\Delta x$ for the corresponding metals, there is a striking similarity between the two constants. The following conclusions are also drawn: (1) the affinity constants, K , of the metallic chlorides for stannic chloride are comparable with the affinity of anhydrides for oxides. (2) In the first and second groups of the elements in the periodic system, K increases with increasing atomic weight in the even series and decreases in the odd series. (3) K is greater for those chlorides which have the greatest tendency to hydration. (4) The metallic chlorides which form complex anions have little affinity for stannic chloride. Various theories regarding the formation of double salts are criticised, and it is pointed out that Wells' classification of the halogen double salts rests on their comparison under really non-comparable conditions. Z. K.

Application to Thorium of a General Method of Synthesis of Fluorides and Silicates. ANDRÉ G. DUBOIN (*Compt. rend.*, 1908, **146**, 489—491).—The double fluoride, KF, ThF_4 , obtained by

dissolving thoria in fused potassium hydrogen fluoride, yields thallium fluoride, ThF_4 , in the form of brilliant crystals on fusion with excess of potassium chloride or bromide (Abstr., 1895, ii, 351). The crystals belong to the cubic system, elongated in the direction of one of the axes as in certain specimens of cuprite, they melt at a red heat, are not attacked by concentrated sulphuric acid, are slowly decomposed by the dilute acid or by hydrochloric acid, and on fusion with sodium carbonate yield transparent crystals of thoria which closely resemble the crystals of the original fluoride.

Potassium thorium silicate, $\text{K}_2\text{O} \cdot \text{ThO}_2 \cdot 2\text{SiO}_2$, $D^\circ 4.44$, prepared by the general method already described (Abstr., 1897, ii, 96), forms highly doubly-refracting crystals belonging to the monoclinic or to the orthorhombic system.

M. A. W.

Fluorides and Oxides of Quinquevalent Bismuth. OTTO RUFF [with MAX KNOCH and JULIAN ZEINER] (*Zeitsch. anorg. Chem.*, 1908, 57, 220—233. Compare Weinland and Lavenstein, Abstr., 1899, ii, 370).—Bismuth trifluoride does not combine directly with fluorine, but traces of a higher fluoride appear to be formed by the action of fluorine on bismuth trichloride at -80° .

When "bismuthic acid" is added to concentrated hydrofluoric acid, a colourless, very unstable solution is obtained, which appears to contain mainly bismuth oxytrifluoride, BiOF_3 . On evaporating this solution in a vacuum, the oxyfluoride suffered partial decomposition; on addition of potassium fluoride (1 mol.) before evaporation, the compound (or mixture), $\text{Bi}_3\text{O}_4\text{F}_7 \cdot 3\text{KF}$, was obtained in small, yellow crystals, and with 3 mols. of potassium fluoride the compound, $\text{BiOF}_3 \cdot 3\text{KF}$, in well-formed, colourless prismatic crystals, which become yellow and decompose rapidly in moist air.

In order to throw light on the nature of "bismuthic acid" and "alkali bismuthates," on the existence of which doubt has been thrown by Gutbier and Bünz (Abstr., 1906, ii, 174, 234, 551, 678), the solution of the trioxyfluoride was decomposed by water and nitric acid and by alkali respectively, and nearly pure bismuthic acid and sodium bismuthate isolated. In order to obtain the latter, a solution of the pentoxide in 60% hydrochloric acid was cooled to 0° , and added drop by drop to *N*-sodium hydroxide, also at 0° ; the yellow precipitate, rapidly washed and partially dried on a porous plate, contained 95—98% of its bismuth in the quinquevalent form, and 1 mol. of sodium hydroxide. On further washing, sodium bismuthate loses alkali and darkens in colour; it does not lose much oxygen, even on heating to boiling, when excess of alkali is present. From this bismuthate, by treating with ice cold 15% nitric acid to neutral reaction and washing rapidly by decantation, a reddish-brown precipitate containing up to 93% of bismuth pentoxide is obtained. On treating the fresh pentoxide with 15% sodium hydroxide, it slowly changes to yellow bismuthate, so that the statement of Gutbier and Bünz (*loc. cit.*), that the higher oxides of bismuth have no acidic properties, is incorrect.

G. S.

Physico-chemical Researches on the "Explosive" Platinum Metals. ERNST COHEN and TH. STRENGERS (*Zeitsch. physikal. Chem.*, 1908, 61, 698—752).—It has been long known that some at least of the metals of the platinum group are explosive under certain conditions, and the authors have set themselves the task of determining exactly the conditions under which the phenomenon is observed and the cause to which it is due.

To prepare the "explosive" metal, the metal in the ordinary form is alloyed with a large excess of zinc, and the alloy is treated with hydrochloric acid. The residue from this treatment explodes when heated in the case of rhodium, iridium, and ruthenium; from palladium and osmium no explosive residues have been obtained; the platinum residue is sometimes explosive, sometimes not, and the factors which determine this result have not been definitely ascertained.

Explosive rhodium is obtained also when cadmium is used instead of zinc in its preparation. With zinc, the rhodium appears to form a solid solution, and it is not possible to extract all the zinc with hydrochloric acid.

When the rhodium residue is kept at 100° or 200° for a few days, it is no longer explosive. It is shown that explosive rhodium contains hydrogen and oxygen, and that, when the utmost precautions are taken to exclude air during the preparation of the residue, the latter is not explosive. A similar remark applies to iridium. Ruthenium, on the other hand, yields an explosive product even when the greatest care has been taken to exclude air. When rhodium is alloyed with lead, and the alloy is treated with nitric acid, a residue is obtained containing oxides of nitrogen; this residue explodes when heated, even although air is excluded.

The amount of heat developed by the explosion of the "explosive" rhodium is of the same order of magnitude as that calculated on the basis of the view that the explosion is due to the combination of hydrogen and oxygen which have been occluded in the rhodium. This view, in conjunction with the fact, established by the author's experiments, that rhodium becomes passive on contact with nitric acid, gives a satisfactory explanation of all observations made by earlier workers. It is therefore unnecessary to suppose, as Bunsen and Debray did, that the explosion affords evidence of an allotropic change. It is possible, however, that this is the correct explanation in the case of ruthenium.

J. C. P.

The Oxidisability of Platinum. CHARLES MARIE (*Compt. rend.*, 1908, 146, 475—477).—When plates of platinum or platinum-iridium are placed in an alkaline solution of potassium permanganate at the ordinary temperature for twenty-four hours, the metal becomes superficially oxidised, for on treatment with a dilute solution of potassium iodide and hydrochloric acid they yield red solutions containing platinum (Abstr., 1907, ii, 698), from which the sulphide is precipitated by hydrogen sulphide. Similar results are obtained when the alkaline permanganate solution is replaced by an acid solution of potassium persulphate, dichromate, chlorate, or permanganate, or by an alkaline

solution of potassium ferri-cyanide, or by warm concentrated nitric acid, whilst an acid solution of ferric chloride, or an acid or alkaline solution of hydrogen peroxide, has no oxidising action on platinum. The total loss of weight of a platinum plate 5 cm. \times 2.5 cm. after several treatments with an oxidising solution amounts to 0.3 mg., and pure platinum is more readily oxidised than platinum containing 20% of iridium.

It appears therefore that platinum is more readily oxidised at the ordinary temperature than is usually admitted, and the solubility of the oxide thus obtained makes it an easy matter to introduce traces of platinum in chemical or physico-chemical experiments in which platinum is employed.

M. A. W.

Freezing-point Diagrams of the Binary Systems Platinum-Arsenic and Bismuth-Arsenic. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1908, 5, 148—149).—Platinum and arsenic form a eutectic containing 13% arsenic and solidifying at 597°. By plotting the times of eutectic solidification, the probable existence of a compound Pt_2As_3 is indicated, but it is not possible to study the solidification of mixtures containing more than 28% arsenic.

Bismuth and arsenic are only slightly miscible in the molten state, and separate completely on solidification.

C. H. D.

Oxides of Iridium. LOTHAR WÖHLER and W. WITZMANN (*Zeitsch. anorg. Chem.*, 1908, 57, 323—352).—The methods of preparation and properties of the three oxides of iridium, Ir_2O_3 , IrO_2 , and IrO_3 , have been investigated systematically. The oxide IrO , also mentioned in the literature, does not seem to exist under ordinary conditions.

Iridium dioxide, IrO_2 , is best prepared by a modification of Claus's method (1846), by the action of alkali on a hot solution of sodium iridichloride, Na_2IrCl_6 , the sesquioxide first formed being oxidised to dioxide by passing a current of oxygen through the solution. The precipitated dioxide can be obtained practically pure by drying at 400° in carbon dioxide, and then boiling with alkali and subsequently with sulphuric acid. The solution obtained by the action of potassium hydroxide on sodium iridichloride in the cold ultimately becomes violet in colour, and contains the dioxide in colloidal solution; after a time, a violet modification of the dioxide separates. On boiling, the violet solution becomes blue, due probably to an aggregation of the colloidal particles; the latter are positively charged. The blue and green solutions obtained by dissolving the dioxide in hydrochloric acid also contain the dioxide in colloidal solution.

The colour of the dioxide depends greatly on the proportion of water present. When dried in a desiccator over sulphuric acid, it contains approximately $2H_2O$, and is black; the water can only be driven off completely by heating at 760°. The anhydrous dioxide is also black. The freshly-precipitated dioxide is much more soluble in acids and alkalis than when dried.

Iridium sesquioxide, Ir_2O_3 , is obtained in an impure form by mixing air-free hot solutions of sodium iridium sesquichloride, $Ir_2Cl_6 \cdot 6NaCl \cdot 24H_2O$, and potassium hydroxide in a current of carbon

dioxide and evaporating to dryness. The residue is then heated to redness in a current of carbon dioxide, and then further purified by boiling successively with sodium hydroxide and sulphuric acid. In the dry way, as used by Claus (1846), the above method yields only a mixture of iridium and the dioxide.

When heated above 400° , the sesquioxide decomposes into the dioxide and iridium, a little oxygen being liberated simultaneously. As in the case of the dioxide, the properties of the sesquioxide depend on the proportion of water present. With hydrochloric acid, it forms a colloidal solution.

Attempts to obtain the lower oxide, IrO , by decomposition of a corresponding double sulphite, $\text{IrSO}_3 \cdot \text{M}_2\text{SO}_3 \cdot n\text{H}_2\text{O}$, with alkali were unsuccessful.

Iridium trioxide, IrO_3 , has not been obtained pure. The methods of preparation by fusing finely-divided iridium with potassium nitrate and alkali and with sodium peroxide, as well as by the anodic oxidation of an alkaline solution of the dioxide, yield products containing considerably less than the theoretical proportion of oxygen. Oxygen is also absorbed when the dioxide, mixed with alkali, is heated in oxygen, but not in the amount required to form the trioxide. In the absence of alkali, the dioxide does not absorb oxygen, from which the conclusion is drawn that a trioxide free from alkali is unstable, and that the comparative stability in the presence of alkali depends on the adsorption of the trioxide by the alkali. G. S.

Solid Solutions in the Dissociation of Iridium Oxides.
 LOTHAR WÖHLER and W. WITZMANN (*Zeitsch. Elektrochem.*, 1908, 14, 97—107).—The dissociation of iridium dioxide is studied in the same way as that of the oxides of copper and palladium (Abstr., 1907, ii, 33). Undecomposed iridium dioxide gives the highest dissociation pressures. At a constant temperature, the dissociation pressure falls as oxygen is removed from the system, but, after about a quarter of the oxygen has been pumped out, the pressure becomes independent of the composition of the solid phase. There are no discontinuities in the curve connecting pressure and composition at the points corresponding with iridium sesquioxide and monoxide. The sesquioxide, when heated, gives higher pressures than the dioxide, but they are not equilibrium pressures; the oxygen is reabsorbed slowly, and the final pressure is the same as that observed when oxygen is removed from the dioxide. The author considers that the dioxide, when heated, decomposes into oxygen and the metal. The dioxide and the metal are mutually soluble to a limited extent, so that, after a certain amount of decomposition has occurred, the solid consists of two saturated solutions, and therefore gives a constant dissociation pressure. Iridium is most rapidly oxidised to the dioxide by oxygen gas at 1070° . The reaction $\text{IrO}_2 \rightleftharpoons \text{Ir} + \text{O}_2$ absorbs about 5000 cal. One gram of iridium heated in oxygen at 775° loses 0.33 mg. per hour, and at 1000° about 0.5 mg. per hour. The volatile substance is possibly a tetroxide, which, being endothermic, decomposes on cooling, depositing the oxide. T. E.

Mineralogical Chemistry.

Proximate Constituents of Coal. PETER P. BEDSON (*J. Soc. Chem. Ind.*, 1908, 27, 147—150. Compare Abstr., 1900, ii, 20; Anderson, *J. Soc. Chem. Ind.*, 1902, 22, 242).—A résumé of the work of various authors on the action of solvents on different classes of coals and on the proximate analysis of coal, and a preliminary notice of a study of coals from the Busly seam, Boitley, County Durham. Pyridine dissolves 19·38% of the “bright coal” from this seam; a number of products, are obtained by treating the residue from the pyridine extract with various solvents, including a red, crystalline substance, m. p. 65°, soluble in light petroleum and volatile with steam, will be described later. The “dunt” from the same seam resembles anthracite, containing 9·92% of volatile matter and dissolving in pyridine only to the extent of less than 1%. The proximate analyses quoted for a number of gas coals agree, in general, with the results obtained in the gas works. Proximate analyses of four “cannel” coals and an oil shale are given for comparison. G. Y.

Polymorphous Substances. J. WEBER (*Zeitsch. Kryst. Min.*, 1908, 44, 212—238).—The literature of the following pairs of dimorphous minerals is recapitulated, and some new observations confirm those of previous authors: blende and wurtzite, metacinnabarite and cinnabar, senarmontite and valentinite. Several analyses of blende and of wurtzite were made to determine the ratio of zinc to sulphur; in blende there is a slight excess of sulphur (0·98—1·97%) over that required by the formula ZnS , whilst in wurtzite there is a deficiency of sulphur (0·21—1·59%). L. J. S.

Change of State in Quartz at 570°. OTTO MÜGGE (*Jahrb. Min.*, 1907, *Festband*, 181—196).—When heated to 570°, quartz suddenly becomes more strongly circularly polarising and birefringent, and on cooling it returns to its original condition. These two modifications of quartz are distinguished as α -quartz (stable below 570°) and β -quartz (stable above 570°); both are tetartohedral-hexagonal, but, as indicated by etching experiments, they probably represent different types of tetartohedrism. L. J. S.

Formation of Dolomite, and the Chemical Precipitation of Calcium Carbonate from Sea-water. E. PHILIPPI (*Jahrb. Min.*, 1907, *Festband*, 397—445).—A general discussion of previous work (compare Abstr., 1899, ii, 306; 1904, ii, 351; 1907, ii, 480). L. J. S.

Chemical Constitution of a North American Monazite Sand. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Petersburg*, 1908, 243—254).—The sample from Carolina contained 78·39% of monazite, the rest being chiefly quartz, garnet, corundum, zircon, titaniferous iron, magnetite,

chromite, and columbite, of which the columbite, garnet, titaniferous iron, and magnetite were analysed and described fully.

The monazite consists of more or less perfectly formed crystals with rounded edges of a dark copper-yellow colour, but occasionally light yellow or green. Some of the crystals also show distinct signs of efflorescence and corrosion. The powdered normal dark yellow crystals are decomposed readily by alkalis, alkaline carbonates, acid sulphates, and mineral acids. Analysis gave :

SiO ₂ .	Ch ₂ O ₃ , Ta ₂ O ₅ .	ZrO ₂ .	P ₂ O ₅ .	ThO ₂ .	Ce ₂ O ₃ .	(La, Pr, Nd) ₂ O ₃ .	Y ₂ O ₃ .
1·60	4·12	3·25	23·43	1·22	45·40	6·56	2·07
	MnO.	Fe ₂ O ₃ .	FeO.	Al ₂ O ₃ .	Total.		
	trace	5·58	3·62	2·49	99·34		

Z. K.

El Inca Meteoric Iron. FRITZ RINNE and H. E. BOEKE (*Jahrb. Min.*, 1907, *Festband*, 227—255).—This meteoric iron, weighing 320 kilos., was found in 1903 in the nitrate works in the Pampa de Tamarugal, near Iquique in Chile. Analysis by Halbach gave :

Fe.	Ni.	Co.	P.	S.	C.	Cr.	Sp. gr.
90·734	8·200	0·220	0·234	0·001	0·243	0·345	7·64

The structure is octahedral, and large nodules of troilite are present. When the meteoric iron is heated for some hours to 1300°, slight differences in the structure become apparent, indicating that there has been a partial recrystallisation of the material while still in the solid condition.

When iron sulphide and iron are fused together, mixed crystals containing 93% FeS and 7% Fe were obtained ; these undergo a change in state at 138°.

L. J. S.

Physiological Chemistry.

Gaseous Metabolism in Uræmic Dogs. S. LA FRANCA (*Biochem. Zeitsch.*, 1908, 8, 180—198).—The gaseous metabolism and respiratory quotient was investigated in dogs before and after removal of the kidneys, or ligature of the ureters. The respiratory quotient rises immediately after the operation, and this is probably due to reabsorption of urinary constituents; it then falls nearly to the normal level, and rises again with the onset of death. The quantities of oxygen absorbed and carbon dioxide given out increase after the operation, and fall considerably when the animal is near death. Complete analytical records of numerous experiments are given.

W. D. H.

Increase in Osmotic Concentration of the Blood during Anæsthesia ANTON J. CARLSON and A. B. LUCKHARDT (*Amer. J. Physiol.*, 1908, 21, 162—168).—During chloroform and ether anæsthesia, the osmotic concentration of the blood rises. This varies with the depth, but not with the duration, of the anæsthesia. The main factor in this is the ether or chloroform itself dissolved in the blood, but there are other factors, discussed at length, which cannot be altogether excluded.
W. D. H.

The Influence of Intestinal Extract on Blood-coagulation. F. CZUBALSKI (*Pflüger's Archiv*, 1908, 121, 395—403).—Extracts of the intestine intravascularly injected produce the same effect in delaying the coagulation of the blood as is produced by injection of Witte's peptone. It is probable that the active substance is not peculiar to the intestine, but can be also obtained from other tissues, for instance, the brain.
W. D. H.

Relative Hæmolytic Power of Serum and Lymph under Various Conditions of Lymph Formation. W. T. HUGHES and ANTON J. CARLSON (*Amer. J. Physiol.*, 1908, 21, 236—247).—The concentration of hæmolysins for rabbits' corpuscles in the normal body-fluids of dog, cat, and horse exhibits the following descending series: serum, lymph from thoracic duct, neck lymph, lymph from limbs, thyroid, and salivary glands, pericardial fluid, aqueous humor. The cerebro-spinal fluid contains none. The large retro-pharyngeal lymph glands do not influence the hæmolytic power of the lymph which passes through them. Immunisation against typhoid bacilli increases the hæmolytic power of the serum and lymph of the dog. Lymphagogues (peptone, salt, sugar) may increase the hæmolytic properties of lymph from the thoracic duct, but not of that from the neck. This may be accompanied by loss of such power in the serum. The action of peptone on serum is probably due to its action on the liver; this organ probably produces antilysins.
W. D. H.

Alkalescence and Acidosis of the Blood. Part II. On the Influence of Alkalis on the Alkalescence of Normal Blood, and of Blood in Cases of Endogenous Acidosis. ANASTAZY LANDAU (*Arch. exp. Path. Pharm.*, 1908, 58, 207—220).—The analyses were performed by the methods described in the first communication (*Abstr.*, 1905, ii, 330). Experiments were carried out to determine the influence of sodium carbonate (both subcutaneous and *per os*) on the alkalinity of the blood both in normal animals and in animals with experimental acidosis. The latter condition was produced by two methods, starvation and phosphorus poisoning. In the case of normal animals (rabbits), both mineral and organic alkalinity of the blood plasma is increased; this increase is, however, of short duration, and rapidly comes to an end through the excretion of the excess of alkali by the kidneys. The alkalinity of the whole blood is not increased in spite of the increased alkalinity of the plasma; this is due to hydræmia, and, since, normally, the blood corpuscles contain larger quantities of alkali than the plasma, the diminished number in a given volume tends to

counteract the increased alkalinity due to the plasma. In the case of starving animals, the effect of alkali is to diminish the acidity due to starvation; on the other hand, in animals poisoned by phosphorus, there is no tendency to increased alkalinity from the injection of sodium carbonate. The difference between the two cases is due to the fundamental difference in the methods of acid production. In starving animals, the acid production is limited, and is due entirely to the breakdown of the fats and proteins to meet the energy needs of the organism; as soon as these needs have been met, the acid production ceases and the acids can be neutralised by the increased alkali in the blood. In the case of phosphorus poisoning, the acid production goes on continually; the alkali is excreted by the kidneys before it is able to reach the cells where the acid is produced; the urine is consequently alkaline, and the acid products subsequently reach the blood. The alkali can, in this case, have only a very temporary effect in diminishing the acidity, and for this reason the injection in cases of diabetic coma is often without result—a toxic acidosis is being dealt with.

S. B. S.

Proteoses in Blood. EMIL ABDERHALDEN (*Biochem. Zeitsch.*, 1908, 8, 360—375).—Polemical against Freund (this vol., ii, 117). His methods and the conclusion that proteoses exist in normal blood-plasma are criticised.

W. D. H.

Guaiaecum Reaction of Blood. GEORGE SENTER (*Proc. physiol. Soc.*, 1907, xxxiii—xxxv; *J. Physiol.*, 36).—The guaiaecum reaction is obtained from boiled blood, although it is not so intense as that given by fresh blood. It is probable that there is a substance of non-enzymatic nature in blood responsible for the reaction; it is certainly greater than that which could be produced by the liberation of chlorine from its sodium chloride.

W. D. H.

Isotonic and Isosmotic Solutions. YVES DELAGE (*Compt. rend.*, 1908, 146, 319—321).—Comparison of the author's results on parthenogenesis in Echinoderms with those of Loeb. The author accepts Loeb's explanation how, if a saline and a sucrose solution are isotonic and the saline solution is isosmotic with an egg, the sucrose solution is not; this is due to sucrose diffusing more slowly through the egg-membrane than the salts which the egg contains.

G. B.

The Work of Digestion. ERNST HEILNER (*Zeitsch. Biol.*, 1908, 50, 488—503).—The author reaffirms his original contention that digestive work in Zuntz's sense does not exist, or rather that the increase of work in the digestive organs during digestion is so small as to be negligible in the study of general metabolism. Rubner's "specific dynamic action" of food-stuffs is, on the other hand, the important factor.

W. D. H.

Action of the Amylase of Pancreatic Juice and its Activation by Gastric Juice. H. BERRY (*Compt. rend.*, 1908, 146, 417—419).—The alkalinity of pancreatic juice, obtained by a

temporary fistula and injection of secretin, is equivalent to $N/8$ sodium carbonate (helianthin as indicator). Pancreatic juice hydrolyses starch to maltose, but only very slowly to dextrose, unless the juice is partially neutralised. The best yield of dextrose is obtained by reducing the alkalinity to one-fifth of the original. The action of gastric juice in accelerating the production of dextrose by pancreatic juice is wholly due to the hydrochloric acid, and occurs normally in digestion when the acid contents of the stomach, passing through the pylorus, partially neutralise the pancreatic juice. G. B.

Metabolism of Calcium, Magnesium, and Phosphorus during Inanition. O. WELLMANN (*Pflüger's Archiv*, 1908, 121, 508—533).—Proofs are adduced that some of the calcium, magnesium, and phosphorus which leave the body during inanition come from the bones. In rabbits, the bones lose about 14% of their weight, and more than half of this falls on the fat. W. D. H.

Parenteral Utilisation of Carbohydrates. LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1907—8, xii—xiii; *Amer. J. Physiol.*, 21).—If sucrose is introduced parenterally, over 90% reappears in the urine. Starch similarly administered appears only in part in the urine as dextrin-like substances. The retention is greatest after subcutaneous injection, less after intraperitoneal, and least after intravenous, injection. Tissue amylases are doubtless concerned in the utilisation of the carbohydrate. Moscati claimed to have found complete utilisation, but this was not confirmed. W. D. H.

Influence of Carbohydrates on Protein Metabolism. JOHN R. MARLIN (*Proc. Amer. physiol. Soc.*, 1907—8, xxi—xxii; *Amer. J. Physiol.*, 21).—Sucrose added to the diet of a well-nourished dog produced no change in the total urinary nitrogen. In emaciated or pregnant dogs it caused a marked reduction of the nitrogen excreted. In the fat dog, the ammonia eliminated was much increased, and in all cases the creatinine output was raised. In pregnant animals, creatine also passed into the urine on the days on which sugar was given. W. D. H.

Feeding and Other Experiments on Dogs with an Eck Fistula. PHILIP B. HAWK (*Amer. J. Physiol.*, 1908, 21, 259—281).—After an Eck's fistula has been made, a diet rich in meat may cause toxic symptoms; these, however, are frequently absent, and may then be induced by giving Liebig's extract. The symptoms include anæsthesia, ataxia, catalepsy, tetanus, and loss of sight and hearing; there is usually a fatal termination. If the diet is meat-free, no toxic signs result even if Liebig's extract is given. Sodium carbamate produces no poisonous effects. The animals waste after the operation, but glycosuria and albuminuria are absent. W. D. H.

Composition and Energy-Value of the Food of the Soldier. MARCUS S. PEMBREY and L. E. L. PARKER (*Proc. physiol. Soc.*, 1908, xlix—l; *J. Physiol.*, 36).—The tables given show that the minimum

diet of the British soldier is above 100 grams of protein, 100 grams of fat, and 400 grams of carbohydrate, and possesses an energy value of about 3000 Calories. W. D. H.

Importance of Glutamic and Aspartic Acids as Food-stuffs. KARL ANDRLÍK and K. VELICH (*Zeitsch. Zuckerind. Böhm*, 1908, 32, 313—342).—The subject is of importance in connexion with the food-value of (beet) molasses, now extensively used as food for cattle. Molasses contain 1·5—2% of nitrogen, which is distributed as follows: proteins and peptones, 10%, betaine, 35—40%, amino-acids, 40%, purine bases, 5—7%. For betaine, it has already been shown (*Abstr.*, 1903, ii, 228; 1905, ii, 266) that it is completely absorbed by herbivora; in carnivora some passes into the urine.

For the present research, a sheep, which was approximately in nitrogenous equilibrium, was given daily 20 grams of glutamic or aspartic acid as the sodium salt; 96% of the former and 98% of the latter acid was absorbed. A portion of the part absorbed (most in the case of the aspartic acid) was used up in protein synthesis; the rest was oxidised to urea, but no acid appeared as such in the urine. The faeces contained protein, 92—94% of which was not digestible by pepsin. G. B.

Composition of Human Brain at Different Ages. WALDEMAR KOCH and SIDNEY A. MANN (*Proc. physiol. Soc.*, 1907, xxxvi—xxxviii; *J. Physiol.*, 36).—Three brains were examined, one at the age of six weeks, one at two years, and the third at nineteen years. With the growth of the brain a decrease in moisture, proteins, extractives, and ash occurs, whilst there is an increase in cerebrins, lipid sulphur, and cholesterol, that is, of substances which predominate in the white matter. W. D. H.

The Smallest Molecule from which the Liver can make Glycogen. KARL GRUBE (*Pflüger's Archiv*, 1908, 121, 636—640).—By perfusion of the tortoise's liver with a weak (0·01—0·02%) solution of formaldehyde, it was found that the liver was able to form glycogen from it. W. D. H.

The Capacity of the Liver to Reverse the Optical Action of Sugars. EDUARD PFLÜGER (*Pflüger's Archiv*, 1908, 121, 559—571).—The administration of lævulose leads to the formation of glycogen in the liver, but the glycogen formed is not lævorotatory; the liver cells have therefore the power to transform the sugar given into dextrose, and it is this from which the glycogen is formed. W. D. H.

Changes in Uric Acid in Animals and Men. ALFRED C. CROFTAN (*Pflüger's Archiv*, 1908, 121, 377—394).—Uric acid was mixed with minced organs and tissues, or their extracts, and the loss in the amount of uric acid estimated; the human liver has greater power in this direction than the livers of other animals; the same is true for the kidneys; the muscles, however, surpass all other tissues in this power. The power of the human spleen, on the other hand, is

relatively small, and that of the blood almost negligible. Neither nucleo-protein nor a protease separated from the extracts destroys uric acid, but a mixture of the two does so. The protease does not decompose hydrogen peroxide. As to what happens to the uric acid, nothing very definite was discovered; a small increase in urea and oxalic acid was noticed, but little or no formation of allantoin.

W. D. H.

The Influence of Colloids on Ferments. LUDWIG PINCUSOHN (*Biochem. Zeitsch.*, 1908, **8**, 387—398).—Ascoli and Izar (this vol., ii, 121) have shown that small quantities of colloidal silver, gold, and platinum have a distinct action in increasing the rate of action of the autolytic enzyme of the liver. Experiments were made to determine the influence of colloids on pepsin digestion. In no case was the rate of action increased.

S. B. S.

Leucomaines of Cod-liver Oil. PHILIP B. HAWK (*Proc. Amer. physiol. Soc.*, 1907—8, xxii—xxiii; *Amer. J. Physiol.*, **21**).—The total amount of leucomaines isolated by the method of Gautier and Mourgues from oils of different tint varied from 1.06 to 1.17 grams per kilogram of cod-liver oil. By fractional distillation, butylamine, amylamine, hexylamine, and dihydrolutidine were separated. From the non-volatile portion, morrhaine was identified, but not the aselline of Gautier and Mourgues.

W. D. H.

Refractory Period of the Frog's Sartorius. H. C. BAZETT (*J. Physiol.*, 1908, **36**, 414—430).—The refractory period is lengthened by fatigue, injury, or normal saline solution. A lowering of temperature acts in the same way, and the lengthening obeys Arrhenius' law of the velocity of chemical reactions. Potassium salts lengthen, and calcium salts shorten, the refractory period. Chloral hydrate, after a short initial effect in lessening it, increases the length of the period.

W. D. H.

Relative Resistance of Cardiac Muscle and Nerve to Drugs. WALTER J. MEEK (*Amer. J. Physiol.*, 1908, **21**, 230—235).—Alkaloids, anæsthetics, and other chemical substances produce paralysis of the *Limulus* heart tissues in the following order: (1) ganglion, (2) motor nerve plexus, and (3) muscle.

W. D. H.

Creatine and Creatinine. EDWARD MELLANBY (*J. Physiol.*, 1908, **36**, 447—487).—Among the many contradictory statements relating to the proportion of creatine to creatinine in muscle, that of Monari, who says that the latter increases at the expense of the former when muscle becomes active, has usually been regarded as most trustworthy. It is now shown that Monari's technique afforded an opportunity for the change to occur, and, moreover, his precipitates were impure; and it is shown that creatinine is never present in muscle at all even after prolonged muscular work; the original amount of creatine remains unaltered after work, and also, in frog's muscle, after survival for three days. When the muscle becomes septic, all the creatine disappears. Aseptic or antiseptic autolysis causes no change in creatine or

creatinine. Gottlieb and Stangassinger's statements (Abstr., 1907, ii, 637) regarding numerous tissue enzymes which affect these substances were in no single respect confirmed.

Creatine and creatinine feeding has no effect on the creatine of muscle after the muscle has reached a certain saturation point. In one set of chickens only, the muscular creatine was slightly increased by glycocyamine feeding, but this is not universal. In early life, also, creatine feeding and possibly creatinine feeding increase the muscular creatine, but the normal differences in chickens are unknown, and this factor has to be eliminated before the fact can be established. Creatinine feeding leaves the muscles still free from that substance.

Before the twelfth day of incubation in the chick, creatine is absent from the muscles; after this date the liver and the muscular creatine develop *pari passu*. After hatching, the liver still continues to grow rapidly, creatine formation increases also, but muscular growth is slow.

Invertebrate muscle even when striated does not contain creatine. The invertebrate "gland of the mid-gut" has no morphological or physiological connexion with the vertebrate liver.

The small amount of creatinine excreted in hepatic disease gives support to the view that the liver is responsible for the formation of creatinine. The excretion of creatine in cancer of the liver makes it probable that, where muscle cells break down, creatine is liberated without conversion into creatinine before excretion. Creatinine, after the earlier period of life, is an excretion product of metabolism; creatine has no influence on muscular contraction or on the passage of nervous impulses into muscle.

The general conclusion reached is that the liver is continuously forming creatinine from substances carried to it by the blood from other organs, and that in the developing muscle this is changed to creatine and then, when the muscle is saturated with creatine, creatinine is continuously excreted. If creatine (an innocuous neutral substance) was converted by the muscles into creatinine (a strongly basic substance) it would be contrary to all that is known of the chemical changes which occur in the body.

W. D. H.

Chemical Processes in the Earth-Worm. ERNST J. LESSER. **The Ferments of the Earth-Worm.** ERNST J. LESSER and ERNST W. TASCHENBERG (*Zeitsch. Biol.*, 1908, 50, 421—445, 446—455).—During inanition, the respiratory quotient of the earth-worm sinks. In the early stages, fat and glycogen are used up, but later, as glycogen disappears, its decomposition is relatively small. The output of nitrogen remains constant, between 2 and 4 mg. per fifteen animals per day. Products of incomplete carbohydrate breakdown are not contained in the excretions. Ammonia is present, which is not the case in *Ascaris* and the leech.

The hydrolysing ferments present are those which act on protein, starch, and glycogen, also invertase and lipase. Catalase and aldehyde (?) are present. Lactase, inulinase, cytase, tyrosinase, and a ferment which renders guaiacum blue are absent.

W. D. H.

The Organic Substance of the Skeletal Tissues of Anthozoa. II. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1908, 55, 77—83).—The previous work (Abstr., 1907, ii, 283) was undertaken with the skeletal tissue of the *Gorgonacea*. The investigations have now been extended to the *Pennatulacea*, the *Alcyonacea*, and the *Antipathidea*. The following general results have been arrived at. In all cases the halogens are in organic combination; iodine is present in all cases (from traces up to 7%), also bromine (in quantities of 0.25 to 4%) with the exception of two *Antipathidea*, and chlorine (generally only about 0.2%). The variations are independent of climate, composition of sea-water, age, &c., and also of the physical properties of the skeletal substance. The organic substance of the *Pennatulacean* skeleton, provisionally called *Pennatulin*, differs from that of the other Anthozoa by its solubility in pepsin-hydrochloric acid. The amount of sulphur in the skeletons of all members of the group is so low that the organic substance cannot be regarded as a keratin. It is probable that halogens are far more widely distributed in the tissues of marine organisms than has hitherto been considered probable. S. B. S.

The Rôle of Calcium Salts in the Mechanical Inhibition of the Ctenophore Swimming-plate. RALPH S. LILLIE (*Amer. J. Physiol.*, 1908, 21, 200—220).—Mechanical stimulation arrests the activity of the swimming-plate; this susceptibility is dependent on the presence of calcium salts. Strontium and barium cannot take the place of calcium. The essential action of the calcium consists in decreasing the permeability of the contractile tissue to ions. Mechanical stimulation favours the entrance of calcium ions into the fibrils. W. D. H.

The Nitrites of the Saliva, and their Origin. JULES VILLE and W. MESTREZAT (*Bull. Soc. chim.*, 1908, [iv], 3, 212—217).—Schönbein observed, in 1862, that saliva contains nitrites, as shown by its action, when acidified, on potassium iodide and starch. The authors show that saliva, when obtained pure by the catheterisation of the ducts of the parotid and sub-maxillary glands, does not contain nitrites; it does, however, contain nitrates in quantities varying from 10—300 mg. per litre in different individuals. The quantities increase considerably after ingestion of nitrates in the food. The nitrites in the saliva are stated to be due to the reducing action of a certain species of bacteria on the nitrates in the buccal cavity. These bacteria, when inoculated in Winogradski's medium containing nitrates (0.1 gram per litre), can reduce as much as 50% in twenty-four hours. S. B. S.

Action of Lymphagogues on the Concentration of Agglutinins in Serum and Lymph. B. BRAUDE and ANTON J. CARLSON (*Amer. J. Physiol.*, 1908, 21, 221—229).—Serum, thoracic lymph, neck lymph, and pericardial fluid of dogs contain agglutinins for typhoid bacilli. The order named is the order of activity. Aqueous humor and cerebro-spinal fluid contain no agglutinin. The agglutinating action runs parallel to the hæmolytic power of the fluids. In cats, on the

other hand, agglutinins are usually absent from all the fluids, but, after immunisation against the typhoid bacillus, the fluids have an agglutinating action, and the relative concentration in the different fluids is the same as in dogs. Lymphagogues (strawberry-extract, 10% peptone, 10% sucrose, 5% sodium chloride) have no effect on the concentration of agglutinins.

W. D. H.

Behaviour of Rennet and Acid to Human Milk. ERNST FULD and JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1908, 8, 376—377. Compare Abstr., 1907, ii, 797).—The authors disagree with Bienenfeld's conclusion (this vol., ii, 121), that human milk cannot be curdled by rennet, on several grounds, one of which is that, if the amount of calcium chloride in the milk is increased, curdling occurs in the usual way.

W. D. H.

Excretion of Sugar in Healthy Men, and the Estimation of Small Quantities of Sugar in Urine. BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1908, 121, 572—603).—Using large quantities of urine, it is possible to detect sugar in many healthy people by the Worm-Müller reaction, and even if this test is negative, it is still possible in many cases by concentrating the acidified filtrate after precipitation by mercuric nitrate; the sugar can then be estimated by the Fehling-Soxhlet method. Quantities varying from 0.005% upwards can be detected. In the urines of over three hundred soldiers, 95% contained sugar, and in few cases as much was found as in diabetes. This is attributed to diet; in civilians, who did not take so much carbohydrate, 85% secreted a sugar-free urine. The sugar was identified as dextrose by means of its osazone.

W. D. H.

Metabolism in a Case of Coma under Rectal Feeding. P. P. LAIDLAW and JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1908, xlvii—xlix; *J. Physiol.*, 36).—Details are given of the composition of urine and faeces of a man in a state of coma, who was fed *per rectum*. The nitrogen excretion is low, and roughly equal to that obtained in the later stages of fasting. Creatine was absent from the urine. Uro-rosein was present; this disappeared on the resumption of mouth feeding. The absence of stercobilin in the faeces suggests that a prolonged stay of bile pigments in the intestine is favourable to the production of uro-rosein. Zawidzky obtained a substance apparently identical with uro-rosein by oxidising pure urobilin.

W. D. H.

Action of Therapeutic Agents on the Gastric Secretion.
III. Action of Iodine in the Promotion of Secretory Activity. JOHANN FEIGL (*Biochem. Zeitsch.*, 1908, 8, 467—519).—Experiments were made to determine the rate of secretion of gastric juice in dogs with a Pawloff fistula after the ingestion of iodine and various iodine compounds. Water was first administered, and the gastric juice collected and measured, the quantity excreted in each half-hour being noted. As soon as the excretion had stopped, the same quantity of water containing iodine or the iodine compound was administered, and the amounts of secretion measured at half-hourly intervals. The

administration of iodine and iodides caused considerable increase in the amount of secretion; iodine itself was particularly powerful; 200 c.c. of water caused a secretion of 4.8 c.c. of gastric juice, the secretion of which ceased after two hours; the same quantity of water, containing 0.05 gram of iodine, caused a secretion of 22.5 c.c. of juice, which ceased to be secreted only after four hours. Potassium iodate had also a powerful action. Experiments were also made with iodised fats and proteins. The fat derivatives acted in varying ways, some acting like the iodides, others having but little action. As a general result, it was found that the iodine compound in all cases when ions could be formed, caused considerable secretory activity. S. B. S.

Biochemistry of Colloids. JOHANN FEIGL and ADOLF ROLLET (*Biochem. Zeitsch.*, 1908, 8, 145—179).—Various colloid preparations of metals and metallic compounds prepared chiefly by Paal's method, such as the commercial preparations collargol, lysargin (silver colloid), hygrol (mercury colloid), &c., were administered to a dog with a Pawloff gastric fistula. In all cases there was a considerably increased secretion of gastric juice as compared with that obtained by the administration of the same quantity of water without the colloid. The colloidal condition has some specific action therefore of promoting gastric secretion which is not possessed by the metals when administered in the form of ordinary ionisable salts. S. B. S.

Antagonistic Action of Calcium and Magnesium SAMUEL J. MELTZER and JOHN AUER (*Proc. Amer. physiol. Soc.*, 1907—8, xi; *Amer. J. Physiol.*, 21).—The paralysis and anæsthesia produced in an animal by the injection of a magnesium salt disappear about one minute after the injection of a calcium salt. In plant life, also, the cure for too much magnesium in the soil is "liming." W. D. H.

Action of Hydrocyanic Acid on Protein Katabolism. ADOLF LOEWY, CHARLES G. L. WOLF, and EMIL ÖSTERBERG (*Biochem. Zeitsch.*, 1908, 8, 132—144).—Three experiments on dogs, which were given respectively small, medium, and large doses of hydrocyanic acid, are described. In all there was a rise of nitrogenous katabolism; the amount of urea is also increased, so that the proportion of urea to total nitrogen does not sink. The ammonia excretion is very slightly lessened; the amount of urinary creatinine sinks markedly, but creatine appears also in the urine; the residual nitrogen is increased. The relation of sulphates to total sulphur is lessened, and the total phosphorus rises. W. D. H.

Action of Benzidine on the Animal Body. OSCAR ADLER (*Arch. exp. Path. Pharm.*, 1908, 58, 167—197).—Symptoms of intoxication are produced in a dog by doses of 1 to 3 grams of benzidine, as such or as a salt, suspended, or dissolved, in water or alcohol; they are the same whether the drug is given by stomach-tube or by subcutaneous injection. Vomiting first sets in, followed by symptoms indicating excessive excitement of the motor centres, and analogous to those produced by cocaine poisoning. A condition of fatigue and

somnolency follows, and the animal dies generally after a period of several days; recovery is, however, possible. These symptoms were accompanied by glycosuria and, in the case of rabbits, blood-corpuscles appeared in the urine containing a changed blood-pigment, which is insoluble in water, and in the case both of rabbits and dogs an abnormal urinary pigment was formed. Very little, if any, unchanged benzdine is recovered in the urine, but a substance has been isolated melting between 130° and 138° of the formula $C_{12}H_6(OH)_2(NH_2)_2$, which is presumably 4:4'-diaminodihydroxydiphenyl. S. B. S.

Purgative Action of Phenolphthalein and of its Disodium Derivative. C. FLEIG (*Compt. rend.*, 1908, 146, 367—370).—The action, which is much more marked on man than on animals, is due to increased secretion and not to increased peristalsis. The disodium derivative is soluble in water, and is more active than the parent substance; it can be given hypodermically. G. B.

Effect of Strychnine on Muscular Work. P. C. VARRIER-JONES (*J. Physiol.*, 1908, 36, 435—446).—Ergographic experiments on man show that small doses of strychnine produce an immediate increase in the power to do work, especially if the drug is taken early in the day. A fall then follows, and the capacity remains subnormal for hours. The effect of successive doses is cumulative. It is suggested that the effects are produced by a diminution of the resistance of the spinal cord to the entry of sensory impulses, and the after effect may be due either to the poisonous action of the drug or to pure fatigue.

W. D. H.

Chemistry of the Infundibular Portion of the Pituitary Body. THOMAS B. ALDRICH (*Proc. Amer. physiol. Soc.*, 1907—8, xxiii—xxiv; *Amer. J. Physiol.*, 21).—A crystalline picrate of the substance which raises blood-pressure was prepared from the extract of the infundibulum, which had previously been freed from protein. The sulphate was prepared from the picrate. Both these salts raise blood-pressure. Platinum chloride also gives a double salt.

W. D. H.

The Sensory Nerves of the Heart and Vessels as a Factor in Determining the Action of Drugs. D. E. JACKSON and SAMUEL A. MATTHEWS (*Amer. J. Physiol.*, 1908, 21, 255—258).—The fall of blood-pressure in early stages of aconitine poisoning is too great to be accounted for by the cardiac weakness, and the vaso-motor nerves respond well on stimulation. Some experiments recorded seem to confirm the suggestion that the alkaloid acts on the terminations of the depressor nerve, and there are indications that other sensory nerve-endings may be affected.

W. D. H.

The Action of Cobra Venom in Destroying Complement. JULIUS MORGENROTH and R. KAYA (*Biochem. Zeitsch.*, 1908, 8, 378—382).—The disappearance of complement from serum under the influence of snake poison is due either to the action of a ferment in

the latter which destroys the former, or to a combination between the amboceptor of the venom and the complement of the serum to form an inactive compound.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Laws of Disinfection. HARRIETTE CHICK (*J. Hygiene*, 1908, 8, 92—158).—In anthrax spores, the disinfection process obeys the equation for a unimolecular reaction if “concentration of reacting substance” is replaced by “numbers of surviving bacteria.” In *B. paratyphosus* this law does not hold, for the younger bacteria are more resistant than the others. The process is influenced by temperature, and the equation of Arrhenius can be applied; from this follows the advantage of using warm solutions in practical disinfection. In the case of some metallic disinfectants, the metallic ion appears to be the active agent. In disinfection with mercuric chloride, a toxic compound is formed between the metal and the substance of the bacterial cell. This compound prevents further growth, but vitality can be restored by a large excess of soluble sulphide. W. D. H.

Relative Efficiency of Filters. WILLIAM BULLOCH, J. A. CRAW, and E. E. ATKIN. **Grain of Filters and Growth of Bacteria through Them.** J. A. CRAW (*J. Hygiene*, 1908, 8, 63—69, 70—74).—Of the filters tested, the Doulton filters alone prevented the direct transmission of micro-organisms. Berkefeld filters and Slade and Brownlow filters gave contaminated filtrates within fifteen minutes of the commencement of filtration. Striking photomicrographs of the size of the pores in the filters show that this is inversely proportional to the efficiency of the filters. W. D. H.

Micro-organisms Oxidising Hydrogen. II. BRONISLAW NIKLEWSKI (*Centr. Bakt. Par.*, 1908, 20, ii, 469—473. Compare Abstr., 1907, ii, 380).—The condensation of hydrogen and oxygen by the soil is due to two organisms, living symbiotically and together constituting the membrane formed on mineral solutions in an oxygen-hydrogen atmosphere. The fact that neither organism when grown by itself can oxidise hydrogen, and that morphologically they greatly resemble each other, accounts for the difficulties of obtaining a pure culture. The author doubts the identification of Kaserer's organism (Abstr., 1906, ii, 113, 697) with *Bacillus oligocarbophilus*; in his own cultures, he never observed nitrification, nor did growth take place in a carbon monoxide atmosphere, as described by Kaserer. In spite of these differences, the author regards his organism as probably identical with that of Kaserer, and probably also with that of Nabokich and Lebedeff (Abstr., 1907, ii, 43). G. B.

Survival of *Bacillus Typhosus* in Soil. W. MAIR (*J. Hygiene*, 1908, 8, 37—47).—The typhoid bacillus survives in soil for seventy to eighty days, but there is no evidence that it multiplies and leads a saprophytic existence there. If the soil has been sterilised previously by steam under pressure, the bacillus dies out more rapidly (eleven days), but this does not obtain in all cases. Sterilisation apparently produces bactericidal substances.

W. D. H.

Chemical Constitution and Biological Properties of the Protoplasm of Koch's Bacillus. JULES AUCLAIR and LOUIS PARIS (*Compt. rend.*, 1908, 146, 301—303).—Tubercle bacilli were freed from soluble proteins and from the fatty wax, and then extracted at 80° with concentrated acetic acid; on almost completely neutralising the extract with sodium hydroxide, flakes are precipitated which resemble a nucleo-casein. When injected in doses of 1 mg., this *bacillo-casein* produces small tumours in the rabbit and the guinea-pig. It and the fatty wax are the essential poisons of tubercle bacilli.

G. B.

Nitrification. LESLIE C. COLEMAN (*Centr. Bakt. Par.*, 1908, ii, 20, 401—420, 484—513).—In accordance with Bazarewski's results, it was found that nitrification in non-sterilised soil may be considerably increased by small amounts of dextrose (to 0·5%). The greatest effect is produced in the second and third weeks; subsequently the effect diminishes, whilst denitrification, due to organic matter, increases.

Sucrose, glycerol, and lactose in small amounts seem to have a favourable effect; no effect was detected in the case of calcium butyrate whilst calcium acetate seems to retard nitrification. Peptone and urea (0·5% and 0·75% respectively) greatly retard nitrification.

Nitrification in a loam was most active in presence of 16% of water, and was much retarded when the amount of water was reduced to 10% or increased to 26%; in presence of an excess of water, dextrose is injurious instead of beneficial.

Approximately pure cultures of nitrate and nitrite organisms in sterilised sand or soil are rendered more active by 0·02—0·05% of dextrose; under similar conditions, pure cultures of the nitrate organism seem to acquire increased activity in presence of 0·05% of dextrose. A supply of carbon dioxide is necessary in presence, as in the absence, of dextrose.

Carbon disulphide has at first a very decided retarding action on nitrification; subsequently, nitrification is increased, owing no doubt to a stimulating action.

N. H. J. M.

Carbohydrates of Yeast. WILHELM MEIGEN and A. SPRENG (*Zeitsch. physiol. Chem.*, 1908, 55, 48—73).—Two carbohydrates can be obtained from the cell membrane of yeast, "*yeast gum*" and "*yeast cellulose*." The yeast gum has been prepared in different ways, such as by boiling the yeast with water (Nägeli and Low, Béchamp, and Schützenberger), by boiling with chalk (Hessenland), and by boiling with dilute potassium hydroxide and precipitation of the polysaccharide with Fehling's solution (Salkowski). The preparations so

obtained show different specific rotations varying from 47.6° to 98.2° . This is due to the fact that the "yeast gum" obtained by different processes contains admixtures of other substances, such as proteins, glycogen, and hemicellulose. Salkowski's method gives the purest preparation (with α_D 91.1°). Hydrolysis with 3% sulphuric acid gives a mixture of mannose and dextrose in the molecular proportions of 2:1. Pentoses seem to be absent.

Two other carbohydrates were prepared from the yeast in the following way.

The yeast was treated for six months with 0.25% potassium hydroxide, which was changed at intervals. The residue was repeatedly treated with alcohol, until the water was removed, and then dried. This preparation gave a brown colour with iodine and sulphuric acid, and also with iodine dissolved in potassium iodide; it was insoluble in ammoniacal copper hydroxide solution. On treatment with 3% sulphuric acid (20 times the quantity for ten hours), or with 15% sodium hydroxide (for four hours), two-thirds of the quantity went into solution; on evaporation of the solution and addition of alcohol, a carbohydrate was precipitated which, after purification, had a rotatory power of $+113^{\circ}$; it gave no precipitate with Fehling's solution, but a precipitate with lead acetate and baryta water. It differs therefore from the yeast gum. On hydrolysis, it yields only dextrose. This substance is, then, *yeast dextrose*, and seems to be identical with Salkowski's erythro-cellulose.

The insoluble residue from the hydrolysis with 3% sulphuric acid, or 15% sodium hydroxide, is another hydrocarbon, *yeast cellulose*; on hydrolysis in the cold with 80% sulphuric acid, it yields mannose and dextrose in approximately equal molecular proportions; it seems to be identical with Salkowski's achroo-cellulose. It does not give, however, the typical cellulose reactions, and is not present in the yeast cell in this form, but is produced from the original hydrocarbons by hydrolysis.

S. B. S.

The Influence of the Chemical Constitution of the Nitrogenous Nutrient on the Fermentative Action and Growth of Certain Fungi. II. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 8, 119—127. Compare Abstr., 1907, ii, 44).—As in the case of yeast, the capability of producing the alcoholic fermentation, being due to the presence of amino-acid groups, is true also for the fungi *Rhizopus tonkinensis*, *Mucor racemosus*, and *Torula I*, but is not the case for *Allescheria Gayonii* or *Torula V*. As was found also by Czapek for *Aspergillus niger*, this source of nitrogen favours the growth of *R. tonkinensis*, *M. racemosus* and *Torula V*, but not of *A. Gayonii*.

W. D. H.

Formation of Fusel Oil by Certain Fungi. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 8, 128—131).—Various fungi which produce the alcoholic fermentation were investigated. All of these possess the power of converting leucine into amyl alcohol, and the smaller the amount of ethyl alcohol formed the richer it is in fusel oil.

W. D. H.

Fixation of Zinc by *Sterigmatocystis nigra*. MAURICE JAVILLIER (*Compt. rend.*, 1908, 146, 365—367).—The growth of this mould (= *Aspergillus*) is stimulated by minute traces of zinc, up to 1 part in 10,000,000 parts of the culture fluid. At higher concentrations up to 1 in 250,000, growth is not accelerated any further, but the fungus assimilates, nevertheless, the whole of the zinc, which no doubt is useful. From concentrations of 1/250,000 to 1/25,000, a portion of the zinc is absorbed, the excess being harmless. In solutions containing more than 1 part in 25,000, the *Aspergillus* no longer attains its normal weight. Although the beneficial effect of traces of zinc (and of other poisonous metals) is well known, the direct proof of the fixation of the zinc is now given for the first time. G. B.

Active Principles of the Fruit of an African *Strychnos*. ALEXANDRE HÉBERT (*J. Pharm. Chim.*, 1908, [vi], 27, 151—155).—The fruit of *Strychnos aculeata*, from the Ivory coast of Africa, contains neither strychnine nor curarine, but traces of brucine. It contains in addition an active principle, which is non-volatile with steam and is toxic to fish, but not to mammals. It exerts this toxic action in doses corresponding with 1 part of the fruit in 10,000 parts of water. S. B. S.

Chemical and Bacteriological Effects of Liming. EDWARD B. VOORHEES, JACOB G. LIPMAN, and PERCY E. BROWN (*New Jersey Agric. Exper. Stat. Bul.*, 1907, 210).—Experiments on the effect of burnt lime and calcium carbonate on oats and crimson clover grown in boxes containing 50 lb. of a market garden soil somewhat sandy and of a red shale arable soil respectively.

In many cases, the application of lime reduced the yield of dry matter and increased the yield of nitrogen; magnesian lime caused a greater depression in the yield of dry matter than non-magnesian lime. On the other hand, ammonification and nitrification were promoted by liming, and more by magnesian than by non-magnesian lime.

The amounts of lime applied were not sufficient seriously to affect the CaO/MgO ratio. The diminished yield of dry matter under the influence of lime is attributed to a decreased supply of available phosphoric acid, accumulation of injurious substances due to bacterial activity being increased by the lime, or to the utilisation of plant-food by the increased numbers of soil organisms. Actual countings by the plate method and by Hiltner and Stormer's dilution method showed an enormous increase of soil organisms under the influence of soil treatment. N. H. J. M.

Proteins of Rice. OTTO ROSENHEIM and S. KAJIURA (*Proc. physiol. Soc.*, 1908, liv—lv; *J. Physiol.*, 36).—Rice yields 7% of total protein, of which 0.14% is a globulin, 0.04% an albumin, and the remainder a protein, which like the glutenin of wheat is soluble only in dilute alkali; the name oryzenin is suggested for it. It gives all the usual protein colour reactions. The almost complete absence of a gliadin

(or alcohol-soluble protein) explains why rice is unsuitable for making dough and bread. The addition of barley to rice diet prevents outbreaks of Beri-beri. It is suggested that the increased supply of glutamic acid in hordein (the alcohol-soluble protein of barley) may partly explain this.

W. D. H.

Analytical Chemistry.

Detection of Free Hydrochloric Acid in the Stomach Contents. F. A. STEENSMA (*Biochem. Zeitsch.*, 1908, 8, 210—211).—The following modification of the Günzberg solution is recommended: phloridzin, 2 grams, vanillin, 1 gram, absolute alcohol, 30 c.c. To carry out the test, the inverted cover of a crucible is placed on a water-bath and warmed. When hot, a drop of the reagent is added; the alcohol evaporates, and leaves a faint yellow ring. In the middle of this ring, where there is no reagent, one or two drops of the liquid under investigation are placed. If hydrochloric acid is present, a bright red edge will form on the inside of the yellow ring on evaporation; if only small quantities of hydrochloric acid are present, only a thin red line will be formed. The reagent will not keep long, and should be freshly made for the test, especially if methyl alcohol is employed instead of ethyl alcohol. S. B. S.

Fluorine in Cœnological Products. P. CARLES (*Ann. Chim. anal.*, 1908, 13, 102—104).—The author calls attention to the fact that traces of fluorine compounds may be introduced into wines by the use of animal charcoal, some kinds of tannins (China galls), clarifying agents (gelatins) to which hydrofluosilicic acid has been added as a preservative, &c. L. DE K.

Detection of Hydrogen Peroxide in Milk. E. FEDER (*Zeitsch. Nahr. Genussm.*, 1908, 15, 234—236).—The presence of 0.01% of hydrogen peroxide in milk may be detected by heating 5 c.c. of the milk, 5 c.c. of hydrochloric acid, D 1.19, and 1 drop of dilute formaldehyde solution to a temperature of about 60° for three or four minutes. If hydrogen peroxide is present, a violet coloration is obtained. Fresh milk treated in the same way gives a yellow coloration. Other substances, however, besides hydrogen peroxide give a violet coloration when heated with milk and hydrochloric acid in the presence of formaldehyde. Of these, nitric and nitrous acids may be mentioned. Milk containing added water may give a coloration, indicating the presence of hydrogen peroxide, but in reality due to the nitrous acid (nitrite) introduced along with the water. In testing watered milk, the presence or absence of nitrous acid should therefore be established by means of other tests. W. P. S.

Estimation of Small Quantities of Oxygen and Carbon Dioxide in Small Volumes of Saline Solutions. THOMAS G. BRODIE and WINIFRED C. CULLIS (*J. Physiol.*, 1908, **36**, 405—413).—A simple method is described of boiling off and collecting the gases from small amounts of oxygenated Ringer's solution used to perfuse surviving organs. The gas bubble is then introduced into a carefully-calibrated capillary tube, and its length measured; potassium hydroxide is then introduced to absorb the carbon dioxide, and an alkaline solution of pyrogallol acid to absorb the oxygen; the diminution of the length of the bubble is a measure in each case of the amount of gas absorbed; the final residue is nitrogen. W. D. H.

Differential Method of Blood-Gas Analysis. JOSEPH BARCROFT (*Proc. physiol. Soc.*, 1908, li; *J. Physiol.*, **36**).—Equal quantities of venous and arterial blood in separate bottles are connected to the manometer of the Barcroft-Haldane apparatus. The blood is then laked as usual, potassium ferricyanide added, and the oxygen liberated. The difference of the levels in the fluid in the manometer is a measure of the amounts of oxygen in the two fluids. The carbon dioxide can then be liberated by tartaric acid, and another reading taken. For oxygen estimation, the ferricyanide may be omitted, and the two samples of laked blood simply shaken with the air; both samples will then saturate themselves with oxygen, and the same difference of level will be produced. W. D. H.

Estimation of Gases in Human Blood by the Chemical Method. JOSEPH BARCROFT and P. MORAWITZ (*Proc. physiol. Soc.*, 1908, lvi; *J. Physiol.*, **36**).—Doubt has been expressed as to whether the ferricyanide method is efficient for human blood. The present series of experiments on five persons shows that it is. W. D. H.

New Process for the Estimation of Sulphur in Organic Substances. ISIDORE BAY (*Comp. rend.*, 1908, **146**, 333—334).—The substance is heated in a tube with sodium carbonate and magnesia; a current of oxygen is passed through the tube during the combustion, and the sulphuric acid formed is estimated subsequently by dissolving the contents of the tube in dilute hydrochloric acid and precipitating with barium chloride. The combustion tube may be filled as follows: firstly, a plug of asbestos 3 cm. in length; then 10 cm. of a mixture consisting of equal weights of sodium carbonate and magnesia; next, the substance to be analysed mixed with sodium carbonate and magnesia, and, finally, another layer of the mixture of sodium carbonate and magnesia about 20 cm. in length, a second plug of asbestos being employed to close this end of the tube. The exit end of the tube may be connected with a Liebig bulb containing sodium hydroxide and bromine to prevent any loss of volatile sulphur compounds. The quantity, if any, of sulphuric acid yielded by the sodium carbonate and magnesia must be estimated separately and deducted from the result obtained. The process is suitable for the estimation of sulphur in mercaptans, ethyl sulphide, allylthiocarbimide, thiophen, &c. In the case of liquids, the substance is introduced into the combustion tube in a small glass tube. W. P. S.

Detection of Sodium Sulphite in the Presence of Sulphate and Thiosulphate. FRANK E. WESTON and C. W. JEFFREYS (*Chem. News*, 1908, 97, 85).—The solution is precipitated by means of lead nitrate or acetate, the precipitate is washed by decantation, and treated with *N*-thiosulphate. The lead sulphate and thiosulphate dissolve, whilst lead sulphite is insoluble.

The precipitate is washed and then treated with a little dilute sulphuric acid. The solution now contains sulphur dioxide, which is tested for in the usual way by the odour, or by means of permanganate, &c. L. DE K.

Estimation of Ammonia in Water. A. RONCHÈSE (*J. Pharm. Chim.*, 1908, 27, [vi], 231—235; *Bull. Soc. chim.*, 1908, [iv], 3, 362—366).—The method described previously (*Abstr.*, 1907, ii, 651) may be applied to the estimation of ammonia in water. From 250 c.c. to 1 litre of the water are acidified with sulphuric acid and evaporated to a volume of about 40 c.c.; the solution is then neutralised, using phenolphthalein as indicator, and 4 c.c. of a neutral 20% formaldehyde solution are added. The solution is next titrated with *N*/100 sodium hydroxide solution until the pink coloration reappears. Owing to the influence of the ammonium salts on the indicator, a correction is applied to the number of c.c. of alkali required for the titration, 0.1 c.c. being added for every 3 c.c. of *N*/100 sodium hydroxide used. W. P. S.

Nitrates, Nitrites, and Ammonia in Sea-water. WILHELM E. RINGER and MEJ. I. M. P. KLINGEN (*Chem. Weekblad*, 1908, 5, 147—168).—The authors review the methods employed in the estimation of nitrates, nitrites, and ammonia in sea-water, basing their criticisms on the results of experiments carried out with artificial solutions of known strength and with numerous samples of sea-water from various places on the coast of Holland. A. J. W.

Volumetric Estimation of Phosphoric Oxide by Uranium. FERNAND REPITON (*Chem. Zentr.*, 1907, ii, 2078; from *Mon. Sci.*, 1907, [iv], 21, ii, 753—754).—A modification of Malot's cochineal process. Tincture of cochineal is prepared by boiling powdered cochineal with 100 c.c. of water for an hour, replacing the loss by evaporation, and heating again to boiling. When cold, 50 c.c. of alcohol are added, and the solution is filtered. The phosphate solution to be tested is mixed with 5 c.c. of sodium acetate solution, diluted to 100 c.c., heated to boiling, and mixed with a few drops of the indicator. Uranium solution is then run in until the solution, after first turning dark and then brick-red, changes suddenly to dull green. In order to make the necessary correction, an experiment is made by titrating under the same conditions a suspension of uranyl phosphate, when about 0.2—0.3 c.c. of uranium solution will be required to effect the change in colour. L. DE K.

Estimation of Carbon in Irons. LUCIEN L. DE KONINCK and E. VON WINIWARTER (*Bull. Soc. chim. Belg.*, 1908, 22, 104—105).—It is proposed to burn the iron with lead borate in a current of

oxygen, and to estimate the carbon dioxide formed by any suitable means.
L. DE K.

New Experiences in the Simplified Method of Elementary Analysis. MAX DENNSTEDT (*Ber.*, 1908, 41, 600—604. Compare Abstr., 1907, ii, 986).—The author gives a detailed account of the precautions to be taken in the analysis of difficultly combustible substances, of substances containing halogens or sulphur, and in the use of commercial calcium chloride and soda-lime.
C. S.

Estimation of Potassium by the Perchloric Acid Method in Manures, Dung, Soils, and Vegetable Substances, &c. VINCENT SCHENKE (*Landw. Versuchs. Stat.*, 1908, 68, 61—65. Compare Abstr., 1907, ii, 910).—The acid solution, to which sulphuric acid should be added if not already present, is evaporated and ignited at a low red heat, and the cold residue repeatedly rubbed and then digested with hot water and 2—3 c.c. of 5% hydrogen chloride. It is then washed into a measuring flask, heated, and treated with a very slight excess of 10% barium chloride. When the amount of barium sulphate is small, as in the case of straws and grain, filtration is unnecessary; phenolphthalein is added and then milk of lime, until strongly reddened, to precipitate phosphates, &c. After half an hour, an aliquot portion is acidified with hydrochloric acid, evaporated to a smaller volume, and treated with a suitable amount (5 c.c. or more) of 20% perchloric acid.

A number of determinations made by the above method are given, as well as by the less expeditious modification in which ammonia and ammonium carbonate are employed. Concordant results were obtained by the two methods, those by the lime precipitation method being, as a rule, slightly higher.

It is important to avoid adding more than a very slight excess of 10% barium chloride, and to employ only about 2 c.c. of 5% hydrochloric acid to dissolve the ignited substance.
N. H. J. M.

Separation of Silver Chloride from Silver Iodide. HENRI BAUBIGNY (*Compt. rend.*, 1908, 146, 335—336).—Whilst the method described by Hager (*Zeitsch. anal. Chem.*, 1871, 10, 341) for the separation of silver chloride, iodide, and bromide from each other yields only approximately accurate results, the author finds that a modification of the method gives trustworthy figures if the chloride and iodide alone are present. The precipitate consisting of the two silver salts (chloride and iodide) is treated for a few minutes at a temperature of 70° to 80° with about 100 c.c. of a solution containing 100 grams of ammonium sesquicarbonate and 20 c.c. of 20% ammonia per litre. The mixture is then cooled, the clear solution is decanted on to a filter, and the residue is once more extracted with the ammoniacal solution. The residue, which now consists solely of silver iodide, is poured on the filter, washed with the ammoniacal solution diluted with an equal volume of water, dried, and weighed. The silver chloride is separated from the filtrate by the addition of nitric acid, and estimated in the usual manner.
W. P. S.

Barium Arsenite and Arsenate. LEOPOLD ROSENTHALER (*Chem. Zentr.*, 1907, ii, 2078; from *Apoth. Zeit.*, 1907, 22, 982).—Barium may be precipitated quantitatively by arsenious acid in the presence of ammonia, but not by arsenic acid unless sodium hydroxide is substituted for the ammonia.

Conversely, arsenious and arsenic acids may be precipitated quantitatively by barium chloride with addition of ammonia or of sodium hydroxide respectively. L. DE K.

Electrolytic Analysis. FRITZ FOERSTER (*Zeitsch. Elektrochem.*, 1908, 14, 90—93).—A reply to Classen and to Fischer (this vol., ii, 226). T. E.

New Method of Qualitative Analysis of the Metals of the Second Group without using Hydrogen Sulphide or Ammonium Sulphide. ETTORE SELVATICI (*Boll. chim. farm.*, 1908, 47, 73—79. Compare Tarugi and Schiff, *Abstr.*, 1895, ii, 84).—The precipitation of the metals of the second group by means of hydrogen sulphide in presence of hydrochloric acid is only complete under certain conditions of acidity, temperature, and concentration, which cannot always be determined exactly. Further, cupric sulphide dissolves to some extent in ammonium sulphide solution, and mercuric and tin sulphides combine, giving a compound soluble in water and partly soluble in ammonium sulphide. In order to obviate these and other difficulties, the author recommends the following procedure, which involves the use of neither hydrogen sulphide nor ammonium sulphide.

The acid filtrate separated from the insoluble chlorides of the first group is treated with thioacetic acid, heated almost to boiling, allowed to cool, and filtered. After being washed on the filter, the precipitate is heated with concentrated nitric acid, which dissolves the sulphides of arsenic, lead (partly), bismuth, copper, and cadmium, and converts stannic and antimony sulphides into insoluble metastannic and antimonie acids and lead sulphide partly into sulphate. After filtration, the liquid is freed from excess of nitric acid by heating, and treated with excess of concentrated sodium hydroxide solution, which precipitates bismuth, copper, and cadmium as hydroxides, arsenic and lead remaining in solution; this precipitate is washed and dissolved in nitric acid, the bismuth being then precipitated as hydroxide by the addition of excess of ammonium hydroxide; the copper may be separated from the cadmium in the ammoniacal solution by means of hydrochloric acid and potassium thiocyanate, or of potassium cyanide and hydrogen sulphide. The addition of dilute sulphuric acid to the sodium hydroxide solution, containing the arsenic and lead, precipitates the latter, the arsenic remaining in solution. The metastannic and antimonie acids, mercuric sulphide, and lead sulphate are treated with alkaline ammonium tartrate to dissolve the lead sulphate, the insoluble residue being washed and dissolved in hot nitro-hydrochloric acid. The solution is then freed from excess of acid and of chlorine, and treated with hydrazine hydrochloride or sulphate to precipitate metallic mercury. The addition of zinc to the filtrate causes the precipitation

of antimony and tin, the latter being separated by its solubility in hydrochloric acid.
T. H. P.

Dry Lead and Silver Assays in Ores. JULIUS LOEVY (*Chem. Zeit.*, 1908, 32, 220).—The Belgian method of fusing the sulphide in an iron crucible yields from 98—100% of the amount of lead regulus obtainable, whereas the English or German method, fusing with metallic iron in a Hessian crucible, yields from 92—95% only.

Any eventual loss in silver is not caused by evaporation during the cupelling process, but is due simply to the lead being deficient. When ores contain much zinc, low results are obtained even with the Belgian method.
L. DE K.

Estimation of Copper in Pyrites. G. REMONDINI (*Chem. Zentr.*, 1907, ii, 2082; from *Mon. Sci.*, 1907, [iv], 21, ii, 754).—Five grams of the sample are heated until the sulphur has been completely burnt, and the residue is boiled for fifteen to twenty minutes with 30—35 c.c. of nitric acid, D 1.4, the solution is diluted with water to 250 c.c., and 200 c.c. of the filtrate are neutralised with ammonia. After again acidifying with 5 c.c. of nitric acid, the copper is deposited electrolytically.
L. DE K.

Technical Assay of Amorphous Carborundum. GABRIEL CHESNEAU (*Ann. Chim. anal.*, 1908, 13, 85—89).—One gram of the finely-powdered sample is heated in a platinum crucible to redness for two hours in a muffle. This burns off the free carbon, and the residue is treated with 20 c.c. of pure hydrofluoric acid and 1 c.c. of sulphuric acid and slowly evaporated on a sand-bath. The mass is then boiled with hydrochloric acid and, after adding some hot water, the undissolved matter is washed by decantation with hot acid water, and finally collected on the filter and washed with hot water. It consists of pure carborundum (amorphous and crystalline), which is ignited and weighed.
L. DE K.

Volumetric Estimation of Manganese in Iron and Steel. EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1908, 22, 75—80).—The author again recommends a process published by him in 1883 and independently worked out by Hampe in 1885, based on the fact that manganese is precipitated as dioxide when its solution in nitric acid is heated with potassium chlorate. The dioxide is then estimated by dissolving it in an acid solution of ferrous ammonium sulphate and titrating the excess of the latter with standard permanganate.

When dissolving pig-iron in nitric acid for the purpose of a manganese estimation, it is advisable to remove the bulk of the silicon by means of a little hydrofluoric acid. The filtrate is then concentrated and boiled with potassium chlorate and nitric acid as usual.

L. DE K.

Estimation of Ferrous Iron. NICHOLAS KNIGHT (*Chem. News*, 1908, 97, 122).—As has been stated by Mauzelius, when assaying native ferrous carbonate, such as siderite, by the Berzelius-Bunsen process (separation of the ferric from the ferrous iron by means of

barium carbonate), it is of great importance that the mineral should be merely coarsely powdered. If reduced to a fine state of division, a not inconsiderable portion of the ferrous iron is oxidised to the ferric state; this is due, in part, to the heat generated by the friction, and also to the larger surface exposed. L. DE K.

Electrolytic Separation of Nickel and Zinc. FRITZ FOERSTER and W. TREADWELL, jun. (*Zeitsch. Elektrochem.*, 1908, 14, 89).—In the separation of nickel and zinc from an ammoniacal solution containing sodium sulphite, the nickel deposited contains sulphur; the error due to this is usually between 1% and 2% of the weight of the nickel (compare Thiel and Windelschmidt, Abstr., 1907, ii, 601, 1137, and Foerster, *Zeitsch. Elektrochem.*, 1907, 13, 563). T. E.

Rapid Electrolytic Separation of Nickel from Zinc. ARTHUR FISCHER (*Chem. Zeit.*, 1908, 32, 185—186).—The author has accelerated the electrolytic deposition of nickel from ammoniacal solution by addition of sodium sulphite.

The solution should contain about 0.15 gram of nickel and zinc (as sulphates). As electrolytes are added 5 grams of ammonium sulphate 1—3 grams of sodium sulphite, and 30 c.c. of ammonia, D 0.91; the whole is then diluted to 250—300 c.c. The nickel may be deposited in twenty minutes if the following conditions are observed; as electrodes are employed two concentric cylindrical diaphragm-cathodes. Temperature 90—92°. The strength of the current to begin with is 1 ampere, which is gradually reduced to 0.1 ampere according to the potential; this is controlled by the author's compensation process described previously.

The zinc may be recovered by oxidising the solution with hydrogen peroxide, expelling the ammonia by heating, and adding 2—3 grams of tartaric acid and excess of alkali. The separation is complete in forty-five minutes when using a current of 2.5 amperes.

L. DE K.

Estimation of Nickel in the Presence of a very large Excess of Cobalt. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 89—91).—When applying the author's molybdate process (Abstr., 1907, ii, 818) to mixtures containing, say, 1 part of nickel to 20,000 parts of cobalt, it is necessary to remove first of all the bulk of the cobalt and then test for the nickel.

To the solution containing about 20 grams of the cobalt nitrate is added ammonium chloride and ammonia, and also an excess of hydrogen peroxide. The liquid is now neutralised with acetic acid, and a saturated solution of ammonium molybdate is added slowly until most of the cobalt is precipitated. The filtrate is evaporated to dryness, and the residue is moistened with nitric acid and heated to expel most of the ammonium salts; it is then dissolved in a few drops of nitric acid, and the nickel precipitated by means of an excess of ammonium molybdate as described in the previous article.

L. DE K.

Rapid Estimation of Potassium Dichromate in Milks. GOUËRE (*Compt. rend.*, 1908, 146, 291—292).—The ash from 10 c.c. of the sample is treated with 3 c.c. of 10% potassium iodide solution and 5 c.c. of hydrochloric acid, and the iodine liberated is titrated with sodium thiosulphate (5.06 grams per litre; 1 c.c. = 0.001 gram of potassium dichromate). No indicator is used. L. DE K.

Volumetric Estimation of Titanium. H. D. NEWTON (*Amer. J. Sci.*, 1908, [iv], 130—132).—The solution, which should contain not less than 10% of sulphuric acid, is placed in a flask fitted with a rubber cork through which pass a delivery tube and a small separating funnel. A sufficiency of pure zinc is added, and the whole is heated gently while a current of hydrogen is passed over the surface of the liquid. When the zinc has completely dissolved, the liquid is allowed to cool in the current of hydrogen, a sufficiency of ferric sulphate is poured through the funnel, and then sufficient air-free water to nearly fill the flask. The contents are transferred to a larger flask containing more air-free water, and the liquid is at once titrated with *N*/10 permanganate. One at. of iron = 1 at. of titanium. If the zinc is not free from iron, this should be allowed for. L. DE K.

Estimation of Small Quantities of Bismuth. HERBERT W. ROWELL (*J. Soc. Chem. Ind.*, 1908, 27, 102—104).—In the process described, the bismuth is obtained in solution free from large quantities of lead, copper, tin, antimony, gold, and silver, then precipitated as oxychloride, and finally estimated colorimetrically as iodide in sulphuric acid solution. In the case of ores, mattes, &c., the sample is treated with hydrochloric and nitric acids, the silica is separated in the usual way, and the solution is evaporated with sulphuric acid to remove the hydrochloric acid and lead before being used for the estimation of the bismuth. For the estimation of bismuth in copper, 10 grams of the sample are dissolved in 60 c.c. of nitric acid (1 : 1), the solution is diluted with 150 c.c. of water, and saturated sodium carbonate solution is added until a slight permanent precipitate forms. One c.c. of the carbonate is then added in excess, the mixture is boiled for five minutes, and the precipitate, consisting of the whole of the bismuth and a little copper, is allowed to settle. The precipitate is then collected on a filter, washed, dissolved in hydrochloric acid, and precipitated as basic chloride. In the case of lead, base bullion, &c., 10 grams of the sample are dissolved in 20 c.c. of nitric acid, D 1.42, and 80 c.c. of water, the solution is boiled to precipitate most of the tin and antimony, and a little sodium chloride is added to precipitate the silver. The lead is precipitated by adding sulphuric acid to the boiling solution, and, after cooling for one hour, the lead sulphate is collected on a filter. The filtrate is treated with 5 c.c. of concentrated hydrochloric acid, a slight excess of ammonia is added, and then dilute hydrochloric acid until the solution is faintly acid in reaction towards methyl-orange. The solution is boiled, kept in a warm place for one hour, and the precipitate is collected on a filter and washed twice. The filtrate is tested with potassium iodide to

ascertain whether it is free from bismuth. The filter and precipitate are now pulped with 10 c.c. of sulphuric acid (1 : 3), 30 c.c. of water are added, the mixture is boiled, cooled to separate any lead sulphate, and filtered, the residue being washed with dilute sulphuric acid. The whole, or a suitable portion, of the filtrate, containing possibly antimony, arsenic, tellurium, iron, and traces of lead, copper, or silver, and not more than 2 or 3 mg. of bismuth, is treated with 5 c.c. of sulphuric acid (1 : 3), 5 c.c. of 20% potassium iodide solution, and ten drops of sulphurous acid. The coloration obtained is compared with that produced by known amounts of bismuth. W. P. S.

Analyses of some Alloys and Slags. RODOLFO NAMIAS (*Chem. Zentr.*, 1907, ii, 2079—2080; from *Mon. Sci.*, 1907, [iv], 21, ii, 751—752).—*Estimation of Bismuth in Complex Slags.*—Two grams of the slag are fused with 10 grams of potassium hydroxide for twenty hours, the fused mass is dissolved in water acidified with nitric acid, and evaporated to dryness. The mass is taken up with nitric acid, D 1.2, and filtered off from the undissolved tin and antimony oxides and silica. The solution is then repeatedly evaporated with hydrochloric acid to expel the nitric acid, and the filtrate, now free from silver, and the bulk of the lead are treated with hydrogen sulphide. The precipitate after being washed with warm ammonium sulphide is redissolved in hot dilute nitric acid, and the lead is precipitated by adding 15% sulphuric acid up to 200 c.c. An aliquot part of the filtrate is then precipitated with ammonia, and the bismuth oxide collected, washed with ammoniacal water, ignited with the usual precautions, and weighed. The same process may be applied also to *alloys*, although traces of bismuth are frequently retained by the tin-antimony precipitate, from which they may be recovered by a second fusion with potassium hydroxide and subsequent treatment with nitric acid.

Estimation of Antimony in Slags.—The slags are fused with a mixture of 2 parts of potassium carbonate and 1 part of sulphur. The mass is dissolved in hot water, and the filtrate is boiled with hydrochloric acid and potassium chlorate; any undissolved matter should be fused again with the sulphur mixture. The antimony is then precipitated as usual by means of metallic iron. *Estimation of Tin:* another portion of the slag is fused with potassium hydroxide and then boiled repeatedly with nitric acid; the joint oxides of tin and antimony are collected, ignited, and weighed.

Estimation of Antimony in Alloys.—In the case of type metal and similar alloys, the finely cut up metal is boiled with dilute hydrochloric acid (1 : 1) and some potassium iodide, which dissolves the tin and lead and leaves the antimony undissolved. *Estimation of Tin:* the alloy is treated with nitric acid, and the joint amount of tin and antimony oxides is thus obtained.

Estimation of Tin in Slags and Ashes (Ash of Dressed Silk).—The sample is fused with potassium hydroxide and treated repeatedly with nitric acid; the result is tin oxide and silica, and the latter is then estimated in the usual way by fusion with alkali and evaporation with acid. L. DE K.

Estimation of Gold by means of Sucrose or Dextrose. P. LEIDLER (*Chem. Zentr.*, 1907, ii, 1867—1868; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 103).—Gold may be precipitated quantitatively by heating the solution on the water-bath with addition of sucrose or dextrose. Lactose cannot be used on account of the very finely-divided state of the precipitate. In the author's hands, the process gave satisfactory results with auric chloride and hydrogen aurichloride, but not with sodium aurichloride. Platinum solutions are not affected. Silver salts yield colloidal solutions. L. DE K.

Method for the Complete Analysis of Vegetable Substances. JACQUES M. ALBAHARY (*Compt. rend.*, 1908, 146, 336—338).—A portion of the substance is dried at 100° to obtain the quantity of volatile matter (water, &c.), and is then incinerated to give the amount of total ash. A second portion of the sample is extracted with alcohol; the alcoholic extract is distilled at a low temperature, and the distillate is collected in a receiver containing a known volume of standard sodium hydroxide solution and surrounded by a freezing mixture. On titrating back the excess of sodium hydroxide, the quantity of volatile acids is obtained, and this added to the weight of the residue remaining in the distillation flask gives the weight of the alcohol-soluble substances. The sum of the substances soluble and insoluble in alcohol subtracted from the weight of the original material gives the actual amount of water present. The dried substance is utilised for the estimation of the fat, colouring matters, cholesterol, and lecithin. The portion of the substance insoluble in alcohol is next digested for two days in alcohol acidified with hydrochloric acid. The solution is then poured through a filter, and the residue is washed with alcohol. The filtrate and washings are evaporated, the residue is weighed, extracted with ether to remove organic acids, and then dissolved in water. Portions of the solution are used for the estimation of the reducing sugars, mineral acids, nitrogen, asparagine, sulphur, and ash. In the portion insoluble in acid-alcohol are estimated the total protein, nuclein, albumin, starch, cellulose, &c. W. P. S.

Estimation of Phenolic Hydroxyl Groups. JOHANNES HERZOG and V. HÂNCU (*Ber.*, 1908, 41, 638—639).—The number of hydroxyl groups present in a phenol can be determined by condensing the phenol with diphenylcarbonyl chloride (Herzog, *Abstr.*, 1907, i, 512), hydrolysing the urethane thus formed, and weighing the amount of diphenylamine formed. The hydrolysis is accomplished by heating 1 gram of the phenolic urethane with 8 c.c. of alcohol and an excess of potassium hydroxide in a pressure flask for one hour at 100°. The product is transferred to a flask and steam-distilled until the distillate is clear. Any diphenylamine which remains in the condenser tube is driven over by removing the water from the condenser and passing steam through the inner tube. After one or two days, the diphenylamine is collected on a dry filter paper, dried at 30°, and weighed. The results are mostly 1% too high.

Fairly good results were obtained with phenol, resorcinol, pyrogallol, eugenol, and *o*-nitrophenol.
J. J. S.

Commercial Carbolic Acid and Disinfecting Powders. MEREDITH W. BLYTH (*J. Hygiene*, 1908, 8, 83—91).—Phenol solutions used as a standard in the bacteriological testing of disinfectants should be made from freshly-distilled phenol. The actual quantity of phenols and cresols present in commercial carbolic acids and carbolic powders may be estimated by extracting the oils and testing their germicidal power. The comparative germicidal value of disinfectant powders may be estimated by keeping the powder and organism in contact by mechanical means during the whole period of the experiment.
W. D. H.

Estimation of Picric Acid. MAX BUSCH and G. BLUME (*Zeitsch. angew. Chem.*, 1908, 21, 354—356).—The process is based on the practical insolubility of nitron picrate in water. One hundred and fifty c.c. of the solution containing about 0.2 gram of any picrate are mixed with 1—2 c.c. of dilute sulphuric acid and heated just to boiling. Ten c.c. of nitron acetate (10% solution of nitron in 5% acetic acid) are added, and, when cold, the precipitate is collected on a Neubauer crucible, washed with 50—100 c.c. of cold water, dried for an hour at 110°, and weighed. The weight $\times 229/541$ = picric acid.

Bromides, iodides, chlorides, chlorates, perchlorates, nitrites, nitrates, and chromates should be absent.
L. DE K.

Differentiation between Arbutin and Quinol. P. LEMAIRE (*Ann. Chim. anal.*, 1908, 13, 105—107).—When heated with ammoniacal silver nitrate, arbutin gives a beautiful silver mirror, whilst quinol is reduced rapidly in the cold. When heated with a solution of sodium hypobromite, arbutin gives a precipitate, whilst with quinol a passing blue coloration is noticed in the cold and also a precipitate which forms rapidly. A mixture of equal volumes of arbutin solution and sulphuric acid turns green on adding a few drops of 10% potassium dichromate solution, but quinol causes a brownish-black coloration. Arbutin gives a blue colour with ferric chloride, whilst quinol turns yellowish-brown, finally yielding a black, crystalline precipitate. When boiled with an equal volume of mercuric sulphate solution (5 grams of mercuric oxide, 20 c.c. of sulphuric acid, 100 c.c. of water), the liquid turns pale yellow, and on cooling gives a deposit; in the case of quinol, a yellowish-brown coloration is noticed. A mixture of arbutin solution with an equal volume of sodium hydroxide gives no coloration in the cold, whilst quinol turns yellowish-brown. An alkaline solution of arbutin turns pale yellow with sodium persulphate, whilst quinol turns reddish-brown.
L. DE K.

New Reactions for Cholesterol and Oxycholesterol. L. GOLODETZ (*Chem. Zeit.*, 1908, 32, 160).—Solid cholesterol turns blackish-brown when moistened with 1—2 drops of a mixture of 5 parts of sulphuric acid and 3 parts of 30% formaldehyde. Cholesterol turns blue when treated with a drop of liquefied

trichloroacetic acid and a drop of 30% formaldehyde. Oxycholesterol when treated with a few drops of liquefied trichloroacetic acid turns at once green and shows, in the spectrum, a dark band in the red.

L. DE K.

The Sugar in Blood. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1908, 8, 356—359).—Parallel determinations were made of the sugar in the blood, using the electronegative kaolin and the electropositive ferric hydroxide for adsorption of the proteins. The results with the former substance were somewhat higher than those with the latter, and this has been shown to be due to the fact that the kaolin contained small quantities of a magnesium salt, which was precipitated as oxide with the cuprous oxide. With the polarimeter, the same results were obtained with kaolin as with ferric hydroxide.

S. B. S.

Use of Potassium Ferrocyanide and Zinc Acetate as Defecating Agents in Urine Analysis. CYRILLE CARREZ (*Ann. Chim. anal.*, 1908, 13, 97—101).—A solution is prepared containing 150 grams of potassium ferrocyanide per litre and another one containing 300 grams of zinc acetate per litre. When a urine has to be tested for sugar with Fehling's solution or when the amount has to be determined polarimetrically, 50 c.c. of the sample are mixed first with 5 c.c. of the ferrocyanide and then with 5 c.c. of the zinc solution, and the filtrate is then tested as usual.

When the polariscope is employed, a second portion of 50 c.c. is treated in the same manner, but with a further addition of 25 c.c. of water. From the result of the two readings, the amount of dextrose is calculated as usual.

L. DE K.

Estimation of Lactose in Milk. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1908, 27, [vi], 236).—Ten c.c. of the milk are treated with 92 c.c. of a solution containing 5 mg. of mercuric acetate and 2 mg. of glacial acetic acid. The mixture is poured on a filter, and the filtrate is shaken for a few moments with an excess of zinc dust and again filtered. The lactose in this filtrate is then estimated volumetrically with Fehling's solution. A correction is applied to the result obtained if the milk has undergone any decomposition; the acidity is estimated, and any excess over 165 c.c. of *N*/10 alkali solution per litre of milk is calculated into lactose and added to the quantity found previously. One c.c. of *N*/10 alkali is equivalent to 0.0088 gram of anhydrous lactose.

W. P. S.

Precipitation of Glycogen. EDUARD PFLÜGER (*Pflüger's Archiv*, 1908, 121, 641—643).—Certain precautions in the method of filtering after the precipitation of glycogen by alcohol are described, the most important being that the supernatant fluid should have become quite clear before filtration is attempted, otherwise the finely-divided glycogen may pass through the filter.

W. D. H.

Estimation of Glycogen by Inversion with Acids. WILHELM GREBE (*Pflüger's Archiv*, 1908, 121, 604—635).—The statement of

Nerking and Gatin-Grużewska is confirmed that, by inversion with 2·2% hydrochloric acid and boiling for three hours, the maximum yield of sugar is reached. W. D. H.

A Colour Test for Formaldehyde and Benzoyl Peroxide. L. GOLODETZ (*Chem. Zeit.*, 1908, 32, 245).—If a few particles of benzoyl peroxide are dissolved in 10–12 drops of sulphuric acid, a strong reaction takes place, accompanied by white fumes having the odour of benzophenone or fluorenone. If now a drop of dilute formaldehyde is added, the acid turns a permanent blood-red; this colour, however, is destroyed on adding water. The test is a very delicate one, and serves for the detection of either compound. L. DE K.

Estimation of Citral in Essence of Lemon. P. BRUYLANTS (*Ann. Chim. anal.*, 1908, 13, 91–97).—The process is based on the fact that if alcoholic citral solution is added in sufficient quantity to a mixture of defibrinated (pig's) blood and yellow ammonium sulphide, the spectroscopic examination shows that the two bands of oxygenated hæmoglobin begin to fade and that a third band appears in the centre. A number of experiments have shown that the time this takes to form is inversely proportional to the amount of aldehyde present. It is therefore sufficient to prepare standard solutions of citral in lemon oil previously deprived of aldehyde by fractional distillation. Before use these are dissolved in aldehyde-free alcohol. L. DE K.

Detection of Formic Acid. HENRY J. H. FENTON and H. A. SISSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 385).—See this vol., i, 243.

Estimation of the Acidity of Wine. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1908, 27, [vi], 237).—The method described previously (*Abstr.*, 1907, ii, 512) by the author gives results which are too low, owing to the fact that certain acid constituents of the wine are precipitated by the mercuric acetate employed. For instance, the number 11·4 found by the method corresponds with the number 12·5 of Gautier's alcohol-acid scale. W. P. S.

Estimation of Volatile Organic Acids in Tobacco. JULIUS TÓTH (*Chem. Zeit.*, 1908, 32, 242–244. Compare this vol., ii, 238).—The distillation process gives unsatisfactory results. When tartaric acid is used, the distillate is actually alkaline. The following process gives good results; it is based on the fact that small quantities of oxalic acid are decomposed and expelled on repeated evaporation with water.

Three grams of the powdered sample are moistened with 3 c.c. of dilute sulphuric acid (1:5), and enough plaster of Paris is added to form a dry mass, which is then placed in a stoppered cylinder and kept in contact for forty-eight hours with 150 c.c. of anhydrous ether with frequent shaking so as to dissolve all the organic acids. Fifty c.c. of the ether are then withdrawn, and, after adding 20 to 40 c.c. of water, titrated with *N*/2 sodium hydroxide, using phenolphthalein as indicator; in the aqueous solution, the oxalic acid is then estimated. Another 50 c.c. of ether are taken, and evaporated to dryness; the

residue is then evaporated thrice with addition of 50 c.c. of water. It is then dissolved in a little water, and titrated with $N/2$ sodium hydroxide, when the loss in acidity will represent the volatile acidity (acetic acid, &c.), including the oxalic acid. L. DE K.

Estimation of Fat and Unsaponifiable Matter in Tissues, together with a Critical Examination of the Methods now in Use. MUNEO KUMAGAWA and KENZO SUTO (*Biochem. Zeitsch.*, 1908, 8, 212—347).—The various methods in use for the estimation of fat (see later) produce, when tested on the same material, very varying results, and they have been subjected to a critical experimental examination. In all cases, the material employed was a specially prepared dried meat powder.

When the fat has been estimated by weighing the amount extracted by a given solvent, varying results have been obtained, depending on the solvent or solvents employed. An examination of the extractive power of different organic liquids was made, and it was shown that ethyl alcohol can produce the largest amount of extract. Putting the amount which can be extracted by this solvent as 100, the amounts extracted by other solvents can be represented by the following numbers: methyl alcohol, 99; ethyl acetate, 77; chloroform, 72; acetone, 62; benzene, 53; ethyl ether, 46; light petroleum, 45.

The examination of the alcoholic extract after it had been purified by solution in ether and filtration, showed that, besides fats, considerable quantities of other products were present, and the nitrogen in one case amounted to as much as 4.3%; the extract also contained phosphorus (compare *Abstr.*, 1907, i, 371). Various methods were attempted for the separation of other substances extracted, but without success. It is found, however, that the higher fatty acids produced by hydrolysis can be readily obtained nearly pure by solution in light petroleum, in which the accompanying substances are insoluble. The true fats can therefore be estimated by weighing the fatty acids thus purified, which are produced by the hydrolysis of the alcoholic extract. It is found that a considerable part of the aliphatic acid produced by hydrolysis, that is not soluble in light petroleum, is lactic acid. The residue of the meat powder after extraction with alcohol yields on hydrolysis a certain quantity of higher fatty acid, which can also be purified by solution in light petroleum. It is proposed therefore to estimate the fat in tissues by determining the quantity of fatty acids obtainable by hydrolysis of the whole substance as follows.

Two to five grams of the dry tissue powder are warmed on the water-bath for two hours with 25 c.c. of $5N$ -sodium hydroxide (20 per cent.). The tissue readily dissolves. The mixture is then washed into a separating funnel and acidified with 30 c.c. of a 20% hydrochloric acid. The separated fatty acids are taken up with 70—100 c.c. of ether. The ethereal solution is filtered through asbestos, and the ether evaporated off at 50° . The residue thus obtained contains, in addition to fatty acids, colouring matters, lactic acid, and other substances. After thoroughly drying at 50° for some hours, 20—30 c.c. of light petroleum are added, when the impurities separate in a resinous form. The light petroleum solution is then filtered through asbestos, the

solvent distilled off at 50°, and the residue dried at this temperature to constant weight. Analysis shows that it consists of almost pure fatty acids, and that it is practically free from phosphorus and nitrogen.

Comparisons were made of this method with those of Rosenfeld (extraction with alcohol and then with chloroform and weighing the combined extracts), of Dormeyer (digestion with pepsin, extraction of the digest with ether, and weighing ethereal extract), of Glikin (extraction with light petroleum), and of von Liebermann-Szekely (hydrolysis of tissue with sodium hydroxide, acidification, extraction of acids with light petroleum, and titration of an aliquot part of extract with sodium hydroxide). Rosenfeld's method gives results which are 17.4—46% too high, in spite of the fact that the residue of tissue after extraction with organic solvents still yields appreciable quantities of higher fatty acids on hydrolysis. The Pflüger-Dormeyer method gives results which are 16.7—40% too high. The Glikin method shows smaller inaccuracies, whilst in the von Liebermann-Szekely method, the principle of which is somewhat similar to the newly-proposed method, other than the higher fatty acids are estimated, and there are besides various minor inaccuracies.

It is claimed finally that it is not possible to estimate fats in tissues with absolute accuracy. The fatty acid number obtained by this method gives results, however, which compare favourably in accuracy with other indirect determinations, such as that of the proteins in tissues, determined by the nitrogen values, and the carbohydrates, determined by the copper reduction method.

The non-saponifiable matter can be determined by treating the fatty acids in petroleum solution with sodium hydroxide dissolved in absolute alcohol, and estimating the amount of substance remaining in the organic solvent after addition of water. S. B. S.

A New Reaction of Proteins. BRUNO BARDACH (*Zeitsch. physiol. Chem.*, 1908, 54, 355—358).—If iodine is dissolved in an albumin solution in the presence of small quantities of acetone, the formation of iodoform is hindered, and, instead of the usual plates and stars, a precipitate of yellow needles is deposited after a varying lapse of time. The same reaction is given by various proteins, but its delicacy varies in different members of the group. W. D. H.

Physiological Assay of Digitalis Leaves. C. FOCKE (*Arch. Pharm.*, 1908, 245, 646—656. Compare Ziegenbein, Abstr., 1903, ii, 118; Barger and Shaw, Abstr., 1904, ii, 793).—A 10% infusion of the powdered leaves is injected into the femoral lymph sac of *Rana temporaria*; the dose should be 1/50 of the body weight. The activity of the drug is then regarded as being inversely proportional to the average time required to stop the heart's action permanently in a series of frogs; this period should be seven to fifteen minutes. The frogs employed should weigh 20—35 grams, and during the experiment they should be cooled (down to 17°) in very hot weather, or warmed (up to 22°) in winter, so as to secure the optimum pulse rate of 48—60 per minute. It is only in this manner that uniform results can be obtained throughout the year. G. B.

General and Physical Chemistry.

Refractive Indices of Alcohol-Water Mixtures. LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1908, 30, 353—360).—Leach and Lythgoe (Abstr., 1905, ii, 655) have made determinations of the refractive powers of aqueous solutions of methyl and ethyl alcohols in which the concentrations were probably deduced from the densities. In the case of very strong alcohols, the refractometric and density constants bear such a relation to each other that the concentration may be much more accurately inferred from the former than from the latter, and it was therefore considered of importance that the refractive constants should be fixed independently of density measurements. The author has prepared absolute alcohol, and made the required solutions by diluting it with known weights of water.

The absolute alcohol was prepared in three ways: (1) the usual calcium oxide method, (2) by means of calcium, and (3) with magnesium amalgam. All these methods gave a product of the same density, refractive index, and critical solution-temperature.

Crismer's observation that the critical solution-temperature of alcohol in petroleum is the best criterion of its dryness is confirmed.

Absolute alcohol has $D_4^{25} 0.78510 \pm 0.00001$, refractive index, μ , against air, 1.35941 ± 0.00001 at 25° on the hydrogen scale, and refractive powers, $(n_D - 1)/d$, 0.45833 and $(\mu_D - 1)/d$, 0.45779 .

The refractive indices against air are recorded for alcohol containing from 0% to 30% of water, and the approximate temperature-coefficients of refraction are given throughout the same range. A maximum refractive index, 1.363315 at 25° , has been found for the mixture containing 20.7% of water, which corresponds closely with $3C_2H_5 \cdot OH, 2H_2O$.
E. G.

Refractive Power of Helium. KARL SCHEEL and RUDOLF SCHMIDT (*Ber. deut. physikal. Ges.*, 1908, 6, 207—210. Compare Abstr., 1907, ii, 145).—The refractive index of helium has been measured for a series of wave-lengths by the interference method previously described. The dispersive power of helium is very small, and the index of refraction of helium at 14° for wave-lengths within the limits of the visible spectrum is found to be 1.0000340 . This is appreciably smaller than the value given by Ramsay and Travers (1.0000362).

H. M. D.

Refraction and Dispersion of Helium. KURT HERRMANN (*Ber. deut. physikal. Ges.*, 1908, 6, 211—216. Compare preceding abstract).—The refraction and dispersion of air, hydrogen, and helium has been measured by the interference method. As the source of

light, a mercury arc lamp was used, and the following values are given for the refractive index of helium :

Wave-length.	Refractive index.
0.579 μ }	1.000034384
0.576 μ }	
0.5461 μ	1.000034525
0.4359 μ	1.000035335.

H. M. D.

Abnormal Dispersion of Metallic Vapours. FRANZ SCHÖN (*Chem. Zentr.*, 1908, i, 332; from *Zeitsch. wiss. Photograph. Photo-physik. Photochem.*, 1907, 5, 349—372, 397—436).—The vapour of alkali and alkaline-earth metals, thallium, gold, silver, and copper are shown to exhibit abnormal dispersion. The salts examined were vaporised in a carbon arc, a cold iron plate being introduced, whereby the flame was bent out and the typical anomalous dispersion observed. With the alkali metals, abnormal dispersion was only noticed with the lines of the principal series, the same being the case with copper, silver, and gold. The alkaline-earth metals show anomalous dispersion only in the case of a few lines, whilst magnesium, zinc, cadmium, and aluminium give normal dispersion. The calculated results confirm a formula derived from the electromagnetic theory of light. Concerning this, however, also the relation between the values of the constants found and the atomic weight of the metal, the original must be consulted.

J. V. E.

Wave-length Tables of the Spectra of the Elements and Compounds. SIR HENRY E. ROSCOE, MARSHALL WATTS, SIR W. NORMAN LOCKYER, SIR JAMES DEWAR, GEORGE D. LIVEING, ARTHUR SCHUSTER, W. NOEL HARTLEY, WOLCOTT GIBBS, SIR WILLIAM DE W. ABNEY, and WALTER E. ADENEY (*Brit. Assoc. Report*, 1907, 77, 116—270).—A table of standard lines, and wave-length tables of the arc and spark spectra of iridium, osmium, and rhodium. T. H. P.

A Phenomenon Attributable to Positive Electrons in the Spark Spectra of Yttrium. JEAN BECQUEREL (*Compt. rend.*, 1908, 146, 683—685. Compare *Abstr.*, 1906, ii, 317, 421; 1907, ii, 147; this vol., ii, 3, 78; Dufour, this vol., ii, 138).—The variation of the absorption bands in a magnetic field observed by the author in the cases of crystals, and solutions at low temperatures, of the rare earths, and by Dufour (*loc. cit.*) in the flame spectra of alkali-earth chlorides and fluorides, is also exhibited in the spark spectrum of yttrium. If, as is probable, the phenomenon is due to the presence of positive electrons, it follows that, although the positive electrons are so closely associated with the atom that they cannot be separated either by electric discharges or by radio-active phenomenon, they acquire sufficient mobility to manifest themselves in optical phenomena.

M. A. W.

Presence of Spark Lines in Arc Spectra. CHARLES FABRY and HENRI BUISSON (*Compt. rend.*, 1908, 146, 751—754).—Spectroscopic

examination of the arc between iron poles has shown (*Compt. rend.*, 1907, 144, 1155) that this emits all the spark lines, but only from some parts of the arc. The arc produced between two vertical iron rods, 7 mm. in diameter, on visual examination appears to be formed of two flames, one proceeding from each electrode. The negative flame is much the more brilliant, and the difference is the greater for the radiations of the longer wave-length; thus, through a red glass the positive flame is almost invisible. In the ultra-violet, the lines given by the negative flame are widened, and a great many undergo reversal, but none of the lines are reversed by the positive flame. The flames seem to originate at a brilliant point situated on the fused drop of iron terminating each electrode. These brilliant points emit all the spark lines, but an anastigmatic spectroscope is required to distinguish their origin. For the smallest wave-lengths of the extreme ultra-violet, the arc spectrum and the spark spectrum are very different. The lines 2493, 2664, and 2684 are emitted only by the electrodes; the flame gives the lines 2679, 2689, and 2735, which are not strengthened at the poles, whilst 2395, 2413, and 2563, common to both, are strengthened at the electrodes.

The above properties are not peculiar to the iron arc, but are observed also with nickel and copper electrodes; the phenomenon has also been observed by Hartmann (*Astrophysical Journal*, 1903, 17, 270) with magnesium. Lockyer considers that the production of spark lines in arc spectra is due to the very high temperature, but the authors believe that it is more probably the result of the rapid fall of potential occurring in the neighbourhood of the electrodes, and suggest that the essential condition for the emission of these rays is the existence of very rapid vibrations, caused in the present case by the electric field, and in other cases due to a thermal effect.

The emission of spark lines by the brilliant points on the electrodes explains their predominance when the conditions are such (immersion of the arc in water) that the intensity and length of the flames of the arc are diminished.

The arc between iron poles can also take another form, in which the brilliant point is observed only on the cathode and the anode flame has vanished. A considerable increase in the difference of potential between the electrodes occurs on passing from the first form of arc to the second.

E. H.

Change in the Hydrogen Spectrum under the Prolonged Action of Strong Electric Discharges. E. ROGOVSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 37—41, *Phys.*).—After passing a strong discharge through a tube of hydrogen for several hours, the lines H_{α} , H_{β} , and H_{δ} disappear from its spectrum, many new lines and bands making their appearance, whilst the colour of the discharge changes from pink to light lilac.

When a tube through which a strong discharge has been passed is kept at rest for four months, the red and blue lines $\lambda = 656.3$ and $486.1 \mu\mu$, together with many other lines in the red, orange, and green, have disappeared from the spectrum, whilst some of the other lines in the blue which had at first disappeared now reappear. The

photograph of the latter spectrum is given and is compared with an ordinary hydrogen spectrum.

The hydrogen spectra here described differ entirely from the secondary spectrum described by Dufour (Abstr., 1907, ii, 1). More probably they are the spectra to be expected for hydrogen from Goldstein's results for some of the alkali metals (Abstr., 1907, ii, 725).
Z. K.

Band Spectrum of Calcium Fluoride. B. WALTER (*Physikal. Zeitsch.*, 1908, 9, 233—234. Compare Dufour, this vol., ii, 138).—Spectral observations with a Bremer arc lamp, the carbons of which contain calcium fluoride, show that the individual lines in several of the bands due to this substance are reversed. This is the case for the bands the centres of which are represented by the wave-lengths 6036·96, 6050·81, and 6064·49, whilst the band with its centre at 6087·24 is not reversed. These four bands are all of the same type, but reversion is also exhibited by the band with its centre at the wave-length 5290·94, which is of a different type.
H. M. D.

Spectroscopic Study of Flames of Various Kinds. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1908, 146, 748—751).—The method of studying flame spectra previously described (*Compt. rend.*, 1907, 144, 1338; 145, 1266) has been applied to the hydrogen flame. If the hydrogen before burning traverses an arc between iron rods, or, better, between an iron and a carbon electrode, the flame emits light, but is not uniformly luminous. The matter detached from the electrodes forms a cylindrical column, composed of threads of incandescent particles, which gives a continuous spectrum. In the latter, the ray 3860·03 of iron occurs very feebly, the three, 4030·84, 4033·16, and 4034·59, of manganese are just visible, and the calcium ray, 4226·9, appears extremely feebly. These rays probably proceed from impurities in the hydrogen. The external envelope of the flame emits only the calcium ray. If the arc is produced between calcium electrodes, the entire hydrogen flame takes an orange coloration, and besides the above rays, the green and red calcium bands are observed in its spectrum. The fact that in the case of iron the internal luminous column of the flame furnishes only a continuous spectrum, seems to support the theory that flame spectra are the result of chemical reactions. When the iron is present only in traces, as impurities in the burning hydrogen, addition of oxygen causes the appearance of some supplementary rays. This spectrum is probably composed of de Gramont's "ultimate rays" (Abstr., 1907, ii, 517). The authors have compared their spectrum with that of the star α -Cygni (Lockyer, 1902), giving a table showing the comparative intensities of the various lines in the two spectra, which show a certain resemblance.
E. H.

Ultra-red Emission Spectra of the Alkali [Metals]. A. BERGMANN (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 145—169. Compare this vol., ii, 242).—In this concluding part of the author's paper, an account is given of relative measurements in the

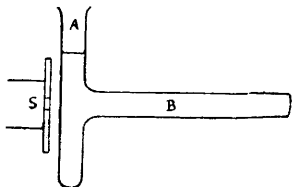
ultra-red prismatic spectrum. It has been found that the majority of the lines are too weak for accurate determinations of the wave-lengths to be obtained from the diffraction spectrum, and the wave-length values have been obtained from observations on the prismatic spectrum, using an interpolation formula of the form $\lambda = A + B/(D - C) - KD^2$, in which λ is the wave-length, D the angular reading, and A , B , C , and K are constants.

The numbers of new lines which have been measured in the ultra-red region are for lithium, 2; sodium, 1; potassium, 9; rubidium, 8; caesium, 10. With the exception of one caesium line ($\lambda = 1377 \mu\mu$), all the new lines fall into series, and for potassium, rubidium, and caesium the existence of a new secondary series of lines is established. These new series exhibit relationships which are opposite in character to those of the series previously known, in that with increasing atomic weight of the alkali metal the new series lines are shifted towards the blue end of the spectrum.

H. M. D.

Modified Spectroscopic Apparatus. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1908, 30, 577—578).—1. In the examination of absorption spectra of dilute solutions in long tubes, the faintness of the spectra is often a great disadvantage. This difficulty is partly obviated by the use of a container made from a T of glass tubing of suitable diameter. The light passes through the tube B lengthwise, and is focussed upon the slit S by the solution in the tube A , which acts as a cylindrical lens, thus increasing the intensity of the light.

2. A simple fulgurator is readily constructed by fusing together, in a nearly parallel position by means of a small piece of glass rod, two glass tubes, into one end of each of which platinum wires have been sealed. One of the wires is bent in the form of a U, so that the end is directly below and parallel to the wire in the other tube. The end of the lower wire may be covered with a glass capillary in the usual way. The apparatus is dipped into the solution to be examined until the capillary is filled with solution. This system can be readily transferred from one solution to another, and can easily be rinsed into the vessel in which it has been used.



W. H. G.

Influence of Temperature and Magnetisation on Selective Absorption Spectra. HENRI E. J. G. DU BOIS and G. J. ELIAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 578—588).—The absorption spectra in the visible region of solid compounds of chromium, uranium, neodymium, and erbium, and of natural crystals of ruby and emerald, were examined at 18° and at -193° . The bands become narrower at the temperature of liquid air, in some cases becoming as sharp as the lines of sodium vapour. The effect of magnetisation in resolving the sharper lines was examined.

C. H. D.

Absorption Spectra of Crystals of the Rare Earths and the Changes which they Undergo in a Magnetic Field at the Temperatures of Liquefaction and Solidification of Hydrogen. JEAN BECQUEREL and H. KAMERLINGH ONNES (*Compt. rend.*, 1908, 146, 625—628. Compare this vol., ii, 78).—Previous observations relating to the influence of temperature on the absorption bands of tysonite and xenotime have been extended by measurements at -253° and -259° . The conclusion drawn from measurements between $+100^{\circ}$ and -190° that the width of certain bands of tysonite is proportional to the square root of the absolute temperature is found not to hold for temperatures between -190° and -259° . In this region the width of the bands decreases much less rapidly than would be the case if the above relationship held good. In the case of xenotime, two of the bands examined are wider at -259° than at -253° , and the width appears to have passed through a minimum at an intermediate temperature. This phenomenon is supposed to represent the general influence of temperature, there being for all bands a certain temperature for which the width of the band is a minimum.

Observations relating to the influence of temperature on the absorption bands observed in circularly polarised light are also recorded and interpreted in terms of the electron theory. H. M. D.

Infra-red Reflection Spectra. W. W. COBLENTZ (*Jahrb. Radioaktiv. Elektronik.*, 1908, 5, 1—14).—A number of minerals have been studied by measuring the rays from a Nernst lamp reflected from a cleavage surface, and comparing them with those reflected by a silver mirror. The radiation was measured by means of a Rubens thermocouple.

Molybdenite, pyrrhotite, chalcocite, and covellite, and also magnetite, hæmatite, chromite, and zincite give continuous reflection. On the other hand, scheelite, wulfenite, rutile, and corundum show selective reflection, as do the silicates. Quartz, both in the crystalline and in the glassy form, shows selective reflection, which is different for the two modifications. In the absence of more definite knowledge respecting the constitution of the silicates, it is not possible to draw any conclusions as to the relation of the spectra to the structure of the silicic acids. C. H. D.

Examination of Liquid Crystals in Convergent Polarised Light. ERNST SOMMERFELDT (*Physikal. Zeitsch.*, 1908, 9, 234—235. Compare Vorländer, Abstr., 1907, ii, 441, 442).—To demonstrate the pseudo-isotropic character of liquid crystals at the ordinary temperature, ammonium and potassium oleate may conveniently be used. The double refraction exhibited by the ammonium salt is about the same as that of the feldspars. On account of the turbidity of potassium oleate, it could not be examined alone, but, when mixed with the ammonium salt, the double refraction observed with the latter was considerably increased, and it was possible to obtain a complete interference ring in the field of view with a mixture of the two oleates. H. M. D.

Rotatory Polarisation in Crystals which are not Enantiomorphous: Methyl Mesityloxidoxalate. ERNST SOMMERFELDT (*Jahrb. Min.*, 1908, i, 58—62).—Crystals of the polymeride of methyl mesityloxidoxalate ($[\text{C}_9\text{H}_{12}\text{O}_4]_2$) (Federlin, *Abstr.*, 1907, i, 1006) are hemihedral-monoclinic, possessing a plane of symmetry, but no axis of symmetry. The optic axial plane is parallel to the plane of symmetry, and the axial angle is wide. The interference-figure shown in convergent polarised light, in the position when the vibration-directions of the plate coincide with those of the nicols, differs from a normal biaxial interference-figure in the absence of the dark bar perpendicular to the axial plane. Sohncke in his theory of crystal structure connected the rotatory polarisation of crystals with their enantiomorphous forms, but it has since been proved theoretically that certain classes of crystals which are not enantiomorphous may be circularly polarising.

L. J. S.

The Mathematical Treatment of Photochemical Reactions on Thermodynamical and Electrochemical Basis. ALFRED BYK (*Zeitsch. physikal. Chem.*, 1908, 62, 454—492).—In this theoretical paper the author deals with photochemical reactions in homogeneous systems, and develops the conception of a photochemical process as a special case of electrolysis by alternating current. This conception is based on the electromagnetic theory of light, and leads to formulæ which are in general harmony with what is known of photochemical processes, both in respect of reaction velocity and of equilibrium (see Luther and Weigert, *Abstr.*, 1905, ii, 785), and do not presuppose the formation of intermediate compounds. In reversible photochemical reactions, according to the author's views, the change which takes place in the dark takes place all the same when the system is exposed to light; it is to be regarded as an electrically neutral process; on exposure to light, an extra reaction is induced, which is simply superposed on the former, and is to be regarded as of an electrolytic character.

J. C. P.

Photochemistry. MAX TRAUTZ (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 169—194).—A theoretical paper in which photochemical change is considered from the standpoint of thermodynamics. It is shown that all the chief photochemical regularities can be deduced by the aid of the second law of thermodynamics.

H. M. D.

Phototropy of the Fulgides and other Substances. HANS STOBBE (*Annalen*, 1908, 359, 1—48. Compare *Abstr.*, 1905, i, 857; 1906, i, 960).—Fulgides, containing aromatic substituting groups, undergo change of colour when exposed to light. Thus, triphenylfulgide, which forms pleochroic, orange-red, monoclinic crystals, becomes dark brown when exposed to sunlight or the rays of an arc lamp, changing again to its original colour in the dark. The brown and orange modifications are chemically identical, and differ only in the solid state. Such phenomena have been termed by Marckwald (*Abstr.*, 1900, i, 2) phototropy. If this phototropic change is frequently

repeated, the difference between the shades of the two forms becomes gradually less, a chemical change taking place which leads finally to the complete conversion of the fulgide into a new substance, the photo-anhydride. This slow photochemical reaction which accompanies the phototropic change is not reversible. The structure of the photo-anhydride will be discussed in a future communication. The present paper is a study of the nature of the phototropic change and the conditions under which it takes place.

To study the action of light waves of different lengths, the fulgide is exposed in a thin layer between two glass plates in a special spectrographic apparatus. Orange-yellow triphenylfulgide, when exposed to the light of the spectrum, after two minutes shows a broad, brown band between the spectrum lines E and G, which on prolonged exposure gradually extends towards the ultra-violet. If the whole layer of fulgide is first exposed to light under a cobalt or bluish-violet Jena glass light filter, it changes to blackish-brown and on exposure to the spectrum light becomes orange-yellow between the lines E and B, but brown from E towards the ultra-violet. Hence the yellow modification is sensitive to blue and violet light rays, but the blackish-brown form, which is intermediate between the yellow and brown modifications, is sensitive to yellow and red rays. The portion of the spectrum which causes the phototropic change from the yellow into the brown modification is termed the zone of stimulation (*Erregungszone*). The behaviour of a number of di- and tri-arylfulgides towards light rays of different wave-lengths has been studied in this manner, and the results obtained, of which those described for triphenylfulgide are typical, are tabulated and expressed graphically.

Phototropic change has been observed only with the lemon-yellow to orange-red diaryl- and the orange-red to dark red triaryl-fulgides; the colourless aliphyl- greenish-yellow to yellow-monoaryl-, and red, purple-red, or brown or tetra-aryl-fulgides are not phototropic.

The modifications of a phototropic substance can exist in the pure state only when exposed to light rays of the wave-length under the influence of which they are formed. Under all other conditions, the substance is a mixture or solid solution of the one form in the other. The phototropic change is caused by the light rays which are absorbed by the modification undergoing the change. Hence the brown form of triphenylfulgide must be in reality blue, the brown appearance resulting from its state of granulation. The equilibrium between the two modifications in a mixture depends on the wave-lengths of the light to which it is exposed. It follows that the parts of the spectrum which produce the phototropic change depend on the colour of the fulgide, the zone of stimulation lying the more towards the violet the deeper the normal shade of the substance, whilst the lighter the shade the further towards the ultra-red does the portion of the spectrum causing the reverse change extend, and that the amount of change in the colour of a phototropic fulgide not only increases with diminishing wave-lengths of the light rays and with increasing intensity of illumination, but diminishes with increasing temperature and depends, further, on the number and nature of the substituting groups, being greatest with diphenyl-*o*-methoxyphenyl-, diphenyl-

piperonylallo-, and diphenyl-*o*-nitrophenyl-fulgides, less with diphenyl-*p*-methoxyphenylfulgide, and least with the diaryl-fulgides. The furyl-fulgides resemble the phenyl compounds.

The phototropy of the fulgides is shown to be analogous to a number of other reversible reactions which take place under the influence of light, and is compared with the phenomena of fluorescence. As the phototropic modifications of the fulgides undergo the reverse change spontaneously in the dark, the energy of the light rays of short wavelength absorbed during the phototropic change might appear during the formation of the original form as heat or fluorescence. This, however, has not yet been observed.

The phototropy of other substances has been studied in a similar manner. The zone of stimulation for colourless β -tetrachloro- α -ketonaphthalene (Marckwald, *loc. cit.*) lies in the ultra-violet, whilst the reverse change is caused by yellowish-green or yellow rays. Red and blue rays have no action.

Phenylbenzylidenehydrazine, which forms light yellow crystals or a white powder, becomes red on exposure to violet or ultra-violet rays, becoming again colourless when exposed to yellow or green light. Phenylanisylidene- and phenylcuminyldiene-hydrazines behave in the same manner, as do also osazones of the benzil series (Biltz and Wienands, *Abstr.*, 1899, i, 910). Tetraphenyldihydrotriazine (Walther, *Abstr.*, 1903, i, 582) and ethyl oxalisobutyrate (Wislicenus and Kiesewetter, *Abstr.*, 1898, i, 240) have also been observed to exhibit phototropy. G. Y.

Simple Gas Burner Contrivance for Showing Various Flame Reactions, Combustion Phenomena, and Flame Colorations. WILHELM THÖRNER (*Zeitsch. angew. Chem.*, 1908, 21, 673—677).—The ring by means of which the air supply of an ordinary Bunsen burner is regulated is replaced by a brass cylinder to which is fixed, at right angles, a brass tube, *A*. The air supply of the burner passes through this tube, consequently, if a U-tube or other suitable vessel be attached containing a volatile liquid, such as carbon disulphide or chloroform, or in which a gas, such as hydrogen sulphide or hydrogen cyanide, is being evolved, the combustion of these liquids or gases can be demonstrated. By making use of the methods of Riesenfeld and Wohlers (*Abstr.*, 1906, ii, 593) or Beckmann (*Abstr.*, 1907, ii, 209), the flame colorations of various substances can also be shown. A list of experiments which may be shown by means of this apparatus is given. W. H. G.

Experiments on the Secondary Rays of Radium. H. STARKE (*Ber. deut. physikal. Ges.*, 1908, 6, 267—284).—It is found that γ -rays are not produced when the β -rays of radium are allowed to fall on substances such as lead, aluminium, and paraffin. The γ -rays of radium cannot therefore be considered as a type of Röntgen radiation resulting from the action of the β -rays on the substance of the radium. Absorption measurements which have been carried out with the secondary rays emitted by the action of β -rays on different substances, indicate that these are very heterogeneous, and that some of the component rays are much more readily absorbed than are the primary β -rays.

The secondary rays from paraffin are very easily absorbed; those from aluminium are less penetrating than the secondary rays from lead.

The most absorbable rays, both in the reflected and transmitted radiation, originate in layers of the material which are very close to the surface. In consequence of this, the transmitted radiation has a maximum intensity for a certain thickness of the material placed in the path of the β -rays, this thickness depending on the nature of the material.

The secondary rays, which originate from the action of the β -rays on air, are in all probability very readily absorbed. H. M. D.

Extraction of Polonium, and its Properties. FRIEDRICH GIESEL (*Ber.*, 1908, 41, 1059—1062).—The lead chloride obtained from pitchblende is dissolved in water, and to the solution is added a little sulphuric acid to remove radium, and then ammonia. The precipitate is digested with a large excess of hydrochloric acid, the acid solution filtered off, and the lead chloride extracted four or five times with hydrochloric acid. Each extract is reduced to a small bulk, the lead chloride which crystallises out being removed; hydrogen sulphide precipitates a mixture of the sulphides of arsenic, lead, bismuth, copper, and mercury from the first extracts, whilst almost pure copper sulphide is obtained from the later extracts. The mixture of sulphides, after treatment with ammonium sulphide, is boiled with hydrochloric acid; the radium-*E* accompanies the bismuth, whilst the polonium remains with the copper sulphide. The latter is digested with nitric acid, and excess of ammonia added to the solution; the polonium separates as a slight, white, flocculent precipitate, which, when collected and dried on a filter, is obtained as a yellowish-grey film. This precipitate is far more active than any film of polonium hitherto obtained as a deposit on metal; it ozonises the air, which at the same time is seen to phosphoresce, and induces a beautiful phosphorescence on a zinc sulphide screen. The solution of the precipitate in 2 or 3 drops of hydrochloric acid is yellowish-brown; this colour, which is discharged on the addition of hydrogen peroxide or nitric acid, is not due to the polonium, but is probably connected with the presence of radium-*D*. No indication of the formation of helium from polonium during a period of two years was obtained. W. H. G.

Heating Effects produced by Röntgen Rays in Lead and Zinc. HENRY A. BUMSTEAD (*Phil. Mag.*, 1908, [vi], 15, 432—437.* Compare Abstr., 1906, ii, 141).—The result previously obtained by the author (*loc. cit.*), that the quantities of heat produced in lead and zinc by Röntgen rays is as 2 : 1, is not confirmed by further experiments, which indicate that the quantities of heat are equal with an uncertainty of from 5% to 10%. The source of error in the previous experiments is traced to the imperfect heat insulation of the metals.

New experiments are described which show that the secondary rays emitted by lead exposed to the action of Röntgen rays are incapable of producing scintillations in a zinc-blende screen. Rays of the α -type are therefore absent.

* *Amer. J. Sci.*, 1908, [iv], 25, 299—304.

Other experiments show that the rate of change of the active deposit from thorium emanation is not altered by exposure to Röntgen rays.

H. M. D.

Anode Rays. V. E. GEHRCKE and O. REICHENHEIM (*Ber. deut. physikal. Ges.*, 1908, 6, 217—225. Compare Abstr., 1907, ii, 421).—In continuation of previous investigations of anode rays, the authors have examined most closely the so-called “striction anode rays.” Experiments with different forms of discharge tubes have shown the conditions under which such rays make their appearance. A convenient form consists of two bulbs of 10 cm. diameter with aluminium electrodes sealed through the walls at right angles to the axis joining the centres of the bulbs, these being connected by a tube which protrudes into each bulb to the extent of 2 cm. “Striction cathode rays” are at once seen when such a discharge tube filled with air or hydrogen is evacuated. If a trace of iodine vapour is added, “striction anode rays” also make their appearance. These anode rays are not influenced by a magnet.

Bromine, hydrogen chloride, bromide and iodide vapours also favour the formation of “striction anode rays,” although the effect is much smaller than that observed when iodine is admitted to the tube containing hydrogen. The rays are not only produced in hydrogen and air, but also in oxygen and helium, whereas in nitrogen no positive results were obtained.

Measurements of the fall of potential at various points between the anode and cathode when “striction anode rays” are being produced indicate that the potential gradient in the anode ray region is very steep.

These facts indicate that the phenomena of discharge at the anode are very similar to the more closely-studied effects observable at the cathode.

H. M. D.

Anomalous Behaviour of Selenium. CHR. RIES (*Physikal. Zeitsch.*, 1908, 9, 228—233).—The anomalous behaviour of crystalline selenium in regard to its electrical properties can be explained on the assumption that there are two different forms. The one form (α), obtained by heating amorphous selenium at temperatures below 200° for a considerable time and cooling rapidly, has a negative temperature-coefficient of electrical resistance. The temperature-coefficient of the second form (β) is within certain temperature limits positive, and this crystalline form of selenium is influenced by light in the opposite direction to that which characterises the α form. The β modification is obtained by heating amorphous selenium at temperatures above 200°. The product obtained by the various methods described for the preparation of crystalline selenium is characterised in terms of the author's theory.

H. M. D.

Contact Potential Differences Determined by means of Null Solutions. S. W. J. SMITH and H. MOSS (*Phil. Mag.*, 1908, [vi], 15, 478—497).—Palmaer's conclusion from the results of experiments with drop electrodes (Abstr., 1907, ii, 424), that the true

contact potential difference between mercury and 0.1*N* KCl solution is about 0.57 volt, is shown to be of doubtful validity.

Several so-called null solutions, for which the potential difference between still and dropping mercury electrodes in contact with the solution is zero, have been examined. A 0.26*N* solution of potassium cyanide possesses this property, and 0.1*N* solutions of potassium chloride, iodide, and hydroxide are convertible into null solutions by the addition of definite small quantities of sodium sulphide.

The potential differences between different null solutions and mercury are not the same. This is proved by measuring each potential difference against the potential difference Hg/0.1*N* KCl, and also by measuring one null solution against another. If the null solution potential differences are assumed to be zero, the values obtained for the potential difference Hg/0.1*N* KCl vary from about 0.53 to 0.79 volt. Assuming that the potential difference corresponding with maximum surface tension is most likely to be zero when the maximum is not depressed, it is probable that the potential difference Hg/0.1*N* KCl does not exceed 0.53 volt.

The equality between the polarising electromotive force required to produce the maximum surface tension between mercury and a given electrolyte and the electromotive force of the corresponding dropping electrode circuit no longer exists when the chemical action at the dropping electrode due to atmospheric oxygen becomes appreciable.

On the addition of small quantities of sodium sulphide to the solution, the potential difference between the dropping mercury electrode and 0.1*N* KCl remains unchanged, although the natural potential difference is thereby altered by more than 0.5 volt. The variation of the natural potential difference with increasing concentration of sodium sulphide is not uniform, but at a certain critical concentration the potential difference varies with extreme rapidity.

H. M. D.

[Condition of Air which has been passed between Sparking Electrodes.] M. DE BROGLIE (*Compt. rend.*, 1908, 146, 624—625).—The fact that flames, fed with air which has passed over metal electrodes between which a spark discharge is taking place, exhibit spectra of the metals has led the author to examine the condition of such air. It contains (1) ions of small mobility, (2) neutral centres which are converted into ions by the action of radium or Röntgen rays, and (3) attenuated solid particles which can be seen in the beam of an arc light. The cloud of solid particles is very dense in the case of sodium, thallium, and bismuth. The particles obtained from thallium electrodes have been found to show Brownian motion. These particles are the cause of the spectral reactions; some of them are electrically charged.

H. M. D.

Hydrogen Peroxide Cell. HOWARD T. BARNES and G. W. SHEARER (*J. Physical Chem.*, 1908, 12, 155—162).—In a previous paper (*Trans. Amer. Electrochem. Soc.*, 1907, 12, 54), it was shown that a cell with magnesium and aluminium electrodes in contact with water containing dissolved air, gives an *E.M.F.* which slowly rises to about

1 volt, although the metals are close together in the potential series. This is now shown to be due to the formation of hydrogen peroxide by the action of water containing dissolved air on aluminium; the peroxide is detected by the potassium iodide starch test. When free hydrogen peroxide is added to the aluminium compartment of the cell, the *E.M.F.* rises to about 2 volts, but falls gradually as the peroxide is decomposed. In some of the experiments, a solution of aluminium sulphate was used as electrolyte.

The rate of change of the *E.M.F.* and current of the magnesium-aluminium cell after a time, and the effect of adding hydrogen peroxide, are described, and the effect of rise of temperature on the behaviour of the cell, with and without the addition of peroxide, has also been investigated.

Some other metals show a similar behaviour to that of aluminium in the above respect, but the effect is much smaller, and hydrogen peroxide cannot be detected.

G. S.

Conductivity of Gaseous Mixtures at the Moment of Explosion. R. DE MUYNCK (*Bull. Acad. roy. Belg.*, 1907, 901—928).—The electrical conductivity of mixtures of carbon monoxide and air or oxygen at the moment of explosion has been measured. The explosion vessel consisted of a cylindrical brass tube, in the axis of which a copper wire was supported, this being insulated from the tube by ebonite. The tube and wire were connected through a galvanometer with the opposite poles of a battery of small cells, by means of which the conducting power of the gaseous mixture, when exploded by means of a spark, was determined.

For a given electrometric force, the galvanometer deflection was found to be much greater when carbon monoxide and oxygen are mixed in the proportion in which they combine than when the gaseous mixtures contain excess of oxygen. The conductivity is uni-polar in character, being considerably greater when the axial copper wire is connected with the positive pole of the battery than when the connections are reversed. The galvanometer deflection for a given mixture increases with the pressure, but does not appear to depend much on the hygroscopic condition of the gases. An influence of the electrodes is apparent from the fact that larger deflections are obtained in the first explosion after the electrodes have not been used for some time than are met with in subsequent explosions. With increase in the applied difference of potential, the galvanometer deflection increases, and the relationship between deflection and voltage can be expressed by a linear equation. When the temperature of the explosion tube is raised, the conductivity of the explosion mixture increases considerably.

The experimental results are utilised in a discussion of the question as to whether the electrical conductivity is a direct result of the chemical action or is a secondary effect due to the development of heat which accompanies the explosion. It is calculated that one ion is produced for every 200 million molecules of carbon dioxide which are formed. This result favours the view that the conducting power of the exploded mixture is to be attributed to the heat liberated in the change.

H. M. D.

Electrical Conductivity of Mixtures of Acid or Base and Water. G. BOIZARD (*Ann. Chim. Phys.*, 1908, [viii], 13, 433—479. Compare this vol., ii, 251).—The author has studied the changes of conductivity, viscosity, and freezing point accompanying the addition of good or weak electrolytes to mixtures of good electrolytes with water. The results are briefly as follows.

With mixtures of good electrolytes with water, there are two concentrations, one high and the other low, between which the addition of a strong or weak electrolyte produces a diminution in the conductivity. These points of inversion depend on the temperature and, in certain cases, on the amount of electrolyte added. With good electrolytes without action on the solvent mixture, a condition of isoconductivity obtains at the points of inversion, the solution having the same conductivity as the solvent mixture. The increases or diminutions of conductivity produced in this way are referred to five principal types, the transition from one of these to another generally taking place in a perfectly definite order; these variations are functions of the temperature, and are not related to the corresponding variations of the viscosity and of the depression of freezing point.

Solutions of electrolytes in mixtures of sulphuric acid with water are stable, and the chemical equilibria attained are not functions of the time and undergo reversible variations when the temperature is changed. Further, the equilibrium depends only on the relative amounts of the ions present and not on the form in which these are introduced into the solutions.

On the basis of a simple theory concerning chemical or ionic equilibria in the solutions, formulæ are derived which lead to results agreeing with the experimental observations.

The changes taking place when sulphates, bisulphates, or acetates are added to mixtures of sulphuric acid and water are considered in detail.

T. H. P.

Equivalent Conductivity of the Hydrogen Ion derived from Transference Experiments with Nitric Acid. ARTHUR A. NOYES and YOGORO KATO (*J. Amer. Chem. Soc.*, 1908, 30, 318—334).—In a paper by Noyes and Sammet (*Abstr.*, 1903, ii, 126), an account was given of transference determinations made with *N*/20, *N*/60, and *N*/80 hydrochloric acid solutions at 10°, 20°, and 30°. The results when combined with the equivalent conductivity of the chloride ion gave a much higher equivalent for the hydrogen ion than that derived from the conductivity of acids at high dilutions. In order to ascertain the cause of this divergence, transference experiments have now been made with nitric acid at 20° with the following results:

Equivalent of HNO ₃ per litre.	Transference number × 10 ³ .	Equivalent con- ductivity of hydrogen ion.
0.058	155.7	350.3
0.0184	159.6	340.2
0.0067	160.0	339.1
0.0022	162.8	332.2
0.0000	166.0	324.6

These values for the equivalent conductivity of the hydrogen ion, except at the highest concentration, agree closely with those obtained in the experiments with hydrochloric acid, and show that the value for the concentration intervals between $0.018N$ and $0.006N$ is nearly 5% greater than that derived from conductivity measurements at extreme dilution. This divergence has also been observed by Noyes and Sammet (*loc. cit.*), and has been confirmed by the conductivity determinations of Goodwin and Haskell and by the transference experiments of Jahn, Joachim, and Wolff. The conclusion is drawn that the transference number of the anion of acids, and therefore the ratio of the velocity of the anions to that of the hydrogen ion, is considerably greater at very low concentrations ($0.001N$ or less) than at moderate concentrations ($0.05-0.005N$).

It is considered probable that this change of the transference number is due chiefly, if not entirely, to a retardation of the hydrogen ion at very high dilution. The nearly constant values of the equivalent conductivity of the hydrogen ion between concentrations of $0.006N$ and $0.018N$ are regarded as normal, whilst the variation at lower concentrations is thought to be due to some secondary effect of a general character.

In view of these results, it is suggested that in calculating the ionisation values of acids which are largely ionised at moderate concentrations, the observed equivalent conductivity of the acid should be divided by a Λ_0 value, obtained by adding to the equivalent conductivity of the anion that of the hydrogen ion obtained by the transference experiments at the given concentration. On the other hand, in the case of an acid solution in which the ion concentration is less than $0.001N$, the older value (324 at 20° or 315 at 18°) for the hydrogen ion is to be preferred.

E. G.

Conductivity and Ionisation of Salts, Acids, and Bases in Aqueous Solutions at High Temperatures. ARTHUR A. NOYES [with A. C. MELCHER, H. C. COOPER, G. W. EASTMAN, and YOGORO KATO] (*J. Amer. Chem. Soc.*, 1908, 30, 335—353).—Noyes and Coolidge (*Abstr.*, 1904, ii, 226) have described an apparatus for determining the electrical conductivity of aqueous solutions at high temperatures, and have recorded measurements made with solutions of sodium and potassium chlorides. The investigation has now been extended to other di-ionic salts, namely, silver nitrate, magnesium sulphate, sodium acetate, ammonium chloride, and ammonium acetate, to two tri-ionic salts, barium nitrate and potassium sulphate, and also to potassium hydrogen sulphate, hydrochloric, nitric, sulphuric, phosphoric and acetic acids, and sodium, barium, and ammonium hydroxides. In most cases, the measurements have been made at four or more different concentrations between $0.1N$ and $0.002N$, and at temperatures ranging from 18° to 306° .

In the case of the di-ionic substances, the values of the equivalent conductivity for complete ionisation become more nearly equal as the temperature rises, and approach equality rapidly between 18° and 218° , but comparatively slowly at higher temperatures. Thus the specific migration velocities of the ions are more nearly equal the higher the

temperature. Complete equality is not reached, however, even at 306° , but the divergence only exceeds 5% in the cases of hydrochloric acid, sodium hydroxide, and sodium acetate.

The equivalent conductivity of the tri-ionic salts increases steadily with the temperature, and attains values which are much greater than those for any di-ionic salt with univalent ions. Thus at 306° the value for potassium sulphate is 1.5 times that for potassium chloride.

The rate of increase in conductivity with all the neutral di-ionic salts is greater between 100° and 156° than between 18° and 100° , or between 156° and 218° , so that the temperature-conductivity curve is first convex, later concave, and then again convex towards the temperature axis with two intermediate points of inflexion. With acids and bases, however, and therefore with the hydrogen and hydroxyl ions, the rate of increase of the equivalent conductivity steadily decreases as the temperature rises, and the curve is consequently always concave towards the temperature axis. In the case of the tri-ionic salts, the rate of increase steadily grows, owing to the great increase in the equivalent conductivity of the bivalent ion, and hence the curve is always convex towards the temperature axis.

With regard to the variation of the equivalent conductivity, Λ , with the concentration, C , of solutions between $0.1N$ and 0.002 or $0.0005N$, the results for all temperatures with all the salts, both di- and tri-ionic, and also with hydrochloric acid, nitric acid, and sodium hydroxide, can be expressed by the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, if to n is assigned a value (varying with different substances) between 1.40 and 1.55. It is evident that if the conductivity ratio, Λ/Λ_0 , can be taken as a measure of the ionisation, γ , the latter changes with the concentration in accordance with the function $\langle C\gamma \rangle^n / C(1 - \gamma) = \text{a constant}$, in which n has values varying between 1.40 and 1.55.

It has been pointed out previously (Noyes, *Congress. Arts. Sci.*, St. Louis Exhibition, 1904, 4, 317) that at the ordinary temperature the form of the functional relation between ionisation and concentration is the same for salts of different ionic types. The present results show that this is true also at high temperatures, and that even the large variation of temperature and the consequent change in the character of the solvent affect very slightly, if at all, the value of the exponent in this empirical relation. This affords a confirmation of the view that the form of the concentration function is independent of the number of ions into which the salt dissociates, and shows that chemical mass action has not any appreciable influence in determining the equilibrium between the ions and the non-ionised part of largely dissociated substances. The functions $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$ and $\Lambda_0 - \Lambda = K(C\Lambda)^{\frac{1}{2}}$ also express the results with potassium chloride, sodium chloride, hydrochloric acid, and sodium hydroxide up to 218° between $0.1N$ and 0.002 or $0.0005N$.

The equivalent conductivity and ionisation of acetic acid and ammonium hydroxide change with the concentration at all temperatures, even up to 306° , in accordance with the law of mass action. Phosphoric acid has intermediate values of n (1.8—1.9) which approach more nearly to the theoretical value (2.0) than to the empirical

value. In general, the ionisation decreases steadily with rise of temperature in the case of every substance investigated, and the decrease is nearly the same for all largely ionised salts of the same ionic type.

It is shown that the effect of temperature on the ionisation of salts is comparable with its effect on the dielectric constant of water.

Neutral salts of the same ionic type are ionised to nearly the same extent in all cases. Hydrochloric acid (up to 156°), nitric acid, and barium and sodium hydroxides also conform to this principle, although their ionisation is somewhat greater than that of the corresponding salts.

The rough proportionality which exists at the ordinary temperature between the non-ionised part of a salt and the product of the valencies of its ions has now been proved to persist up to high temperatures.

The ionisation constant for ammonium hydroxide increases considerably from 0° to 18° , then remains nearly constant to 50° , and afterwards rapidly decreases, until at 306° its value is only $1/200$ of that at 18° . The values for acetic acid are similar to those of ammonium hydroxide at all temperatures. Phosphoric acid has a much greater ionisation constant, which decreases steadily and rapidly with rising temperature.

From these results, the conclusions are drawn that the ionisation of salts, strong acids and bases is primarily determined, not by specific chemical affinities, but by electrical forces arising from the charges on the ions; that this is not affected, except in a secondary degree, by chemical mass action, but is regulated by general, comparatively simple laws; and that, in most respects, the phenomenon differs from that of the dissociation ordinarily exhibited by chemical substances, including that of the ionisation of weak acids and bases.

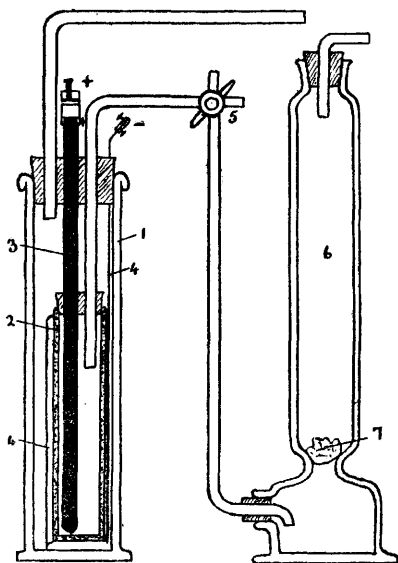
E. G.

Determination of Ionisation Factor of Water in Hydrochloric Acid Solutions. EMMANUEL DOUMER (*Compt. rend.*, 1908, 146, 687—690. Compare this vol., ii, 252).—In an earlier paper, the author has defined the ionisation factor of water in solutions of hydrochloric acid as the ratio $2v/V$, where v and V represent the volumes of oxygen and hydrogen respectively obtained during the electrolysis of the solution; and in the present paper methods are described whereby the value of v can be determined accurately. For this purpose, electrodes of silver or mercury are used; in the former case, after the anode has become coated with brown silver oxide, it absorbs all the chlorine and all the electrolytic oxygen is evolved, and in the latter case the mercury anode absorbs both the oxygen and the chlorine, and from the increase in weight of the mercury and the volume of hydrogen liberated at the cathode the weight of electrolytic oxygen and of chlorine can be calculated after making the necessary correction for the trace of mercury oxide dissolved by the solution. The results of the experiments tabulated in the original show that the ionisation factor of water in hydrochloric acid solutions is a constant, and independent of the intensity of the current, of the strength of the solution, and probably also of the nature of the anode; the factor is equal to 0.662, whence it follows that, in the electrolysis of solutions of hydrochloric

acid, about two-thirds of the hydrogen evolved comes from the electrolysis of the water, and the remaining one-third from the hydrochloric acid.

M. A. W.

Apparatus for the Quantitative Electrolysis of Hydrochloric Acid. J. B. LEWIS (*J. Amer. Chem. Soc.*, 1908, 30, 615—616).—The apparatus consists of (1) a glass cylinder, (2) a porous pot, (3) a carbon anode, (4) a cathode of sheet platinum, fitted together as shown in the sketch. The chlorine delivery tube is connected to the bottom of the tall cylinder (6), the top of which is provided with an air outlet; a loose plug of cotton wool (7) is placed in 6 to retard the mingling of chlorine and air. A two-way stopcock is interposed as shown at 5. The air (or chlorine) and hydrogen evolved during the electrolysis may be collected over water in inverted burettes. To start the apparatus, the anolyte is saturated with chlorine by adding a few crystals of potassium chlorate to it. The mixture may then be used immediately; electrolysis need only be carried on



a minute or two, during which time the chlorine is allowed to escape by means of the stopcock 5, and then the apparatus is ready for the demonstration.

W. H. G.

Electrolytic Valve Action of Columbium and a Classification of the Behaviour of Electrolytic Anodes. GÜNTHER SCHULZE (*Ann. Physik.*, 1908, [iv], 25, 775—782).—The electrolytic valve action of columbium is studied in the same way as that of tantalum (*ibid.*, 1907, [iv], 23, 226. Compare also Abstr., 1907, ii, 842). The results obtained with the two metals are very similar. A classification of anodes is given according to whether they are attacked or not, and whether the product of reaction is soluble, insoluble, a conductor or not, forms an adherent film, &c. The anodes which exhibit valve action are supposed to belong to the class in which a non-conducting, porous skin is formed and simultaneously gas is evolved; the gas film retained in the pores of the skin is the non-conductor to which the valve action is due.

T. E.

Electrolytic Reduction of Solutions of Titanic Sulphate. B. DIETHELM and FRITZ FOERSTER (*Zeitsch. physikal. Chem.*, 1908, 62, 129—177).—The only result of the electrolytic reduction of titanic sulphate in sulphuric acid solution is to reduce the metal from the

quadrivalent to the tervalent condition (compare Knecht's experiments on the chloride, Abstr., 1903, ii, 217). The course of the reduction varies with different electrodes, the current efficiency being considerably higher with a lead or a copper electrode than with one of bright platinum. In all these cases the reduction goes on until it is complete. With an electrode of platinised platinum, whilst the current efficiency is high, the reduction may be incomplete.

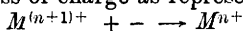
It appears from a study of the potentials at an electrode immersed in a solution containing titanium in both stages of oxidation, that such a solution is in equilibrium with hydrogen at atmospheric pressure. In contact with platinised platinum, the equilibrium $\text{Ti}^{++++} + \text{H} \rightleftharpoons \text{Ti}^{+++} + \text{H}^+$ is reached from either side.

The cathode potentials and the way in which they vary with the current density have been studied in detail for the reduction which takes place without the evolution of hydrogen. Here, again, the influence of the material of the cathode is very evident.

The velocity of the reduction of titanium sulphate is much smaller at a bright platinum cathode than at a platinised platinum cathode. The effective reducing agent at lead cathodes is electrolytically separated, finely-divided lead, and at copper cathodes apparently an alloy of copper and hydrogen.

The influence of the cathode material recorded in this paper is analogous to that observed by Chilesotti in the electrolytic reduction of molybdic acid (Abstr., 1906, ii, 263, 365), and to that observed by Haber and Russ in the reduction of organic substances (Abstr., 1904, ii, 309).

Electrolytic reductions which involve a change of valency appear to depend on the secondary action of the hydrogen which is primarily separated at the cathode surface, or of the electrolytically separated metal. Such a direct loss of charge as represented by



does not correspond with what usually happens.

J. C. P.

Thermal Conductivity of Mixtures of Argon and Helium.

JOHANNES WACHSMUTH (*Physikal. Zeitsch.*, 1908, 9, 235—240).—The thermal conductivity of various mixtures of argon and helium has been measured according to the method of Schleiermacher. The experimental data are discussed in reference to the formula $k = f \eta C_v$, in which k denotes the thermal conductivity, η the coefficient of viscosity, and C_v the specific heat at constant volume. Previous experiments have shown that the value of f for argon and helium is 2.5, in accordance with the Maxwell-Boltzmann theory. For mixtures of these two gases, the value of f is, however, not constant, and the curve which represents f as a function of the composition of the gas mixture exhibits a maximum for the mixture containing 60% helium. This corresponds with the results of previous measurements of the thermal conductivity of hydrogen-oxygen mixtures, the maximum value of f in this case being obtained for the mixture containing 60% of hydrogen. The variation in the value of the factor f in the gas mixtures is attributed to the alteration in the mean free path of the molecules of a gas which takes place when this is mixed with a second

gas. An interpolation formula is deduced by taking account of this alteration in the mean free path, from which the thermal conductivities of mixtures of argon and helium can be calculated in good agreement with the observed values.

H. M. D.

Specific Heat and Dissociation of Chlorine. MATHIAS PIER (*Zeitsch. physikal. Chem.*, 1908, 62, 385—419).—The molecular specific heat of chlorine, according to the work of earlier investigators, is about 2 cal. greater than that of most diatomic gases. This might be connected with the abnormal density of chlorine, and accordingly the author has studied the behaviour of this gas at various temperatures and pressures. If the value 2.49 (air = 1) is taken as the correct density at 0° and 1 atmosphere pressure (see Moissan, *Abstr.*, 1904, ii, 114), then under the same pressure the densities at higher temperatures are as follow: 50.24°, 2.4688; 100.4°, 2.4601; 150.7°, 2.4554; 184.0°, 2.4538. When the pressure is reduced to about 0.1 atmosphere, the theoretical value of the density, namely, 2.4494, is reached; the variation of density with pressure at 13.5° is shown by the following figures, the first number given in each case being the pressure in atmospheres; 1.00, 2.4820; 0.466, 2.4640; 0.294, 2.4584; 0.195, 2.4543; 0.123, 2.4518; 0.0569, 2.4494.

As to the influence of the abnormal density of chlorine on its specific heat, the assumption is made that there is a partial association to Cl_4 molecules. On this assumption a formula is based, which gives the variation of density (Δ) with the pressure (P atmospheres) and with the absolute temperature. With this formula, which runs: $\log(\Delta - 2.4494) = 463.11/T - 0.6415 - \log T + \log P$, it is possible to calculate the density of chlorine in very good agreement with the values actually found at various pressures and temperatures.

From the foregoing formula, the author calculates also the correction which must be applied to the molecular specific heat of chlorine to get the value for the ideal undissociated gas; the correction, however, amounts, even at the ordinary temperature, only to 0.3—0.5 cal., and hence the exceptionally high value of the specific heat of chlorine cannot be attributed to its abnormal density.

The degree of association of chlorine is practically zero at 300°, and from this temperature up to 1450° the density is normal. This is shown by a study of the specific heat. Hydrogen and chlorine were exploded in a bomb (1) with an excess of chlorine, and (2) with an equivalent excess of hydrogen. From the maximum pressure produced by the explosion, the maximum temperature reached was calculated, and from the data obtained in the two cases the specific heat of chlorine was compared with that of hydrogen. Regnault's value for the specific heat of chlorine is distinctly too high, and the author finds that up to 1450° the experimental values are satisfactorily given by the formula $C_v = 5.431 + 0.0005T$. The values so obtained, however, are still greater than those of most diatomic gases, for which the formula $C_v = 4.327 + 0.0005T$ is valid.

Above 1450°, the experimental values for the specific heat of chlorine are considerably greater than those calculated by the foregoing formula. On the basis of the difference between these values,

and on the assumption that the heat of dissociation of the chlorine molecule is -113000 cal., the author, applying Nernst's theory (Abstr., 1906, ii, 727; see also Brill, Abstr., 1907, ii, 233), deduces the formula $\log(1-x^2)/x^2 = 113000/4.571T - 1.75\log T + \log P - 3$ as applicable to chlorine above 1450° . In this formula, x is the degree of dissociation of the chlorine. J. C. P.

Specific Heat of Some Elements and Salts between the Temperature of Liquid Air and Room Temperature. PAUL NORDMEYER (*Ber. deut. physikal. Ges.*, 1908, 6, 202—206. Compare Abstr., 1906, ii, 521; 1907, ii, 432).—The specific heat values recorded for certain elements in the previous paper (*loc. cit.*) have been confirmed. For the other substances examined, the following mean specific heats were deduced: aluminium, 0.182; phosphorus (yellow), 0.178; potassium, 0.169; potassium bromide, 0.102. H. M. D.

Vapour Pressure of Dry and of Ordinary Sal Ammoniac. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1908, 62, 194—198).—Treating this problem from the point of view of thermodynamics, the author shows that the conclusions drawn by Abegg (this vol., ii, 157) and Johnson (*ibid.*) are incorrect. It does not follow that the partial pressure of undissociated ammonium chloride above sal ammoniac must always be the same at a given temperature, whatever be the degree of dissociation of the vapour. In the case of ordinary sal ammoniac, a complete dissociation equilibrium is established; this is not so with dry sal ammoniac, and the theory of heterogeneous dissociation equilibria is therefore not applicable to this case. Such dissociation equilibria are defined, not by the *partial pressure* of the undissociated substance, but by the *total pressure* of the system.

J. C. P.

Vapour Pressure of Aqueous Acetone Solutions. A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 216—227).—The object of the research was to study complex solutions, but the difference in vapour pressure of acetone and water is so great that the study of the systems acetone + water + a third substance was abandoned. Curves and tables are given showing the relation between the composition of the solutions and the refractive index at various temperatures, the vapour pressure of the solutions, and the partial vapour pressures of acetone and water respectively.

The results are claimed to be considerably more accurate than those of previous investigators (compare Taylor, Abstr., 1900, ii, 529). Z. K.

Condition of Substances in Absolute Sulphuric Acid. GIUSEPPE ODDO and E. SCANDOLA (*Zeitsch. physikal. Chem.*, 1908, 62, 243—255).—The authors have discovered independently the method of preparing absolute sulphuric acid lately described by Hantzsch (this vol., ii, 14), and the value they find for the freezing point is 10.43° . In the Beckmann apparatus used, the tube is closed by a glass stopper, into the central passage of which the thermometer is ground; another

small tube sealed into the stopper is closed at its upper end by a plugged piece of thick-walled rubber tubing, in the wall of which a hole is pierced for the passage of the platinum stirrer; with the aid of a little grease, the stirrer moves easily and the acid is protected from the air.

Experiments with phosphoryl chloride and sulphuryl chloride as normal solutes give 68.07° as the mean value for the molecular freezing-point depression in absolute sulphuric acid. When the value for the latent heat of fusion of sulphuric acid (24.03°) found by Pickering is inserted in the formula $K=0.027^2/\lambda$, K is calculated to be 66.86° , a figure in better agreement with the authors' experimental determination than with Hantzsch's value (70°).

The numbers obtained for the molecular weight of water in absolute sulphuric acid are about two-thirds of the normal value, even in solutions considerably more concentrated than those examined by Hantzsch. Using pyridine and quinoline as solutes, the authors show that acid sulphates give a figure for the molecular weight which is half the normal value, and not two-thirds as found by Hantzsch. The conclusions based by the latter on his experiments, and his "hydronium" theory in particular, are adversely criticised.

J. C. P.

Heats of Vaporisation of the Liquid Halogen Hydrides and of Hydrogen Sulphide. P. H. ELLIOTT and DOUGLAS McINTOSH (*J. Physical Chem.*, 1908, 12, 163—166).—The heats of vaporisation of the compounds in question were determined by an electrical method (compare Franklin and Kraus, *Abstr.*, 1907, ii, 929). The mean values (from three to four experiments for each substance) are 14.9, 17.3, 18.8 and 19.6×10^{10} ergs. per gram-molecule for hydrogen chloride, bromide, iodide and sulphide respectively. The results agree well with those calculated from the variation of the vapour pressure with temperature by means of the Clausius equation, except in the case of hydrogen iodide, for which the calculated value is 20.7×10^{10} ergs.

G. S.

Heat of Formation of Organic Fluoro-compounds. II. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1907, 941—955. Compare *Abstr.*, 1907, ii, 9).—The heats of combustion of the aromatic fluoro-compounds named below have been determined. The three numbers placed after the name of each compound are the heat of combustion at constant volume, the heat of combustion at constant pressure, and the heat of formation (large calories): fluorobenzene, 746.26, 746.84, 7.26; *o*-fluorotoluene, 901.61, 902.47, 14.73; *p*-fluorotoluene, 901.86, 902.72, 14.48; fluoro- ψ -cumene, 1206.15, 1207.49, 36.51; *o*-fluorobenzoic acid, 739.92, 739.92, 108.38; *m*-fluorobenzoic acid, 737.36, 737.36, 111; *p*-fluorobenzoic acid, 739.43, 739.43, 108.87.

The mean difference between the heats of formation of the above fluoro-compounds and the corresponding hydrogen compounds is approximately 14. This is considerably smaller than the mean difference of 20, which was obtained on comparing the heats of

formation of aliphatic fluoro-compounds with the corresponding hydrogen compounds. The smaller difference corresponds with the greater chemical activity of nuclear substituted fluorine.

The above three heat values have also been determined for ψ -cumene; these are respectively 1244.48, 1246.5, 16.24. The difference between the heat of formation of solid fluoro- ψ -cumene and liquid ψ -cumene is greater than 20 Cal.

H. M. D.

Heat of Formation of Quadrivalent Oxygen Compounds.

DOUGLAS MCINTOSH (*J. Physical Chem.*, 1908, 12, 167—170).—The amounts of heat given out when methyl alcohol, acetone, and ethyl ether are mixed with liquid hydrogen bromide have been measured. The apparatus used consisted of a Dewar test-tube nearly filled with liquid hydrogen chloride, in which was immersed a small tube containing liquid hydrogen bromide. In the upper part of the latter tube was a bulb containing a known weight of the organic liquid, which was ultimately dropped into the hydrogen bromide, the mixing being effected by an electrical stirrer. The whole apparatus was placed in a vacuum tube containing solid carbon dioxide and ether. From a comparison of the rate of "natural" evaporation of the hydrogen chloride with that after admixture, and the known heat of vaporisation of hydrogen chloride (preceding page), the heat given out in the reactions has been calculated.

The mean heats of combination of 1 mol. of the organic compounds with hydrogen bromide are as follows: Methyl alcohol, 57×10^{10} ergs.; acetone, 60×10^{10} ergs.; ether, 95×10^{10} ergs., but the agreement between different observations, especially in the last case, is only moderate.

It is considered that the heat developed is due mainly, if not entirely, to chemical combination, but the evidence in that respect is not conclusive.

G. S.

Simple Demonstrations of the Gas Laws. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1908, 30, 578—582).—Some simple forms of apparatus are described, involving the use of a moving drop of mercury (compare Abstr., 1907, ii, 755), by means of which the effects of heat, pressure, and aqueous vapour on a gas, separately and conjointly, may be demonstrated and calculated.

Charles' Law.—The apparatus consists of a calibrated bulb joined to a graduated stem, the internal diameter of which is less than 3 mm., containing a drop of mercury. A length of rubber tubing is attached to the end of the stem, and the apparatus, except the end of the rubber tube, is then placed in a water-bath, the temperature of which is known, and the position of the mercury noted. The temperature of the bath is raised, and the increase in temperature and volume read.

Boyle's Law.—The above apparatus is attached to a manometer by a T-tube, one limb of which is fitted with a stopcock. The volume of contained air and the atmospheric pressure are noted. Air is blown into the instrument through the stopcock, the drop of mercury is forced along the stem towards the bulb, and the mercury rises in the manometer. The stopcock is closed, and the volume of contained air

and the difference in the height of mercury in the two limbs of the manometer read off and added to the atmospheric pressure.

Aqueous Vapour.—The apparatus and method employed has been described (*loc. cit.*). The same apparatus may be used to show the conjoint effects of heat, pressure, and aqueous vapour on a gas.

W. H. G.

Surface Tension of Dilute Aqueous Solutions. ADOLF HEYDWEILLER (*Ber. deut. physikal. Ges.*, 1908, 6, 245—248).—The percentage alteration of the surface tension of solutions of chlorides of lithium, magnesium, ammonium, sodium, potassium, strontium, and barium produced by 1 gram-equivalent of the dissolved salt can be represented by an equation of the form $\Delta = Ai + B(1 - i) + Cm$, in which A , B , and C are constants, and i is the degree of dissociation of the solute. A and B represent the influence exerted respectively by the ions and the undissociated electrolyte, and C is a measure of the internal cohesion pressure of the dissolved substance.

In the series of chlorides examined, A has a positive value, which with increasing equivalent weight first diminishes and then increases. B , which has a positive value for lithium and magnesium, becomes negative when the equivalent weight is further increased, and assumes gradually increasing negative values for the other chlorides from left to right.

From the values of C , numbers are calculated representing the constant a of van der Waals' equation as applied to solutions.

H. M. D.

Weight of a Falling Drop and Tate's Laws. Determination of the Molecular Weights and Critical Temperatures of Liquids by the Aid of Drop Weights. J. LIVINGSTON R. MORGAN and RESTON STEVENSON (*J. Amer. Chem. Soc.*, 1908, 30, 360—376).—From the results of experiments on the weight of drops of water falling from a tube, Tate (*Phil. Mag.*, 1864, [iv], 27, 176) deduced the following laws: (1) Other conditions being the same, the weight of a drop of liquid falling from a tube is proportional to the diameter of the tube in which it is formed. (2) The weight of the drop is proportional to the weight which would be raised in the same tube by capillarity. (3) Other conditions being equal, the weight of a drop of liquid is diminished by an increase of temperature. Tate used a thin-walled glass tube, the lower end of which was ground to a sharp edge, so that the part of the tube in contact with the drop might be regarded as infinitely thin.

The present investigation was undertaken with the object of testing these laws and of ascertaining if the temperature-coefficient of drop weight of any one liquid could be employed instead of the temperature-coefficient of surface tension in a formula similar to that of Ramsay and Shields as a means of determining molecular weights and critical temperatures.

An apparatus is described by means of which the volume (and hence the weight) of a single drop of a liquid falling from a tube can be accurately measured. Thick-walled capillary tubes were used, the ends of which were bevelled at an angle of 45°, and were found to have the

same effect as those used by Tate in causing all liquids to drop from one and the same area. The liquids employed were ether, benzene, ethyl iodide, chlorobenzene, guaiacol, benzaldehyde, aniline, quinoline, and water.

The results show that for such tips as were employed, Tate's second and third laws are true, and that the first law is also true for bevelled tips of diameters between 4.68 and 7.12 mm. It is found that for the same liquid, falling drop weights can be substituted for the surface tensions in Ramsay and Shields' relation, and that molecular weights in the liquid state can be calculated with an accuracy equal to that obtained with surface tensions under the same, saturated air, conditions. Further, from a knowledge of the molecular weight of a non-associated liquid, the falling drop weight at one temperature, and the densities, it is possible to calculate the weight of a drop falling from the same tip at another temperature. Critical temperatures can be calculated by the aid of Ramsay and Shields' equation $\gamma(M/d)^3 = k(\tau - 6)$, by substituting a drop weight for surface tension, and the molecular temperature-coefficient of drop weight for k , with the same precision as is attained by using surface tensions, against saturated air, provided that the drop weights from which the coefficient is found are determined at as many temperatures and at as high a temperature as the surface tensions.

A bibliography of the subject is appended.

E. G.

Experimental Examination of Gibbs's Theory of Surface-concentration, Regarded as the Basis of Adsorption, with an Application to the Theory of Dyeing. W. C. M. LEWIS (*Phil. Mag.*, 1908, [vi], 15, 499—526).—Adsorption effects at liquid-liquid interfaces have been measured, and the results obtained are interpreted with reference to Gibbs's theory of surface-concentration in order to ascertain whether this theory affords an explanation of the general phenomenon of adsorption.

The adsorption measurements were made at the surface of separation of a hydrocarbon oil and an aqueous solution of bile salts ("sodium glycocholate"). The choice of these substances was determined by the fact that the hydrocarbon is chemically inert in respect of the solution, and that the solute lowers the interfacial tension between the water and the hydrocarbon.

By modifying Gibbs's fundamental expression, an equation has been obtained which gives the mass of solute adsorbed per square centimetre of surface in terms of the concentration of the solution and the alteration in the interfacial tension due to the dissolved substance. Determinations of the adsorption coefficient were made (1) at a very curved surface and (2) at an approximately plane surface, the corresponding interfacial tension measurements being carried out by the drop-pipette method. The values obtained in the two cases are in good agreement, which appears to point to the fact that the tension, even at very great curvatures, is not appreciably different from that at an approximately plane surface, but these experimental values are from twenty to eighty times greater than the values indicated by Gibbs's theory.

Experiments with dyes (Congo-red and methyl-orange) gave similar results, the discrepancy between theory and experiment being of the same order of magnitude.

An explanation of the observed differences has not yet been obtained.

H. M. D.

Determination of Viscosity at High Temperatures. CHARLES E. FAWSITT (*Proc. Roy. Soc.*, 1908, 80, A, 290—298).—The method of determination is based on that described by Coulomb, in which the viscosity is calculated from the rate of decay of the amplitude of a horizontal circular disk which is allowed to execute vibrations about a vertical suspending wire. The disk used by the author was 26 mm. in diameter and 1 to 3 mm. thick. In order to make the disk heavy enough to sink in molten metals, a small, iron cylinder was clamped on to the vertical stem which forms the axis of rotation. The weight of the cylinder and its distance from the disk must be such as to keep the centre of gravity of the rigid part of the apparatus as low as possible. For temperatures up to 400°, iron may be used as material for the disk; for temperature up to a white heat, fire-clay or a mixture of fire-clay and plumbago is suitable. The apparatus was found to give good results for a number of liquids at the ordinary temperature, and measurements are recorded of the viscosity of mercury at temperatures up to 216°, and for sodium nitrate up to 450°.

H. M. D.

Dissociation Pressures of Some Metallic Hydroxides and Carbonates. JOHN JOHNSTON (*Zeitsch. physikal. Chem.*, 1908, 62, 330—358).—The dissociation pressures of calcium, strontium, barium, lithium, sodium and magnesium hydroxides, of lithium and sodium carbonates, and of the hydrates of barium and strontium hydroxides have been determined, mostly by a statical method, which is described in detail in the paper.

The results obtained for sodium hydroxide are very uncertain, but some of those for the other hydroxides are recorded in the following table. The figures represent the temperatures at which the hydroxide in question exerts the dissociation pressure given on the left.

<i>p</i> mm.	Ca(OH) ₂ .	Sr(OH) ₂ .	Ba(OH) ₂ .	LiOH.	Mg(OH) ₂ .
9.2	369°	452°	630°	561°	35°
31.5	408	524	710	628	53
92	448	597	789	700	74
234	488	670	870	782	100
526	527	742	951	875	147
760	547	778	998	924	—

The results obtained for the carbonates are similarly represented in the following table, in which are incorporated also the results obtained by other observers (Le Chatelier, *Compt. rend.*, 1886, 102, 1243; Finkelstein, *Abstr.*, 1906, ii, 354; Brill, *Abstr.*, 1905, ii, 522). The values in brackets are extrapolated by means of the author's formulæ:

<i>p</i> mm.	CaCO ₃ .	SrCO ₃ .	BaCO ₃ .	Li ₂ CO ₃ .	MgCO ₃ .	Na ₂ CO ₃ .
5	[480°]	[814°]	1028°	740°	—	940°
10	[520]	[860]	1070	783	—	about 1100
50	616	[960]	1164	930	—	—
100	650	[1008]	1210	1010	—	—
760	825	1155	1350	[1270]	230°	—

The foregoing tables show that if the elements are arranged according to the readiness with which their compounds dissociate, the order is the same whether the hydroxides or the carbonates are considered, and the same also as that based on the periodic classification and on the physical properties (solubility, density, melting point, &c.) of the compounds. The author's experiments show also that the dissociating tendency of the hydrates of strontium hydroxide is much greater than that of the corresponding hydrates of barium hydroxide.

With the help of the equation $d(\log_e p)/dt = Q/RT^2$, the heats of dissociation of the hydroxides of calcium, strontium, barium, lithium, and magnesium are calculated from the author's observations. These calculated values are in good agreement with Thomsen's direct determinations. The values calculated from the author's observations by Nernst's formula (Abstr., 1906, ii, 727) are not in harmony with the experimental values.

A theoretical proof is given of Ramsay and Young's equation connecting the boiling points of different substances under any pressure the same for both. When this formula is applied to fatty alcohols or acids, to crystalline hydrates, or to the hydroxides of calcium, strontium, and barium, water being taken as the standard of comparison in each case, the curves obtained are straight lines. On the other hand, hydrocarbons, benzene derivatives, ethers and esters give a linear relationship when compared with fluorobenzene, but not when compared with water.

J. C. P.

Osmotic Pressure. JOSEPH E. TREVOR (*J. Physical Chem.*, 1908, 12, 141—154).—A mathematical paper instigated by Porter's recent paper (Abstr., 1907, ii, 743) on the same subject. Porter's equation connecting osmotic pressure and vapour pressure is deduced by an alternative method, which shows the relation of the osmotic pressure to the reversible and irreversible work and heat of dilution.

Somewhat complicated expressions are given for the rate of change of the osmotic pressure with temperature at constant pressure and composition of the solution, and with the composition at constant pressure and temperature of the solution, and the assumptions made in van't Hoff's theory of solutions are discussed in the light of these results. The conditions for proportionality between osmotic pressure and the absolute temperature are zero heat of dilution and constant specific volume of the solvent.

G. S.

Rôle of Imbibition in the Osmosis of Liquids. G. FLUSIN (*Ann. Chim. Phys.*, 1908, [viii], 13, 480—522. Compare Abstr., 1899, ii, 204; 1901, ii, 148, 439).—The author's experiments were made with the object of ascertaining whether there is, in general, a quantitative relation between the osmotic activity of a liquid towards a membrane and the amount of the liquid imbibed by the membrane.

The membranes employed were weighed in three different conditions: (1) dry before imbibition; (2) after imbibition, and (3) dry after imbibition. The last weight is always less than the first, and is used in the calculation of the coefficient of imbibition, which is defined as

the volume in c.c. of liquid absorbed by 100 grams of the membrane at a definite temperature and in a certain time; the coefficient increases appreciably, but very slightly, with rise of temperature. The absorptive capacity of membranes, such as parchment paper or pig's bladder, varies for different membranes and diminishes markedly when the same sample is used more than once. The presence in the membranes of certain substances has a great influence on the extent of absorption.

The osmometer used was a modified form of that of Raoult (Abstr., 1895, ii, 487), and in place of the expression velocity of osmosis the author uses "osmotic debit" (*débit osmotique*), the apparent osmotic debit being the increase in volume (c.c.) of the liquid column in the measuring tube per hour per sq. dm. of membrane. For membranes from the same source, but of different thicknesses, the osmotic debit is inversely proportional to the thickness. The membranes employed consisted of vulcanised caoutchouc, parchment paper, pig's bladder, viscose, and copper ferrocyanide.

As regards their absorption by caoutchouc, organic liquids fall into two clearly-defined classes: (1) "active" liquids, or those which are absorbed energetically from the moment they come into contact with the membrane, and (2) "inactive" liquids, including water, with which an appreciable increase in weight of the membrane only occurs after several hours. The relative value of the coefficient of imbibition depends on the duration of imbibition. The osmotic debits are in the same order as, and roughly proportional to, the coefficients of imbibition, except for long durations of immersion. Apparent osmosis always takes place from the liquid with the higher towards that with the lower coefficient of imbibition.

With pig's bladder, the distinction between "active" and "inactive" liquids is less clearly marked than with caoutchouc. Water has the highest coefficient of imbibition, and next in order is acetic acid, which forms with the material of the bladder a moderately stable compound. In this case, too, the osmotic debits and the initial (five minutes) coefficients of imbibition vary in the same order, but the ratio has one value for the "active" and another for the "inactive" liquids.

With parchment paper or viscose, the only "active" liquid is water, the absorption of which is very rapid at first, but almost ceases after about ten minutes.

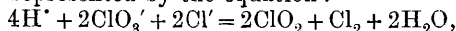
With solutions of various concentrations of sodium chloride, potassium carbonate, tartaric and acetic acids in contact with parchment paper, the osmotic debit varies as the diminution of the coefficient of imbibition, but bears no simple relation to the molecular weight of the solute even when ionisation is allowed for. Similar results were obtained with membranes of pig's bladder. With copper ferrocyanide membranes, the osmotic debits are inversely proportional to the molecular weights of the dissolved compounds if the concentrations of the solutions are the same in each case.

In order that osmosis may take place, it is not necessary for the two liquids to be miscible in all proportions,

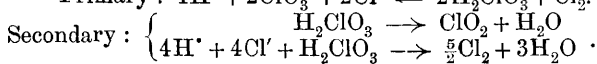
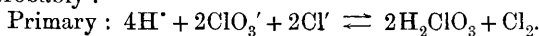
A method is described of determining molecular weight by means of osmotic debits.
T. H. P.

Kinetics of the Reaction between Chloric and Hydrochloric Acids. A Reaction of the Eighth Order. ROBERT LUTHER and F. H. MACDOUGALL (*Zeitsch. physikal. Chem.*, 1908, 62, 199—242. Compare Abstr., 1906, ii, 436).—The method employed in studying this reaction was to pass a rapid current of an indifferent gas through the mixture, and so sweep away the chlorine and chlorine peroxide, the substances concerned in the intermediate equilibrium. By this procedure, these substances were kept permanently at a small concentration, and this permitted a quantitative study of the primary reaction. The necessary data for this study were obtained by absorbing the chlorine and chlorine peroxide in potassium iodide solution; the velocity of the reaction was thus ascertained as well as the ratio $\text{ClO}_2 : \text{Cl}_2$.

The velocity of the primary reaction is proportional to the fourth power of the H^+ concentration, to the second power of the ClO_3' concentration, and to the second power of the Cl' concentration, that is, the reaction as a whole is one of the eighth order. The net change may be represented by the equation :



but consideration of the experimental data shows that the separate stages are probably :



Among the experimental facts which support the foregoing representation of the reaction are the following : the reaction is not noticeably retarded by chlorine peroxide; the ratio $\text{ClO}_2 : \text{Cl}_2$ in the products is practically independent of the intensity of the gas current, and the total reaction is retarded proportionally to the square root of the chlorine concentration.

In discussing the results from a general point of view, the authors point out that in oxidation-reduction reactions the primary product is probably always that compound which is in the next stage of oxidation.
J. C. P.

Influence of Slow Dissociation on the Equilibrium between Phases. C. VAN ROSSEM (*Zeitsch. physikal. Chem.*, 1908, 62, 257—283).—Ramsay and Young have found (*Phil. Trans.*, 1886, 177, i, 82) that in certain cases the statical and dynamical methods of determining the vapour pressure of a solid lead to divergent and irregular results, the substances which exhibit this behaviour being all capable of dissociation, namely, aldehyde-ammonia, phthalic and succinic acids, and chloral hydrate and alcoholates. The author adopts Bancroft's explanation (Abstr., 1899, ii, 411) that, when a solid sublimes rapidly, there is not sufficient time for the establishment of the dissociation equilibrium. This interpretation is considered in detail in connexion with Ramsay and Young's experiments.

These investigators found also (*loc. cit.*) that, in the case of the chloral alcoholates, the vapour pressure of the supercooled liquid was smaller than that of the solid phase at the same temperature. Bancroft's explanation (*loc. cit.*) of this is rejected, and the author points out that the phenomenon was probably due to these alcoholates being contaminated with the alcohol from which they were crystallised.

Again, Ramsay and Young found (*loc. cit.*) that the statically-determined vapour pressure of succinic acid varied with the amount of the solid phase. Bancroft's explanation of this is rejected, and the author suggests that this phenomenon also is due to the slowness with which the dissociation equilibrium is reached. Increase of the quantity of the solid phase would involve increase of the subliming surface, and would therefore accelerate the establishment of the equilibrium.

J. C. P.

Ammonia Equilibrium. F. JOST (*Zeitsch. anorg. Chem.*, 1908, 57, 414—430. Compare Haber and van Oordt, Abstr., 1905, ii, 159, 384, 814; Haber and Le Rossignol, Abstr., 1907, ii, 454).—The equilibrium $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ has been investigated between 685° and 1040° by means of the special electric furnace designed by Nernst (*Zeitsch. Elektrochem.*, 1907, 11, 521), which admits of the investigation of gas reactions under high pressures. The furnace is described and figured. A mixture of hydrogen and nitrogen at partial pressures of 60 and 20 atmospheres respectively was passed slowly through the apparatus and the composition of the resulting mixture determined, and the equilibrium was also reached from the other side with a mixture containing excess of ammonia. Platinum, iron, and manganese were used as catalytic agents.

Between 700° and 1040°, the equilibrium is represented satisfactorily by the equation $\log x = 3065/T - 6.918$, where x is the partial pressure of the ammonia. At 685°, 876°, and 1040°, the partial pressure of the ammonia is only 0.0178%, 0.0055%, and 0.0026% respectively. The heat equivalent of the reaction, calculated from the measurements by van't Hoff's equation, is 28,000 cal. at 1150°, compared with 24,400 cal. found by Berthelot at the ordinary temperature.

The results are in moderate agreement with those calculated by Nernst's formula connecting equilibrium and temperature, but the data are not sufficient to allow of a satisfactory comparison. The agreement between the author's results and those of Haber and Le Rossignol (*loc. cit.*) is also only moderate.

G. S.

Equilibrium of Ammonia under Pressure. FRITZ HABER and ROBERT LE ROSSIGNOL (*Zeitsch. Elektrochem.*, 1908, 14, 181—196).—Nernst and Jost (*Zeitsch. Elektrochem.*, 1907, 13, 521) have made determinations of the equilibrium condition of ammonia at temperatures between 685° and 1040°, and pressures of 12 to 70 atmospheres. The results do not agree with those obtained by the authors at atmospheric pressure (Abstr., 1907, ii, 454), and they have therefore made further experiments at 30 atmospheres pressure. The essential part of the apparatus used is a quartz tube containing iron or

manganese asbestos; the tube (5 mm. internal diameter and 3 mm. thick) withstood the pressure of 30 atmospheres at 980°. Full details are given of the methods used to eliminate errors; the authors believe that the quantities of ammonia found are correct to within 2½%.

Equilibrium is attained from both sides. The final results are:

Temperature.	% NH ₃ at 30 atmos. (N ₂ :H ₂ =1:3).	$K \times 10^4$.
700°	0.654	6.80
801	0.344	3.56
901	0.207	2.13
974	0.144 to 0.152	1.48 to 1.56

The equilibrium constant K is defined by the ratio of the partial pressures of the gases $p(\text{NH}_3)/p(\text{N}_2)^{\frac{1}{2}} \times p(\text{H}_2)^{\frac{3}{2}}$. These numbers agree very well with the authors' previous experiments at atmospheric pressure; they do not agree with Nernst's theoretical calculations. The discrepancy is possibly due to an error in the heat of formation of ammonia or to an increase in the specific heat of ammonia at high temperatures.

T. E.

Theory and Practice of the Iodometric Estimation of Arsenious Acid. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1908, 30, 31—46).—A study has been made of the equilibria involved in this analytical process, and the proper conditions to be observed at the end-point have been deduced from the results.

It is shown that the success of the titration depends on maintaining the hydrogen-ion concentration at a sufficiently small value. Calculation of the limits of the hydrogen-ion concentration gives 10^{-4} as the upper limit and 10^{-9} as the lower limit. If an accuracy of 0.001% is desired, the hydrogen-ion concentration must lie between these limits, the best value being their geometrical mean, which is almost identical with the concentration of the hydrogen ions in pure water. It follows, therefore, that at the conclusion of a titration of an arsenious acid solution with iodine the solution should be neutral.

A solution will maintain itself at any desired hydrogen concentration, even although small quantities of acid or base are added, if it contains something which will remove both hydrogen and hydroxyl ions. A solution containing the salt of a weak acid or base together with an excess of the acid or base has this property. It is shown that the ionisation constant of the acid should be numerically equal to the desired hydrogen-ion concentration. From theoretical considerations, it is found that phosphoric, carbonic, and boric acids are capable of meeting the requirements. In the case of phosphoric acid, it is shown that at the end of the titration the solution should contain about 2 mols. of Na_2HPO_4 to 1 mol. of NaH_2PO_4 in order that neutrality may be preserved. A 0.12 molar solution of sodium hydrogen carbonate, saturated with carbon dioxide, and a solution saturated with borax and boric acid are also capable of achieving the desired result. Experiments have proved that these conclusions are justified.

It is recommended that for accurate work the solutions should be weighed instead of measured, and a convenient form of weight-burette is described. Methods of preparing the standard solutions are given, and the mode of carrying out the titrations and the precautions to be observed are described.

The results of the investigation show that, under the proper conditions, iodine can be quantitatively reduced to iodide by arsenious acid, and that a definite, permanent, and exceedingly delicate end-point is obtained.

E. G.

Mutual Solubility of Piperidines and Water. OTTO FLASCHNER (*Zeitsch. physikal. Chem.*, 1908, 62, 493—498).—Piperidine is miscible with water in all proportions between 0° and 250°, but some experiments in which potassium chloride was added to the mixed liquids indicate that the hypothetical lower critical solution-temperature (see Timmermans, Abstr., 1907, ii, 229) for the system piperidine + water is about 277°. The lower critical solution-temperature for methyl-piperidine + water is 48.3°, the critical mixture containing 23% of the base. In this case, indications are obtained that the complete mutual solubility curve would be a closed one, but it is not fully realised. The lower critical solution-temperature for ethylpiperidine + water is 7.45°, the critical mixture containing 27% of the base. In the system *n*-propylpiperidine + water, the lower critical solution-temperature could not be reached, owing to the formation of solid; it appears to lie about -20°.

The author suggests a relationship between mutual solubility and dielectric constant.

J. C. P.

Stability of Colloidal Solutions. II. THE SVEDBERG (*Chem. Zentr.*, 1908, i, 88; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 142—149. Compare Abstr., 1907, ii, 535).—By further studying the behaviour of slightly ionising solvents on colloidal solutions the author's view that the phenomena of coagulation are dependent on other factors than those considered by Billitzer (Abstr., 1907, ii, 535) is confirmed. If the activity of the ions is made as small as possible by using a medium having a small ionising effect and a colloidal substance with very small solubility pressure, such as platinum in ether, the following regularities are found. Concerning the temperature, there exist well-defined "critical points" (sharp coagulation points), and these are elevated on the addition of a small quantity of a non-colloidal substance. The "critical curves," which show the relation between the temperature of coagulation and the amount of added material, are asymptotic to the negative temperature axis. An increase of solubility pressure of the colloid, or an increase of the ionising power of the solvent, causes in each case a decrease in the sharpness of the "critical point."

J. V. E.

Process of Formation of Hydrosol and Hydrogel. II. Adsorption of Silver Nitrate and Potassium Iodide by Amorphous Silver Iodide. ALFRED LOTTERMOSER and A. ROTHE (*Zeitsch. physikal. Chem.*, 1908, 62, 359—383. Compare Abstr., 1907, ii, 851; also Abstr., 1905, ii, 586; 1906, ii, 429; 1907, ii, 78).—Pure

silver iodide was prepared by precipitating ammoniacal potassium iodide with ammoniacal silver nitrate, the product being successively washed with ammonia, water, nitric acid, and water again. When such amorphous silver iodide is shaken with a solution of silver nitrate, some of the latter substance is adsorbed, and the adsorption is in harmony with the usual formula $x/m = \beta \cdot c^{1/p}$. The equilibrium is established very rapidly when a series of silver nitrate solutions of gradually increasing concentration is used, but very slowly when the concentration is changed in the opposite direction. It is therefore practically impossible to free silver iodide completely from adsorbed silver nitrate by mere washing with water.

When a solution containing Ag^+ ions is added to a solution containing I^- ions, so that the latter are always in excess, a negative hydrosol is formed, provided the concentration is below a certain maximum value. Similarly, when a solution containing I^- ions is added to one containing Ag^+ ions, so that the latter are always in excess, a positive hydrosol is formed, provided the concentration is less than a certain maximum value. This maximum concentration, at which formation of hydrosol can take place, is much lower in the latter case than in the former. The maximum concentration is markedly lowered by multivalent cations where a negative hydrosol is being formed, and by multivalent anions where a positive hydrosol is being formed. Multivalent cations are without influence on a positive hydrosol, and multivalent anions have no effect on a negative hydrosol.

Moist amorphous silver iodide can be converted into a hydrosol by I^- ions. This effect reaches a maximum for a certain concentration of the iodide; the higher the valency of the metal in the iodide the lower is the concentration which gives the maximum effect. The structure of amorphous silver iodide is altered by I^- ions, and this is probably the reason why the adsorption of potassium iodide by moist amorphous silver iodide does not take place in accordance with the usual adsorption law.

J. C. P.

[Action of Some Electrolytes on Colloidal Silver Solutions. The Process of Coagulation.] ALFRED LOTTERMOSER (*Zeitsch. physikal. Chem.*, 1908, 62, 284—286).—A criticism of Woudstra's recent paper (this vol., ii, 160).

J. C. P.

Mutual Flocculation of Colloids. OSCAR TEAGUE and BERNARD H. BUXTON (*Zeitsch. physikal. Chem.*, 1908, 62, 287—307).—The rule that the degree of flocculation and the extent of the region of optimal concentration (Abstr., 1907, ii, 933) depend on the degree in which the substances are colloidal (rule of colloidal flocculation) was first observed to hold for aniline dyes, and is now found to apply to a number of other colloids. The mutual flocculation of an acid and a basic dye is greatest when the two are mixed in equivalent proportions. An inorganic salt (sodium chloride) is formed by double decomposition, and extends the flocculation zone. Histological experiments indicate that highly colloidal dyes are more firmly united than the less definitely colloidal ones.

G. B.

Parallel Growths of Crystals and Isomorphous Miscibility. THOMAS VIPOND BARKER (*Min. Mag.*, 1908, 15, 42—53).—The experiments on the parallel growth of soluble salts on each other (Abstr., 1907, ii, 240) are continued with the sulphates and chromates of the alkali metals. Although isomorphous miscibility and the formation of parallel growths of crystals are favoured by the same factor, namely, similarity in molecular volume and crystal-structure, yet these two properties do not always go hand in hand, for many immiscible or only slightly miscible substances readily form parallel growths. Mixed crystals cannot therefore be regarded as being built up of alternating parallel layers. The bearing of parallel growths on questions of isomorphism and the limitations of the term isomorphism are discussed.

L. J. S.

Isomorphism. B. GOSSNER (*Zeitsch. Kryst. Min.*, 1908, 44, 417—518).—A lengthy dissertation on isomorphism in general.

L. J. S.

Supposed Alteration in the Total Weight of Substances taking part in a Chemical Reaction. HANS LANDOLT (*Sitzungsber. K. Akad. Berlin*, 1908, 354—387. Compare Abstr., 1906, ii, 528).—The author gives the final results of his extensive investigations on the question whether changes in total weight take place when substances undergo chemical change. The fact that in the majority of the changes previously investigated a small loss of weight was found has led the author to examine whether this might not be due to the circumstance that these changes take place with development of heat, resulting in a diminution of the amount of water condensed on the surface of the glass vessels and also in an increase of volume of the apparatus. The recovery from these disturbances was examined by determining the weights of the reaction vessels from day to day over much longer intervals of time than those during which observations were made in the earlier experiments. As a result of these new measurements, the supposed preponderance of the reactions which take place with loss of weight disappears, and in nearly all of the forty-eight experiments the changes in weight fall within the estimated limits of experimental error. The final conclusion drawn by the author is that in none of the fifteen different chemical changes which have been examined can a change in the total weight of the reacting substances be recognised.

H. M. D.

Deduction of the Stoicheiometric Laws. O. DE VRIES (*Zeitsch. physikal. Chem.*, 1908, 62, 308—329).—The author criticises at length the attempt made by Wald (Abstr., 1897, ii, 311, 400; 1898, ii, 64, 159, 327; 1899, ii, 276; 1907, ii, 755) to provide an *a priori* foundation for the stoicheiometric laws, as well as the similar attempts made by Ostwald (Trans., 1904, 85, 506), Benedicks (Abstr., 1906, ii, 530), and Baur (Abstr., 1906, ii, 661). It is considered that the proofs given by these writers are either faulty in themselves or are based on facts which are equivalent to those involved in the stoicheiometric laws. These laws should be regarded as purely

experimental in character. [For other papers bearing on this subject, see Nasini, *Abstr.*, 1905, ii, 514; Kuhn, *Abstr.*, 1907, ii, 678; this vol., ii, 98.] J. C. P.

Are the Stoicheiometrical Laws Intelligible without the Atomic Hypothesis? F. WALD (*Chem. Zeit.*, 1908, 32, 299—301. Compare *Abstr.*, 1907, ii, 678, 755).—Polemical. A further reply to Kuhn. P. H.

Choice of the Most Probable Value for an Atomic Weight: Atomic Weight of Hydrogen. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1908, 30, 4—8).—The following suggestions are made as a guide to the selection of the most probable value for an atomic weight. (1) When an observer discovers sources of error in the work of an earlier observer and succeeds in avoiding them in his own work, the later work should be accepted and the earlier work regarded as of only confirmatory value. (2) When the results obtained by two independent observers agree, whilst those of a third are discordant, much greater weight should be given to the former than to the latter; and, further, values obtained by one author which differ markedly from those obtained by several authors should be rejected. (3) After eliminating certain results by (1) and (2), the remainder should be arranged in the order of their probable errors. Any result with a probable error more than five times that of the smallest probable error should be excluded, and the values remaining for a given ratio should be combined by weighting them inversely as the squares of their probable errors. The ratios thus selected should be weighted, not by the mathematical probable error, but by the deviation of the results of different observers from the value selected. The combination of the experimental ratios for the calculation of atomic weights should be carried out by the application of the same general principles.

On applying these principles to the determinations which have been recorded of the atomic weight of hydrogen, the value 1.00775 is obtained ($O = 16$) (compare this vol., ii, 100). E. G.

Number of Corpuscles in the Atom. J. BOSLER (*Compt. rend.*, 1908, 146, 686—687).—The total potential energy of 1 gram of hydrogen is $\frac{N(ne)^2}{a} = n^2 10^{13}$ ergs, where N is the number of atoms (about 10^{24}) in 1 gram, n the number of electrons in the atom, e their charge (about 3.2×10^{-10}), and a the radius of the atom (10^{-8}); the corresponding value in the case of radium is $(225/3) \times n^2 10^{13}$ or $n^2 10^{15}$ ergs, whilst the observed value calculated from Curie's measurement of the heat emanation, and Rutherford's estimate of the life of radium, is 3×10^{16} ergs; it follows therefore that the number, n , of corpuscles in the atom of hydrogen is of the order of units, and this result is in agreement with the results of J. J. Thomson's later experiments, from which he concluded that the number of corpuscles of the atom is of the order of greatness of the atomic weight.

M. A. W.

Chemical Elements. Periodicity, Weight, and Valency. GEORGE WOODIWISS (*Chem. News*, 1908, 97, 122—124).—An attempt to find relationships between the specific gravities of the elements in the solid state and their atomic weights. It is assumed that the valency of the elements in the long series of Mendeléeff's table increases uniformly from the first to the eighth group, the elements in which have a valency of eight, and then decreases uniformly. The elements of the copper and zinc groups are thus septa- and sexavalent respectively. When the specific gravities of the elements are divided by these hypothetical valencies, numbers are obtained which, in the case of the metals, increase uniformly with the atomic weights, and when plotted on a diagram with atomic weight as abscissa these numbers fall approximately on a straight line. The numbers for the non-metallic elements do not correspond at all with this relationship.

H. M. D.

Theory of Valency and Constitution of Salts. GRÉGOIRE N. WYROUBOFF (*Ann. Chim. Phys.*, 1908, [viii], 13, 523—561).—The author advances a new theory of the formation and constitution of salts which comprehends the so-called molecular compounds as well as the ordinary atomic compounds. He also applies the notion of mixed functions, generally used only in connexion with organic compounds, to inorganic substances. The ideas involved in the terms partial valency, crypto-valency, pseudo-valency, and secondary valency are criticised.

All theories of valency confound the chemical energy inherent in an atom with its valency, or, in other words, the sum of the chemical actions which it can exert according to the laws of definite and multiple proportions with the number of atoms of a certain kind with which it can combine directly. By separating these two notions, the problem of valency becomes greatly simplified, as also does that of molecular compounds. The valency of a molecule is regarded as being independent of the atomicity of the atom from which it originates, and the combination of a molecule $M(OH)_n$ with $nHCl$ is represented, not by the equation $M(OH)_n + nHCl = MCl_n + nH_2O$, but by $M(OH)_n + nHCl = M(OH)_n.nHCl$. So that salts are produced by the neutralisation of two different functions without elimination of water, and are characterised by being electrolytes and by being capable of taking part in double decompositions. The following considerations are brought forward in support of this hypothesis. A large number of hydrated salts are known from which it is impossible to remove all the water without decomposing them, or, at any rate, completely changing their character. This is the case, for example, with magnesium sulphate and chloride and with the chlorides of the alkaline-earth metals, and the stable hydrates generally represented as $MgSO_4.H_2O$ and $MCl_2.2H_2O$ are regarded as containing water of constitution $M(OH)_2.H_2SO_4$ and $M(OH)_2.2HCl$. Thermochemical data are quoted to show that the water in such stable hydrates is present in a form different from that in which any further water absorbed exists. Thus 1 mol. of calcium sulphate, in taking up $2H_2O$ to form gypsum, $Ca(OH)_2.H_2SO_4$, evolves 4.4 Cals., whilst 1 mol. of gypsum dissolves in water with absorption

of 0.3 Cal. When dehydrated compounds dissolve in water, they are regarded as combining with water and passing from the condition of anhydrides to that of true salts. Salts which are always anhydrous in the solid state are looked on as resulting from the instability of the hydrated salts in the solid form. The formation of organic salts without elimination of water is cited in support of the above theory of salt formation.

The author also discusses the compounds $\text{Pt}(\text{OH})_2\text{Cl}_2, 2\text{HCl}, 2\text{H}_2\text{O}$ and $\text{PtCl}_4, 2\text{HCl}, 2\text{H}_2\text{O}$, which he regards as derived from the non-existent or unstable normal salt $\text{Pt}(\text{OH})_4, 4\text{HCl}$; the compound $\text{Cr}_2(\text{C}_2\text{O}_3)_2(\text{OH})_6$; the compound $\text{Cr}_2(\text{OH})_6$, which presents itself under four distinct aspects: with exclusively (1) basic or (2) alcoholic functions; (3) with functions partly acid and partly basic, as in the green chromium compounds, and (4) in a form in which the hydroxyls are acid and alcoholic at the same time.

Colson's work (this vol., ii, 45) is criticised.

T. H. P.

Apparatus for the Centrifugal Draining of Small Quantities of Crystals. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1908, 30, 286—288. Compare Richards, *Abstr.*, 1905, ii, 238).—The apparatus consists of an aluminium cup containing a platinum crucible and fitted with a rubber sleeve, which in turn holds a platinum Gooch crucible. The aluminium cup is attached by means of trunnions to the centrifugal machine. The crystals are placed in the Gooch crucible, and the mother liquor drains into the platinum crucible beneath. The removal of the platinum crucible is facilitated by a hole situated at the bottom of the aluminium cup. A full description and diagram of the apparatus are given.

E. G.

Inorganic Chemistry.

Origin of the Green Colours of Natural Waters. WALTHERÉ SPRING (*Arch. sci. phys. nat.*, 1908, [iv], 25, 217—227).—The green colours of natural waters are attributable in some cases to the presence of colouring matters, and in others to the presence of very finely-divided suspensions, which give rise to diffraction phenomena; the colour effects due to these causes result in a modification of the blue colour of pure water.

The colours of water containing finely-divided suspensions of various kind have been examined in columns 6 metres long. A suspension of silica, obtained by heating precipitated silicic acid and removing the larger particles by levigation, exhibits the blue colour of pure water. A suspension of mastic, obtained by mixing an alcoholic solution with water, is dark brown in colour; on diluting with pure water, the colour changes to a greenish-blue. Colloidal solutions of

aluminium hydroxide and silicic acid prepared by dialysis exhibit a deep reddish-brown colour. On diluting these suspensions with gradually increasing quantities of pure water, the colours exhibited are in succession yellow, yellowish-green, green, greenish-blue, and blue. These experiments show that the green colours of many natural waters can be attributed to diffraction phenomena, due to the presence of finely-divided substances in suspension.

H. M. D.

Formation of Hydrogen Peroxide. FRANZ FISCHER and O. RINGE (*Ber.*, 1908, 41, 945—954).—The formation of hydrogen peroxide, which as an endothermic compound should be produced from steam and oxygen at high temperatures under suitable conditions, has been observed by several investigators either by the explosion of oxy-hydrogen gas with an excess of oxygen or by the sudden cooling of the gases issuing from a flame of burning hydrogen; Nernst, however, has proved that the process of combustion itself, as such, is not responsible for the formation of hydrogen peroxide, since the latter is produced when water is sprayed on to a glowing Nernst filament.

The authors have now approached the subject with the experience gained in the experiments on the formation of ozone at high temperatures (compare Fischer and Brähler, *Abstr.*, 1906, ii, 224; Fischer and Marx, *Abstr.*, 1906, ii, 606, 627, 845; 1907, ii, 163, 340), with the following results. (1) Nernst's experiments with a glowing filament are confirmed. (2) A tube of magnesia, 8—10 cm. long and 0.6 mm. wide, is attached to a capacious tin condenser. The middle of the tube is heated by a bunsen burner, and the end, as near as possible to the condenser, raised to a white heat. When steam under a pressure of 40 mm. of mercury is passed through the tube, the condensed liquid contains 0.0045% of hydrogen peroxide. With magnesia tubes, 0.3 mm. or 1.0 mm. wide, only traces of hydrogen peroxide are obtained. (3) Steam, issuing from a sloping quartz capillary tube, was directed, at a distance of 4—6 mm., on to a flame of hydrogen, 4—6 cm. in height, which was thus blown into the neck of a tin condenser. When the pressure driving the steam was 7 mm. of mercury, 0.067% of hydrogen peroxide was found in the condensed liquid, although the condensation was incomplete in consequence of the velocity of the gaseous stream. (4) Contrary to Nernst's observations (*Abstr.*, 1906, ii, 17), the authors find that hydrogen peroxide is formed when a current of steam and oxygen is submitted to a spark discharge, provided that the velocity of the current is sufficiently great to allow of a rapid cooling of the escaping gases. (5) Traces of hydrogen peroxide are formed when steam is submitted to the silent electric discharge, the temperature being 130°, to prevent condensation of water within the ozoniser. Better results are obtained with a mixture of steam and oxygen or steam and air.

C. S.

Catalytic Decomposition of Hydrogen Peroxide under High Pressures of Oxygen. E. B. SPEAR (*J. Amer. Chem. Soc.*, 1908, 30, 195—209).—It has been suggested by several authors that in the catalytic decomposition of hydrogen peroxide an important part is

played by the dissolved or chemically bound oxygen. In order to study this point, an investigation has been carried out with the object of ascertaining the effect produced on the decomposition by increasing the concentration of oxygen. For this purpose, a method has been devised for determining rates of reaction under high pressures. The apparatus employed and the manner of conducting the experiments are described in detail.

The results show that the catalytic decomposition of hydrogen peroxide by colloidal solutions of platinum, palladium, iridium, gold, and silver is not appreciably affected by increasing the pressure of oxygen above the reaction mixture from 1 to 200 atmospheres.

E. G.

Atomic Weight of Chlorine. WILLIAM A. NOYES and H. C. P. WEBER (*J. Amer. Chem. Soc.*, 1908, 30, 13—29).—The only determination of the atomic weight of chlorine made by direct comparison of hydrogen and chlorine is that of Dixon and Edgar (*Abstr.*, 1905, ii, 696).

Determinations have now been made by the direct union of hydrogen and chlorine, the hydrogen being weighed absorbed in palladium, and the chlorine in the form of potassium platinichloride. The hydrogen was passed over the heated potassium salt, and the hydrogen chloride was collected and weighed. Two independent series of ratios were thus obtained.

An account is given of the methods by which the materials were purified and weighed, as well as a description of the way in which the determinations were carried out.

In the first series, consisting of seven experiments, the hydrogen chloride was absorbed directly by water, whilst in the second series the hydrogen chloride was first condensed to a solid with liquid air, and was absorbed by water after connexion with the other parts of the apparatus had been cut off, the object being to avoid the risk of transference of water from the absorption apparatus to the potassium platinichloride tube. The results of the two series agree very closely, and give $\text{Cl} = 35.452 (\text{H} = 1.00762)$ or $35.461 (\text{H} = 1.00787)$. The values for silver, calculated from Richards and Wells' results (*Abstr.*, 1905, ii, 450) and these two values, are 107.87 and 107.89 respectively. The mean values are considered the most probable, namely, $\text{Cl} = 35.457$ and $\text{Ag} = 107.88$.

E. G.

Changes in the Properties of Chlorine. JOSEF VON FERENTZY (*Chem. Zeit.*, 1908, 32, 285—286).—The statements made by Fabinyi and Förster (compare *Abstr.*, 1906, ii, 435) are erroneous, and their experimental results may be explained by the fact that they did not sufficiently purify their chlorine and carried out the preparation in sunlight. Chlorine prepared by the usual methods always contains oxygen compounds, but the amount is particularly large when the chlorine is prepared by adding sodium chloride to a mixture of potassium dichromate and sulphuric acid. Hypochlorous acid has a marked effect in promoting the conversion of the chlorine in chlorine water into hydrogen chloride.

P. H.

Influence of Ozone on the Condensation of Water Vapour. G. LEITHÄUSER and R. POHL (*Ber. deut. physikal. Ges.*, 1908, 6, 249—255).—The question whether ozone facilitates the condensation of water vapour has been examined. When increasing quantities of nitrogen are mixed with ozone, the condensation takes place more and more readily. This is attributed to the formation of oxides of nitrogen, and it is shown that condensation does not occur when these are removed by passing the ozonised gas through a tube cooled to -79° . Two kinds of cloud formation are described. A nearly colourless cloud consisting of large drops is caused by nitrogen pentoxide, whilst a blue cloud of very small drops is caused by some other oxide of nitrogen, which is formed by the action of ozone on nitrogen pentoxide.

The condensation of water vapour is also facilitated by ozone when traces of other substances, such as chlorine and iodine, are exposed to its action, with the result that acid anhydrides are formed as in the case of nitrogen. H. M. D.

The Gases Sulphur Dioxide, Dimethyl Ether, and Methyl Chloride. G. BAUME (*J. Chim. Phys.*, 1908, 6, 1—91).—A detailed account is given of measurements of the density and the compressibility at low pressures of sulphur dioxide, dimethyl ether, and methyl chloride. The critical pressure and temperature of methyl chloride have also been determined.

The weights of a litre of sulphur dioxide, methyl ether, and methyl chloride at 0° and 760 mm. are respectively 2.9266, 2.1096, and 2.3045 grams; the coefficients, representing the deviations from Boyle's law between pressures of 0 and 1 atmosphere, are for the three gases, 0.02380, 0.02656, and 0.02215; the critical temperature and pressure of methyl chloride are respectively 416.3° (absolute) and 65.85 atmospheres.

These numbers are used for the determination of the molecular weights of the three gases according to the methods which have been indicated by Leduc, D. Berthelot, and Guye.

When the densities of the gases are calculated by the method of molecular volumes, values are obtained which agree with the experimental values within 0.1% to 0.3%. The method of limiting densities and the method based on the reduction of the critical data give values slightly smaller than the experimental values, the agreement being closer when the density method is employed. H. M. D.

"Tellurium." Is it a Mixture of Two Elements? WILLIAM BETTEL (*Chem. News*, 1908, 97, 169—170).—Some twenty-five years ago, the author's attention was drawn to a silver "telluride" ore which exhibited anomalous behaviour on cupellation. The beads of silver instead of solidifying to buttons spread out in irregular films, which in some cases were over an inch in diameter, leaving a protuberance in the centre of the cupel. In the case of another ore examined four years later, a film of only 2 mm. width was formed around the silver bead, a similar result being obtained on cupelling ordinary silver lead to which pure tellurium of commerce had been added. Suspecting that the original ore contained a new element,

and having exhausted his supply, the author appeals to others for samples of silver "telluride" ores the behaviour of which is in any way peculiar. P. H.

Oxidation of Hydrazine. II. ARTHUR W. BROWNE and F. F. SHETTERLY (*J. Amer. Chem. Soc.*, 1908, 30, 53—63).—In an earlier paper (Abstr., 1907, ii, 863), it was shown that hydrazine sulphate is oxidised by ammonium metavanadate with formation of azoimide.

An account is now given of the action of potassium chlorate, bromate, and iodate, and of the halogens on an acid solution of hydrazine sulphate. The experiments were carried out with the object of ascertaining whether azoimide is produced in these reactions, and of determining the yield under particular conditions. The following results were obtained.

When a solution of hydrazine sulphate is treated with potassium chlorate or bromate in presence of sulphuric acid, the hydrazine is not completely oxidised to nitrogen and water, but a secondary reaction takes place: $2\text{N}_2\text{H}_4 + 2\text{O} = \text{N}_3\text{H} + \text{NH}_3 + 2\text{H}_2\text{O}$. In the case of potassium chlorate, the highest yields obtained were 22.44% of azoimide and 48.76% of ammonia, whilst with potassium bromate 6.68% of azoimide and 9.77% of ammonia were formed. With potassium iodate, neither azoimide nor ammonia was produced. The amount of azoimide formed decreases therefore with increase in the atomic weight of the halogen.

When hydrazine sulphate is treated with chlorine, a small quantity of azoimide is produced in both acid and alkaline solutions, whilst, with bromine, traces are formed in an alkaline solution and none in an acid solution, and, with iodine, none is produced either in acid or alkaline solution. Hence the slight tendency of halogens to produce azoimide decreases with increase in the atomic weight of the element.

By the oxidation of hydrazine sulphate in presence of sulphuric acid and silver sulphate, the following maximum yields of azoimide and ammonia were obtained. With potassium chlorate, 13.32% N_3H , 16.96% NH_3 ; with potassium bromate, 11.65% N_3H , 27.42% NH_3 ; with potassium iodate, 11.16% N_3H , 16.16% NH_3 . The influence of silver sulphate in increasing the yield of azoimide varies directly therefore with the atomic weight of the halogen. E. G.

The Phosphorus-Arsenic Group. GOTTLÖB E. LINCK (*Ber.*, 1908, 41, 822—823. Compare Abstr., 1899, ii, 415; this vol., ii, 176).—Polemical. A reply to Stock (this vol., ii, 176) and Erdmann (this vol., ii, 275). W. H. G.

Glowing of Phosphorus and Some of its Compounds. ERNST SCHARFF (*Zeitsch. physikal. Chem.*, 1908, 62, 179—193).—The phosphorescence phenomena exhibited by phosphorous oxide have been studied, and are found to resemble those observed with phosphorus itself. In perfectly dry oxygen, phosphorous oxide is not luminous at any pressure between 100 and 800 mm., or at any temperature between 19° and 60°. When the oxygen is moist, phosphorescence

is exhibited so soon as the pressure falls below a certain limiting value. At first, it is intermittent, but, as the pressure is still further reduced, the glow becomes steady and permanent. On reversing and raising the pressure, the steady glow passes gradually into an intermittent phosphorescence, which ceases when the limiting pressure has been reached. The value of the limiting pressure increases with rising temperature, and at the ordinary temperature is about 350 mm.

The change from intermittent to permanent phosphorescence, or vice versâ, is well shown by phosphorus sesquisulphide, for which there exists a limiting pressure in dry oxygen. In this case, no phosphorescence is exhibited until a temperature of 65° is reached, whilst at 90° the substance is burned up. It takes fire also when the permanent phosphorescence is allowed to become fully developed at temperatures below 90° . The combustion occurs in a pulsatory fashion ("stossweise") with a greenish light, in a similar manner to the trioxide. The phosphorescence disappears generally at a higher pressure than that at which it first appeared, the difference between the two pressures increasing with rising temperature. This behaviour is attributed to the heat effect of the reaction, in virtue of which the temperature is raised and the limiting pressure is accordingly higher. In moist oxygen, the limiting pressures for phosphorus sesquisulphide are higher than in dry oxygen.

The luminosity exhibited by phosphorus itself was studied under conditions similar to those employed in the previous experiments, the ozone produced in this case being removed by Para rubber. It is found that the various phases of the phenomenon are very similar to those observed with the oxide and sulphide, and it is therefore probable that for the phosphorescence of phosphorus the trioxide is mainly responsible. The usual vigour of the phosphorus oxidation is to be attributed to the presence of ozone; the limiting pressure in the case of phosphorus, that is, the pressure above which no phosphorescence is exhibited, is very nearly a linear function of the temperature, as found by Joubert.

The vapours of organic substances tend to prevent the phosphorescence of phosphorous oxide and phosphorus sesquisulphide. The author's observations in this direction agree generally with those made by Centnerszwer on the effect of these vapours on the luminosity of phosphorus (see Abstr., 1898, ii, 427). J. C. P.

Reversion of Phosphoric Acid in Superphosphates. KARL HERBST (*Chem. Zentr.*, 1908, i, 285; from *Oesterr.-ung. Zeitsch. Zuckerind. Landw.*, 1907, 36, 645—652).—Neither calcium nor magnesium salts cause the soluble phosphate in superphosphate to change back to the insoluble, but ferrous and ferric sulphates, formed from the natural phosphate by using sulphuric acid in the preparation of the superphosphate, bring about this change. The monocalcium phosphate in the presence of ferrous and ferric sulphates changes into the insoluble ferric phosphate, $\text{FePO}_4 \cdot x\text{H}_2\text{O}$. In the case of monoaluminium phosphate, $\text{AlH}_6(\text{PO}_4)_3$, a similar change takes place in the presence of ferric sulphate, sulphuric acid being liberated and ferric aluminium phosphate, $\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot (\text{P}_2\text{O}_5)_2 \cdot \text{H}_2\text{O}$, produced. The author

suggests that to increase the value of the superphosphate the iron salts should be rendered indifferent or extracted. J. V. E.

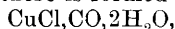
Colloidal Graphite. E. G. ACHESON (*Chem. Zentr.*, 1908, i, 210—211; from *J. Franklin Inst.*, 1907, 164, 375—382).—The addition of tannic acid solution to clay has been shown to render it more plastic and incapable of filtration. The author treats graphite in a similar manner, with the object of obtaining it in a more suitable form for lubrication. The best results were arrived at by stirring graphite for a long time with 3—6% of its weight of tannin in aqueous solution. Colloidal graphite obtained in this manner remains for weeks and months in suspension, and passes through all filters; the addition of hydrochloric acid causes it to separate in a flocculent state.

J. V. E.

Cuprous Compounds of Carbon Monoxide. WILHELM MANCHOT and J. NEWTON FRIEND (*Annalen*, 1908, 359, 100—128. Compare Manchot and Zechentmayer, *Abstr.*, 1907, ii, 93; Jones, *Abstr.*, 1900, ii, 17; Berthelot, *Abstr.*, 1901, i, 493).—The characteristic property of forming additive compounds with gases, such as oxygen, carbon monoxide, and nitric oxide, possessed by hæmoglobin as a metallic complex, makes it desirable to investigate the dissociating additive compounds of metallic salts with those gases. Such studies, moreover, may be expected to throw light on the primary action of free oxygen on the unsaturated metallic compounds. Hence the authors have studied quantitatively the absorption of carbon monoxide by cuprous chloride under varying conditions, and have obtained the following results.

The absorption of carbon monoxide by cuprous chloride in hydrochloric acid solution increases with decreasing concentration of the hydrogen chloride, with lowering of the temperature, with increasing concentration of the cuprous chloride, and with increasing pressure of the carbon monoxide. Similar results are obtained with sulphuric acid solutions. The absorption by means of cuprous chloride and water takes place very slowly, and diminishes as the amount of water increases. The results are not markedly affected by the employment of saturated ammonium sulphate solutions in place of water. Cuprous hydroxide does not combine with carbon monoxide, but in presence of sodium hydroxide it is slowly reduced to copper, small amounts of carbonate being formed.

In all the cases studied, there is formed the compound



which crystallises in colourless leaflets, decomposes, evolving carbon monoxide on exposure to air, is decomposed by alcohol, concentrated sulphuric acid, or sodium hydroxide, and forms a brownish-black solution in hydrochloric acid. The ratio Cu:CO determines the maximum limit of absorption, which is approached under optimum conditions as to temperature, carbon monoxide pressure, concentration of cuprous chloride, and nature of the solvent, but is never exceeded. This agrees with Jones's observation (*loc. cit.*) that the absorption

may be much greater than that corresponding with Berthelot's formula $\text{CO}(\text{CuCl})_2$.

Similar results are obtained with cuprous chloride, bromide, or iodide in dilute ammoniacal solution, and with cuprous chloride dissolved in aniline, *o*-toluidine, or piperidine. In each case, the limit of absorption is in the ratio $\text{Cu}:\text{CO}$, which in the organic solvent is attained to under the ordinary pressure. In concentrated ammonia, the absorption diminishes with increasing copper concentration.

The addition of carbon monoxide to cuprous chloride takes place only simultaneously with the addition of water, or of some substance, such as ammonia or aniline, which can act as a substitute for water. Thus cuprous chloride does not absorb carbon monoxide in alcoholic solution. This explains the occurrence of many reactions, such as the combustion of carbon monoxide, only in presence of moisture. Where such a reaction takes place in two stages, the second leading to the re-formation of the water, this acts as a catalyst. G. Y.

Combustion of Gases by Incandescence in the Presence of Oxidisable and of Non-combustible Substances. JEAN MEUNIER (*Compt. rend.*, 1908, 146, 757—758).—The curious behaviour of incandescent bodies in the presence of explosive gases and the mechanism of flameless combustion (this vol., ii, 11, 276) are to be explained by the localisation of the combustion on the incandescent surface. The results with an oxidisable incandescent substance are different from those when this is incombustible. When a spiral of pianoforte wire, 1 metre long and weighing 0.33 gram, is heated to redness by an electric current in a closed vessel containing 100 c.c. of a mixture of 9.2% of methane, 18.5% of oxygen, and 72.3% of nitrogen, the spiral oxidises, increasing 0.0115 gram (corresponding to 8.5 c.c. of oxygen) in weight, whilst the residual gas contains 10 c.c. of oxygen, but no carbon dioxide, showing that none of the methane is burnt. As the spiral only occupies 40 cubic millimetres, that is, 1/2500th of the volume of the gas, the oxygen cannot be supplied to it by connexion currents alone, but must actually be attracted by the incandescent metal. A lead wire exhibits the same phenomenon. The metals generally do not remain incandescent when heated and then placed in an inflammable gaseous mixture, although platinum and nickel (the disk in the experiment previously described, *loc. cit.*, was of nickel, not copper as there stated) have this property. Certain oxides, however, possess the property to a high degree. Thus, if the ashy skeleton of a half-burnt match is placed 4 mm. from the flame of a candle, it becomes incandescent, and at a distance of 1—2 mm. the incandescence is very vivid.

The intensity of the incandescence depends, not only on the nature of the incandescent substance, but also on the composition of the surrounding gas. E. H.

Low Ignition Temperature of Carbon Disulphide. F. SCRIBA (*Chem. Zentr.*, 1908, i, 100; from *Zeitsch. phys.-chem. Unters.*, 1907, 20, 390).—If a pellet of cotton-wool soaked in carbon disulphide is

placed in a funnel, the stem of which is closed at the end, and allowed to remain, the vapour may be ignited by sparks from flint and steel on opening the funnel stem. Besides showing the high density of the vapour, this explains its occasional ignition upon treading the earth round the vines when destroying grape phylloxera. J. V. E.

Silicon as a Reducing Agent for the Oxides of Refractory Metals. BERNHARD NEUMANN (*Zeitsch. Elektrochem.*, 1908, 14, 169—172).—Silicon and metallic oxides do not react by the application of a fuse, and the author therefore brings about reaction by adding the mixture to a fused bath of alumina (150 parts) and lime (100 parts) in an electric arc furnace. The temperature of the fused bath is about 1600°, and this is raised by the reaction. A ferro-silicon with 91·65% silicon and 1·03% carbon is used. Chrome-iron ore yielded a ferro-chromium containing 35% to 43% chromium, 2·5% to 3·7% silicon, and 0·8% to 1·5% carbon. Pure chromium oxide yielded a metal with 7% to 8% silicon. Tungstic acid yielded a fused regulus containing, in addition to tungsten, 4·97% iron, 0·93% carbon, and 2·26% silicon. Wolframite, $\text{FeO} \cdot \text{WO}_3$, gave a partially fused 97·5% tungsten. Powdered rutile gave a brittle regulus of titanium containing 20·37% silicon and nearly 3% iron. Molybdic acid yielded a brittle, partially fused metal containing 3·24% silicon, 6·41% iron, and 0·64% carbon. T. E.

Use of Sodium as a Desiccating Agent for Gases. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1908, [iv], 3, 353—355).—Rosenfeld has shown (Abstr., 1901, ii, 547) that finely-divided preparations of sodium or potassium may be obtained by grinding up the metal with sodium chloride. The author finds such a preparation of sodium useful as a drying agent for ammonia and similar gases in cases where the presence of a small amount of hydrogen in the dried gas is not objectionable. Perfectly dry ammonia can be obtained by heating ammonia solution and passing the evolved gas, first over soda-lime and then over metallic sodium which has been ground up with fused sodium chloride. T. A. H.

Specific Gravities of the Iodides of Sodium, Potassium, Rubidium, Cæsium, Calcium, Strontium, and Barium. GREGORY P. BAXTER and FRANCIS NEWTON BRINK (*J. Amer. Chem. Soc.*, 1908, 30, 46—53).—The sp. gr. of lithium iodide has been determined already (Baxter, Abstr., 1904, ii, 484).

Determinations of the sp. gr. of several other iodides have now been made, the salts being fused previously in an atmosphere of nitrogen. The pycnometer employed has been described by Baxter and Hines (Abstr., 1904, ii, 257). The results for D_4^{25} are as follows: Sodium iodide, 3·665; potassium iodide, 3·115; rubidium iodide, 3·438; cæsium iodide, 4·510; calcium iodide, 3·956; strontium iodide, 4·549; barium iodide, 5·150. E. G.

Preparation of Chemically-active Silver by Electrolysis N. TANANAEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 197—203).—Silver, even when obtained electrolytically, varies greatly in its chemical reactivity according to the conditions of the experi-

ment. The most active product is obtained by using a solution of 1.5 grams of silver nitrate in 100 c.c. of water to which about 5 c.c. of dilute nitric acid are added, and heating it to about 40° before starting the experiment; the vessel consists of a porous clay cylinder placed within an outer shallower vessel, the electrodes being platinum plates of 4 sq. cm., of which the cathode is placed in the cylinder at a depth of not more than 1 cm. below the liquid and is kept perfectly motionless throughout the electrolysis. The anode is placed in the outer vessel. The silver so obtained need not be heated in a stream of hydrogen, as it is perfectly free from oxides (compare Danneel, Abstr., 1900, ii, 467) and is also perfectly amorphous. At higher concentrations, it is partly crystalline, whilst at 20% concentration it is wholly so. The activity is measured by its action on ferric sulphate.

Z. K.

Latent Photographic Image as a Colloidal Compound. LÜPPO-CRAMER (*Chem. Zentr.*, 1908, i, 93; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 135—138).—A study has been made of the combination of metallic silver with silver halides. When colloidal silver and silver chloride or bromide are mixed, a colour change and a flocculent separation takes place. Nitric acid dissolves the excess of silver from the precipitate, leaving an intensely red photo-halide. The photo-chloride is more easily prepared than the bromide, and is inert in much smaller particles towards oxidising agents. This photo-halide is only produced so long as the silver is in the colloidal state. The formation of silver sub-chloride or -bromide assumed by Lea is not supported by experiment, and is shown by the author to be unnecessary.

J. V. E.

Relative Solubility of the Silver Halides and Silver Thiocyanate. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1908, 30, 68—74, 303).—The relative solubility of two sparingly soluble salts can be determined whenever (1) the concentrations of the free ions can be calculated from the total concentration of the substances in solution as estimated analytically, and (2) the degree of dissociation of the two salts in saturated solution is known, so that the total solubility can be calculated for the solubility products. The relative solubility of the silver halides and silver thiocyanate has been determined on these lines with the following results.

The solubility of silver chloride being taken as unity, the relative solubilities at 25° are: AgCl : AgCNS : AgBr : AgI = 1.00000 : 0.07480 : 0.05500 : 0.00077. Accepting Kohlrausch and Rose's value for the solubility of silver chloride, the absolute solubilities of the salts at 25° are: AgCl, 1.6×10^{-5} ; AgCNS, 1.2×10^{-6} ; AgBr, 8.8×10^{-7} ; AgI, 1.23×10^{-8} .

E. G.

So-called Silver Peroxide. G. BABOROVSKÝ and B. KUZMA (*Zeitsch. Elektrochem.*, 1908, 14, 196—197).—A solution of silver nitrate is electrolysed with an anodic current density of 0.07 ampere per sq. cm. at platinum electrodes separated by a porous cell. A crystalline, insoluble substance is formed at the anode which contains one molecule of nitric acid for each atom of silver, and two molecules of free nitric acid

are also formed at the anode for each atom of silver in the precipitate, $3\text{AgNO}_3 + \text{H}_2\text{O} = 2\text{Ag} + 2\text{HNO}_3 + \text{AgNO}_4$. The silver pernitrate is very unstable, and soon decomposes into the substances which have been described as silver peroxide. T. E.

Potassium Silver Silicomolybdate. H. COPAUX (*Bull. Soc. franç. Min.*, 1907, 30, 292—299).—A solution containing potassium silicomolybdate, silicomolybdic acid, and silver nitrate deposits first a white precipitate and, on evaporation, crystals with the composition $2(\text{SiO}_2, 12\text{MoO}_3), 3\text{Ag}_2\text{O}, \text{K}_2\text{O} + n\text{H}_2\text{O}$. The amount of water of crystallisation depends on the temperature at which the solution is evaporated: at 18—20°, red, triclinic crystals containing $14\text{H}_2\text{O}$ are deposited; and at 12—14°, yellow, triclinic crystals containing $30\text{H}_2\text{O}$. Yellow, crystalline crusts with $22\text{H}_2\text{O}$ were also formed. The red colour of one of these hydrates is unusual for a silicomolybdate, which are characteristically yellow in colour. L. J. S.

Preparation of Alkaline-earth Metals. FR. VON KÜGELGEN (*Zeitsch. Elektrochem.*, 1908, 14, 143—144).—The essential feature of the author's patented process for making calcium and strontium is the use of an immersed cathode and an electrolyte heavier than the metal, so that the globules of fused metal separate quickly from the cathode, where the temperature is highest, and float up to the surface, where the temperature is kept down by means of a cooling ring. T. E.

Action of Metallic Calcium and Calcium Hydride on Metallic Oxides, Sulphides, and Halogen Salts. F. MOLLWO PERKIN and LIONEL PRATT (*Trans. Faraday Soc.*, 1908, 3, 179—186. Compare Abstr., 1907, ii, 952).—Calcium hydride reduces cupric oxide, manganese peroxide, ferric oxide, stannic oxide, litharge, tungstic oxide, boron trioxide, and silica. The reactions are not so violent as when calcium is used. Zinc oxide is not attacked. Lead and antimony sulphides react, but little metal is produced; a calcium antimony (or lead) sulphide may be formed.

Metallic calcium reduces tungsten trioxide very vigorously, both the metal and the calcium oxide produced being fused; with titanium oxide, the temperature does not rise so high, the titanium being obtained as a powder. Alumina is also reduced, but globules of metal are not obtained.

Strontium oxide and metallic calcium react readily, but no metal is obtained; by heating calcium with quicklime, the metal disappears; it appears probable that in these cases a sub-oxide is formed.

The hydroxides of the alkali and alkaline-earth metals react vigorously with calcium, but the metals could not be obtained.

By heating calcium with barium or strontium chloride in the proportion 2Ca to BaCl_2 or SrCl_2 , alloys of barium or strontium with calcium are formed. The chlorides of the alkali metals are also reduced, but the metals volatilise and burn. Lead chloride reacts explosively, forming an alloy. Aluminium chloride gives a small yield of an alloy. Calcium and sulphur, fired by a taper, react almost explosively, but with calcium hydride the reaction is under control, yielding calcium sulphide and hydrogen sulphide. A mixture of

calcium hydride and red phosphorus cannot be ignited by a fuse, but, if some metallic calcium is added, the reaction leads to red calcium phosphide. Calcium hydride and selenium yield calcium selenide.

T. E.

Reaction between Lime and Sulphur. R. W. THATCHER (*J. Amer. Chem. Soc.*, 1908, 30, 63—68).—An account of the composition of solutions formed by boiling mixtures of water, lime, and sulphur, which are largely used as insecticides in agricultural practice (compare Haywood, *Abstr.*, 1905, ii, 312). The solutions contain chiefly calcium pentasulphide and thiosulphate, together with small quantities of sulphite and sulphate. When freshly-slaked lime and sulphur are boiled with water in open vessels, either in presence or absence of salt, they dissolve in the proportions of 1 part CaO to 1.94 parts S when the lime is in excess, or 1 part CaO to 2.24 parts S if the sulphur is in excess. The ratio of the sulphur appearing as pentasulphide to that appearing as thiosulphate is always about 1:5. If such solutions are left for several days, they sometimes deposit bright red or yellow crystals of calcium oxysulphides, formed by the union of the excess of calcium hydroxide with some of the pentasulphide.

The results of analyses of concentrated lime-sulphur solutions are recorded. The proportion of sulphur as pentasulphide is much greater in these solutions than in those prepared in open vessels. E. G.

Abnormal Behaviour of Salts of Zinc, Magnesium, Thorium, Cerium, Nickel, and Cobalt on Hydrolysis. HENRY G. DENHAM (*Zeitsch. anorg. Chem.*, 1908, 57, 378—394).—The degree of hydrolysis of the salts in question, in different dilutions and in some cases at different temperatures, has been determined by measuring the H^+ ion concentration with a hydrogen electrode. In many cases, the H^+ ion concentration of the solutions alters irregularly from day to day and does not appear to attain an equilibrium value; this behaviour is probably connected with the presence of colloidal salts or hydroxides in solution.

For $M/8$ and $M/4$ solutions of zinc sulphate, the potential difference between metal and solution varies irregularly from day to day over a range of about 0.05 volt at 25°; the same is true of solutions of zinc chloride. Measurements have been made at intervals of temperature between 25° and 95°, and it is found that at the same temperature the H^+ ion concentration is less with falling than with rising temperature, showing that the original solutions were not in true equilibrium, but in some way "over hydrolysed." As confirming the view that the phenomena in question are connected with formation of colloidal solutions, it is found that, when a solution of zinc sulphate is heated to 100° and again cooled to 25°, the *E.M.F.* is not much altered, but a slight colloidal precipitate is noticed.

Magnesium sulphate shows the same phenomenon, a $1/32$ molar solution is hydrolysed only to the extent of about 0.0023%. For thorium sulphate, the H^+ ion concentration rises steadily for seven to eight days and then falls, the average hydrolysis of a $1/64$ molar solution is 46%. A $1/32$ molar solution of cerium chloride, $CeCl_3$, is

hydrolysed about 0.14%. For cobalt chlorides, the daily variation is small; the average hydrolysis in a 1/32 molar solution is 0.17%. Like zinc sulphate, the hydrolysis of the latter salt is greater with rising than with falling temperature, and the difference at 50° is as much as 54%. For nickel sulphate, the daily alteration in hydrolysis is very small. G. S.

Electrolytic Corrosion of Copper-Aluminium Alloys. W. S. ROWLAND (*J. Physical Chem.*, 1908, 12, 180—206. Compare, for the composition of the alloys, Curry, Abstr., 1907, ii, 872).—A series of copper-aluminium alloys, containing 0—100% of copper, were annealed at 500°, and those containing 0—54% and 84—100% of copper quenched from that temperature; the remainder, owing to their brittle character, had to be cooled slowly. Alloys containing 84—90% of copper were also annealed at 610°. The alloys were then subjected to electrolytic corrosion in solutions of certain sodium salts, a test piece being used as anode, a platinum wire as cathode, and a small electric current passed through the solution. The amount and copper content of the corrosion products, as well as the current efficiency, are given in tabular form, and in most cases the current efficiency is also represented graphically as a function of the composition of the alloys.

The alloys are practically unacted on in sodium carbonate solution; sodium hydroxide dissolves the CuAl_2 and η phases, but not the α , β , and ϵ phases. The α phase is most readily soluble in the majority of the organic salt solutions, but the CuAl_2 and η phases are unacted on in contact with these solvents. In alkaline tartrate solutions, the solubility increases from the α to the γ phase and then diminishes. The alloys which are most resistant to corrosion in general have the poorest physical properties. Only those containing 10—20% of copper are suitable for commercial use.

In many of the solutions, especially those containing organic salts, the alloys tend to become passive, the aluminium at the same time becoming superficially oxidised. G. S.

Physico-chemical Investigation of Old Bronzes from the Excavations in Lalajants, on the S.W. Shore of Lake Gotscher, in the Summer of 1906. VLADIMIR A. SKINDER (*Chem. Zentr.*, 1908, i, 220; from *Mitt. Kaukasisch. Museum*, 1907, 3, 1—60).—The author discusses the relation between the properties of bronzes and their chemical composition, and also the alteration which bronze objects undergo when under water or buried in the earth. In both cases, they become coated with a film of copper sulphide, owing to the presence of free hydrogen sulphide. The inner surface of two of the bronze objects examined was found to be coated with a thin film of atacamite, $3\text{CuO} \cdot \text{CuCl}_2 \cdot \text{NH}_3\text{O}$. Many results of the analysis of bronze objects are given, and from them the conclusion is drawn that the hardening of bronze was known to the ancients. J. V. E.

Synthesis of Atacamite. VLADIMIR A. SKINDER (*Bull. Acad. Sci. St. Petersburg*, 1908, 3, 381—388).—The chemical and microscopical examination of the deposits found on ancient bronzes that have been

long buried (preceding abstract), shows that the quantity of atacamite in them is very inconsiderable, this being due (as proved by its synthesis) to the extreme slowness with which atacamite is formed. The proportion of atacamite, however, also depends on the quality of the soil in which the bronze is buried and on the climate. The process by which atacamite is synthesised is best explained by Berthelot's equations (*Ann. Chim. Phys.*, 1895, [vi], 4, 551). Z. K.

The Three-Component System CuO , SO_3 , H_2O at 25° . JAMES M. BELL and WALTER C. TABER (*J. Physical Chem.*, 1908, 12, 171—179).—No evidence has been obtained of the existence of definite basic or acid sulphates of copper at 25° .

In order to determine whether any of the basic sulphates of copper described in the literature actually exist, solutions of copper sulphate have been shaken with copper oxide or hydroxide in varying proportions at 25° until equilibrium was attained, and the solutions and residues then analysed. The equilibrium solutions all contained copper oxide and sulphur trioxide in equivalent proportions. The results show that definite basic sulphates of copper do not exist; the residues consist of solid solutions of copper oxide and sulphate. The composition of the limiting solid solution in contact with water is $4\text{CuO}\cdot\text{SO}_3$, which is that of the "basic sulphate" obtained by Pickering (*Trans.*, 1907, 91, 1981) by the action of not more than 0.75 equivalent of alkali on a solution of copper sulphate.

When sulphuric acid in gradually increasing concentration is added to solutions of copper sulphate, the solubility of the latter is lessened, and the three hydrates, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4\cdot \text{H}_2\text{O}$, and, finally, the anhydrous salt are obtained successively as solid phases. The hydrates with $5\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$ are in equilibrium with a solution containing 41.29% of sulphur trioxide and 1.42% of copper oxide, the vapour pressure of which is about 8.5 mm. at 25° , and the hydrates with $3\text{H}_2\text{O}$ and $1\text{H}_2\text{O}$ are in equilibrium at the same temperature with a 48.5% solution of sulphur trioxide, the vapour pressure of which is about 4.5 mm.; finally, the transition $\text{CuSO}_4\cdot \text{H}_2\text{O} \rightarrow \text{CuSO}_4$ takes place at about 0.1 mm. pressure. These transition pressures are in moderate agreement with those determined directly by Lescoeur (*Abstr.*, 1886, 842).

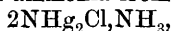
No evidence has been obtained of the existence of hydrates other than those mentioned. G. S.

Purification of Mercury. WILLIAM BETTEL (*Chem. News*, 1908, 97, 158).—It is found that mercury can be freed from gold, zinc, tin, lead, copper, and iron by treatment with dilute potassium cyanide solution in the presence of sodium peroxide. The metal (7 kilos.) is placed in a shallow enamelled iron pan, thus exposing a maximum surface to the cyanide solution, which consists of 1.5 litres of a 2% solution of potassium cyanide (98%). Twenty grams of peroxide are added at intervals in order to facilitate the oxidation of the base metals, and the whole is agitated gently at intervals. During the first four days, the base metals are removed, and at the end of about fourteen days the

whole of the gold if, after eight days, the above solution is removed and replaced by one of one-tenth its concentration.

The mercury, after this treatment, is purer than that usually obtained by distillation under reduced pressure. J. J. S.

Ammoniacal Dimercuriammonium Chlorides. H. GAUDECHON (*Compt. rend.*, 1908, 146, 761—764. Compare this vol., ii, 85).—By the action of liquid or dry gaseous ammonia at 10—15° on the chloride, $\text{NHg}_2\text{Cl}, \text{H}_2\text{O}$, an amorphous, canary-yellow compound of the composition $(\text{NHg}_2\text{Cl})_2, \text{NH}_3$ is formed. The same substance is produced by the action of liquid ammonia on the oxychloride, $3\text{HgO}, \text{HgCl}_2$, and by the prolonged action of alcoholic ammonia on the chloride, $\text{NHg}_2\text{Cl}, \text{H}_2\text{O}$. The latter, for the preparation of the new compound, should be obtained at a low temperature, washed with cold water, and dried in a vacuum over phosphoric oxide. The substance, $2\text{NHg}_2\text{Cl}, \text{NH}_3$, is only very slowly decomposed by concentrated aqueous ammonia; it is hydrolysed by water at 15° into ammonia and the chloride, $\text{NHg}_2\text{Cl}, \text{H}_2\text{O}$. The latter, however, is not altered by prolonged contact with concentrated aqueous ammonia. Cold potassium hydroxide solution liberates ammonia from the compound



and, on heating, gives the brown, crystalline mercuric oxide, ammonia, and potassium chloride. The new substance is decomposed by dilute hydrochloric acid into $\text{NHg}_2\text{Cl}, \text{H}_2\text{O}$ (2 mols.) and NH_4Cl (1 mol.), which slowly combine, giving $\text{NHg}_2\text{Cl}, \text{NH}_4\text{Cl}$. Dissolution of $2\text{NHg}_2\text{Cl}, \text{NH}_3$ (solid) in 24KCN develops +121.5 Cal. From this, the heat developed by the reaction $2\text{NHg}_2\text{Cl}, \text{H}_2\text{O}$ (solid) + NH_3 (gas) = $(\text{NHg}_2\text{Cl})_2, \text{NH}_3$ (solid) + $2\text{H}_2\text{O}$ (liquid) is calculated as +10.2 Cal., or +5.9 Cal. (liquid ammonia), +1.4 Cal. (dissolved ammonia). Deducing by analogy the value +3.3 Cal. for the heat of combination of $2\text{NHg}_2\text{Cl}$ with $2\text{H}_2\text{O}$ (solid), the value +13.5 Cal. is obtained for the heat of formation of NHg_2Cl (solid), NH_3 (gas).

The compound $(\text{NHg}_2\text{Cl})_2, \text{NH}_3$ combines with a further molecule of ammonia at 0°, and a study of the system $(\text{NHg}_2\text{Cl})_2, \text{NH}_3$ (solid) + NH_3 (gas) shows that it obeys the law of fixed tensions, the equilibrium pressures of ammonia being 21 cm. at -21°, 38 cm. at 0°, 62 cm. at +8°, and, by extrapolation, 76 cm. at 13°. Application of Matignon's law as to the constant variation in the entropy of similar systems (*Abstr.*, 1899, ii, 273) gives the value +9.4 Cal. for the heat of combination of the second molecule of ammonia.

The compounds $(\text{NHg}_2\text{Cl})_2, \text{NH}_3$ and $\text{NHg}_2\text{Cl}, \text{NH}_3$ can be regarded as ammoniacal dimercuriammonium chlorides, in which the group NHg_2Cl behaves as a true metallic chloride, whilst Rammelsberg's compound $\text{NHg}_2\text{Cl}, \text{NH}_4\text{Cl}$ can be considered as the hydrochloride of the substance $\text{NHg}_2\text{Cl}, \text{NH}_3$, and written thus: $[(\text{NHg}_2\text{Cl})\text{NH}_3]\text{HCl}$.

E. H.

Mercury Salts of Hydrogen Peroxide and the Preparation of a Compound HgO_2 . ANDREAS VON ANTROPOFF (*J. pr. Chem.*, 1908, [ii], 77, 273—320).—In the periodic contact catalysis of hydrogen

peroxide by mercury (Bredig and Weinmayr, Abstr., 1903, ii, 279; Bredig and Wilke, 1905, ii, 151), the formation of a yellow or brownish-black skin has been observed when the evolution of oxygen ceases. It is highly probable that this is an intermediate product of the type Hg_xO_y formed during the catalysis. It has not been found possible to isolate and analyse the skin, on account of the readiness with which it is decomposed, sometimes explosively, into mercury and oxygen, but the conclusion is drawn that it is the mercurous salt of hydrogen peroxide or *mercurous peroxydate*.

When the skin is left in contact with concentrated hydrogen peroxide, it is transformed into an explosive, brownish-red compound, which can be prepared more readily by the action of hydrogen peroxide (30%) on red mercuric oxide.

Careful synthesis and analyses, by van Bylert's method, of the red compound show that it has the composition HgO_2 , and it is regarded as the mercuric salt of hydrogen peroxide, that is, *mercuric peroxydate*,

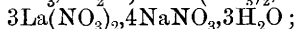
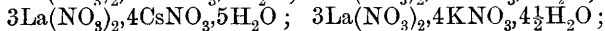
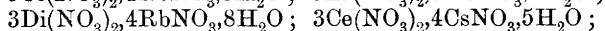
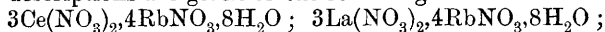
$\text{Hg} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$. It decomposes rapidly when in contact with water at the ordinary temperature with evolution of oxygen. It is slowly hydrolysed by water at 0° ; the washings contain free hydrogen peroxide, and mercuric oxide is formed ultimately. The dark red compound is not formed when the red oxide is left in contact with hydrogen peroxide of 15% or less concentrated, although even in these cases evolution of oxygen occurs after some little time. The peroxydate is formed more readily at the ordinary temperature than at 0° , but this is followed by vigorous decomposition in the course of twenty to fifty minutes, whereas at 0° decomposition occurs after three to seven days. The decomposition is accelerated by traces of alkali, but retarded by acids. Yellow mercuric oxide cannot be used in place of the red oxide, but, if the red oxide is powdered until it has a yellow colour, it reacts readily with hydrogen peroxide; the product formed has a paler colour, and decomposes much more readily than the product from the ordinary red oxide. When dry, the compound is comparatively stable, even at the ordinary temperature. It can undergo rapid decomposition, leaving a grey residue; this usually occurs at the beginning of drying; or it can decompose slowly, giving up oxygen and leaving a residue of red mercuric oxide. When heated or struck, it explodes, and the product obtained from the finely-powdered oxide explodes when rubbed, even in the moist state. Daylight has no apparent effect on the decomposition of the dry powder.

Some specimens of red oxide immediately decompose the hydrogen peroxide with evolution of oxygen, but the addition of a minute quantity of nitric acid will prevent this and induce the formation of the peroxydate. The compound cannot be obtained by the action of hydrogen peroxide on mercuric acetate, or by the action of ozone on mercury or mercuric oxide.

Mercurous oxide reacts with hydrogen peroxide with explosive violence even in the presence of free acid; after repeated additions of peroxide, the reaction ceases, and the black oxide assumes a dark red colour, due to the formation of mercuric peroxydate.

J. J. S.

Double Nitrates of Alkali and Cerium Metals. GRÉGOIRE WYROUBOFF (*Bull. Soc. franç. Min.*, 1907, **30**, 299—323).—Crystallographic descriptions are given of the following salts:



and the pyridine salt, $3\text{Ce}(\text{NO}_3)_2, 4(\text{C}_5\text{H}_5\text{N}, \text{HNO}_3), 7\text{H}_2\text{O}$.

When the solutions of these salts are evaporated at temperatures above 70° , the anhydrous salts (except the sodium salt) are deposited as cubic crystals. Mixed crystals of some of these salts are described.

L. J. S.

Cerium Selenates. MASANIELLO CINGOLANI (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 254—266*).—The author has prepared anhydrous cerous selenate, $\text{Ce}_2(\text{SeO}_4)_3$, and the hydrates containing 4, 5, 7, 8, 10, 11 and 12 H_2O . All these hydrates, like the corresponding hydrated sulphates, are very unstable. The properties of the various hydrates are given.

The tetrahydrate, $\text{Ce}_2(\text{SeO}_4)_3, 4\text{H}_2\text{O}$, forms hexagonal prisms belonging to the rhombic system [*A. Rosati*: $a:b=0.6834:1$].

The solubility of the anhydrous selenate is given in tabular and curve form, the latter undergoing various changes of direction.

T. H. P.

Yttrium Earths. I. VICTOR LENHER [and, in part, R. C. BENNER] (*J. Amer. Chem. Soc.*, 1908, **30**, 572—577. Compare James, *Abstr.*, 1907, ii, 467).—The earths of the yttrium group, obtained from samarskite, may be fairly readily separated by repeated fractional precipitation of the hot neutral solution of the nitrates with sodium succinate. In this way are finally obtained (1) a most soluble fraction, the atomic weight of the element in which is 93, consisting chiefly of yttrium with small amounts of samarium, europium, and holmium; (2) a least soluble fraction, the oxide of which is yellow, atomic weight 139, and which is undoubtedly a mixture of yttrium with terbium, holmium, europium, and erbium.

W. H. G.

Action of Aluminium Powder on Silica and Boric Anhydride. FRANK E. WESTON and H. RUSSELL ELLIS (*Trans. Faraday Soc.*, 1908, **3**, 170—178).—Fine aluminium powder and powdered boron trioxide, mixed in the proportion $2\text{Al}:\text{B}_2\text{O}_3$, react in the cold when a fuse of barium dioxide and magnesium ribbon is used; with coarser powder, or when a mixture containing twice as much boron trioxide is used, the reaction only takes place at a red heat. By boiling the product with hydrochloric or hydrofluoric acid, or by fusion with borax and extraction with water, a residue is obtained which consists mainly of boron mixed with borides of aluminium, and alumina. When treated with chlorine, this residue yields boron trichloride, aluminium chloride, and boron trioxide, the latter substances being formed thus: $2\text{BCl}_3 + \text{Al}_2\text{O}_3 = 2\text{AlCl}_3 + \text{B}_2\text{O}_3$. The yield of boron trichloride is poor.

Silica and aluminium powder, mixed in the proportion $8\text{Al}:3\text{SiO}_2$,

* and *Gazzetta*, 1908, **38**, i, 292—307.

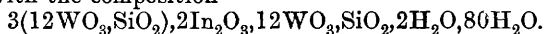
react in the cold when kieselguhr or precipitated silica is used; a higher temperature is required for sand or when other proportions are used. Amorphous silicon is always formed. T. E.

Utilisation of Leucite. CAMILLO MANUELLI (*Gazzetta*, 1908, 38, i, 143—152).—The author discusses the various processes suggested for the industrial application of leucite. The following methods of treatment give the most promising results. The mineral is converted into alum by the action of dilute sulphuric acid. The alum is then either (1) heated with wood charcoal at a dull red heat, by which means it yields potassium and aluminium sulphides; the latter can then be converted into aluminium hydroxide by the action of water and separated; or (2) heated alone at 450° , the products being potassium sulphate, alumina, and sulphur trioxide; or (3) treated with calcium carbonate, which also removes the alumina. Leucite may also be treated profitably with nitric acid, the reaction being represented by the equation: $\text{Al}_2(\text{SiO}_3)_3, \text{K}_2\text{SiO}_3 + 8\text{HNO}_3 = 2\text{KNO}_3 + 2\text{Al}(\text{NO}_3)_3 + 4\text{SiO}_2 + 4\text{H}_2\text{O}$; the aluminium nitrate may then be converted into potassium nitrate by treatment with potassium chloride. T. H. P.

Some New Compounds of Indium. FRANK C. MATHERS and C. G. SCHLUEDEBERG (*J. Amer. Chem. Soc.*, 1908, 30, 211—215).—*Indium perchlorate*, $\text{In}(\text{ClO}_4)_3, 8\text{H}_2\text{O}$, obtained by dissolving indium in perchloric acid, is a colourless, crystalline, deliquescent salt which fuses at 80° . The *iodate*, $\text{In}(\text{IO}_3)_3$, prepared by the action of potassium iodate on indium trichloride, forms white crystals, and is soluble in 1500 parts of water at 20° , or in 150 parts of nitric acid (1:5) at 80° . The *selenate*, $\text{In}_2(\text{SeO}_4)_3, 10\text{H}_2\text{O}$, obtained by dissolving indium hydroxide in selenic acid, forms white, hygroscopic crystals, and is easily soluble in water. *Indium caesium selenate*, $\text{CsIn}(\text{SeO}_4)_2, 12\text{H}_2\text{O}$, crystallises from a solution of caesium and indium selenates in colourless, efflorescent octahedra. E. G.

Silicotungstates of Indium. GRÉGOIRE WYROUBOFF (*Bull. Soc. franç. Min.*, 1907, 30, 277—282).—Metallic indium was dissolved in nitric acid and the theoretical amount of silicotungstic acid added to the solution; the nitric acid was driven off by evaporating to dryness, and the neutral solution crystallised over sulphuric acid at 15° . The large, colourless crystals so obtained are isotropic octahedra, with the composition $3(12\text{WO}_3, \text{SiO}_2), 2\text{In}_2\text{O}_3, 93\text{H}_2\text{O}$.

In an acid solution at a higher temperature, anorthic crystals with $63\text{H}_2\text{O}$ were first obtained, and afterwards monoclinic crystals of an acid salt with the composition



Indium is therefore tervalent, and the silicotungstate of its sesquioxide is analogous to those of iron, aluminium, chromium, gallium, and glucinium, with the difference, however, that none of these give an acid silicotungstate. L. J. S.

Specific Heat of Iron-Carbon Alloys. P. OBERHOFFER and A. MEUTHEN (*Metallurgie*, 1908, 5, 173—177).—The vacuum calorimeter employed in the determination of the specific heat of iron (*Abstr.*, 1907, ii, 736) has been improved in several respects.

Alloys containing from 0—4.03% C were examined at 650°, the whole of the carbon being present as cementite. The specific heat between 0° and 650° is directly proportional to the carbon content, increasing by 0.0011 for each 0.5% C. Extrapolation gives the value 0.1581 for the specific heat of the carbide, Fe_3C , the theoretical value, calculated from the atomic heats, being 0.1546. C. H. D.

Electrolytic Inactivity of Ferric Oxide. PETERS (*Chem. Zentr.*, 1908, i, 213—214; from *Zentr. Akkumulat.*, 1907, 8, 165—166).—Contrary to the statement that chemically-prepared ferric oxide is difficult to reduce electrolytically (D.R.-P. 180672 and 190236), on comparing the capacity of accumulators containing negative plates of artificial and natural ferric oxide, no evidence of electrolytic inactivity is observed. J. V. E.

Freezing-point Curve of the Cobalt-Arsenic Alloys. K. FRIEDRICH (*Metallurgie*, 1908, 5, 150—157).—Very pure specimens of cobalt, prepared by reduction of the oxide with hydrogen at 1100—1200°, and arsenic were melted together to form an alloy containing 45.6% of cobalt, and this was then melted with further quantities of cobalt or arsenic. The complete thermal examination by Tammann's method was made. Each melt was nucleated to prevent undercooling, although even with this precaution undercooling was sometimes observed to the extent of 20°.

The first series of crystals consist of cobalt containing not more than 1% of arsenic in solid solution. There is a eutectic point at 916° and 30% As. There is a maximum at 926° and 33.7% As, corresponding with the compound Co_5As_2 . A second maximum, corresponding with the compound Co_2As , occurs at 959° and 38.9% As. The existence of Co_3As_2 , dissociating without melting at 1014°, is also indicated, and the curve then rises, apparently reaching a maximum near 1180°, corresponding with the compound CoAs . It was not possible to follow the curve to higher percentages of arsenic.

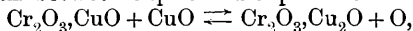
The three compounds first mentioned exist each in an α - and a β -form, the transformation occurring on cooling with development of heat whether the compound is present in primary crystals or as a constituent of a eutectic. The respective transition temperatures are: for Co_5As_2 , 828°; Co_2As , 352° (?), and Co_3As_2 , 915°. Alloys containing from 12% to 46% As also undergo a transformation at temperatures ranging from 250° to 350°, both temperature and heat development reaching a maximum at the composition Co_2As . This change is accompanied by a considerable increase of volume on cooling, sometimes causing disruption of the alloy. Its nature is not to be discovered by a microscopic examination of the alloys.

The hardness of cobalt is progressively increased by the addition of arsenic. Only alloys containing 0—38% As are attracted by a magnet. C. H. D.

Dissociation of Chromium Oxides and of the Double Oxides of Chromium and Copper. LOTHAR WÖHLER and PAUL WÖHLER (*Zeitsch. physikal. Chem.*, 1908, 62, 440—453).—Up to 1220°, no oxidation of chromic oxide can be detected, and it is supposed that the

formation of higher oxides must be an endothermic process, taking place at higher temperatures. If chromic oxide is heated along with potassium sulphate in an atmosphere of oxygen at about 1000° , an equilibrium pressure is established, which increases when the temperature is lowered, and decreases when the temperature is raised. This is therefore a case of exothermic dissociation, and the author shows that the equilibrium is probably: $2K_2SO_4 + Cr_2O_3 + 3O \rightleftharpoons 2K_2SO_4 \cdot CrO_3$. The value of the equilibrium pressure at any temperature varies with the quantity of oxygen already absorbed, probably because at 1000° potassium sulphate is fused and keeps the complex compound in solution.

The equilibrium between cupric and cuprous chromites,



has been investigated. The equilibrium oxygen pressure was determined at various temperatures, and it was found that the equilibrium could be reached from both sides; the equilibrium pressure reaches the value of 1 atmosphere at 875° .

The stages of decomposition of cupric chromate on heating are represented as follows: (1) $4CuCrO_4 \rightarrow 2Cr_2O_3 \cdot CuO + 2CuO + 3O_2$; (2) $2Cr_2O_3 \cdot CuO + 2CuO \rightarrow 2(Cr_2O_3 \cdot Cu_2O) + O_2$. The first of these changes takes place below 400° under 1 atmosphere pressure, and some observations made by the authors tend to show that this decomposition is exothermic.

When copper chromate is heated in a current of oxygen at $650-700^{\circ}$, the product contains basic cupric chromite, $4Cr_2O_3 \cdot 5CuO$, and cupric oxide, the former being insoluble in nitric acid. If this product is further heated to a temperature not below 900° , cuprous chromite is obtained, thus: $4Cr_2O_3 \cdot 5CuO + 3CuO = 4(Cr_2O_3 \cdot Cu_2O) + 2O_2$. Cuprous chromite is insoluble in nitric acid, and can therefore be easily separated from excess of cupric oxide; its specific gravity is 5.237. By heating cuprous chromite in a current of oxygen below 870° , crystalline cupric chromite is obtained. Amorphous cupric chromite may be prepared by igniting a mixed precipitate of chromic and cupric hydroxides at about 700° in a current of oxygen.

Cuprous chromite is not attacked by sulphur dioxide; it is probable therefore that the cause of its catalytic efficiency in the contact process is a primary oxidation to $Cr_2O_3 \cdot CuO + CuO$, followed by a reduction to $Cr_2O_3 \cdot Cu_2O$. J. C. P.

Crystallisation of Potassium Dichromate. HENRY A. MIERS (*Min. Mag.*, 1908, 15, 39—41).—When a drop of a strong solution of potassium dichromate evaporates, there is first of all a rapid growth of branching fibres and needles at the edges of the drop; after a short time, the ends of the fibres grow slowly and uniformly as platy crystals. The first stage in the crystallisation corresponds with the "metastable" condition of the solution, and the second with the "labile" condition (*Trans.*, 1906, 89, 413). In the same drop there may be a recurrence of these conditions, resulting in a periodic phenomenon in the crystallisation, similar to that recently described and attributed to another cause by D. W. Alexéeff (*Abstr.*, 1907, ii, 239).

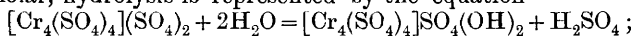
L. J. S.

Electrometric Determination of the Hydrolysis of Blue and Green Chromic Sulphates. HENRY G. DENHAM (*Zeitsch. anorg. Chem.*, 1908, **57**, 361—377. Compare Recoura, *Abstr.*, 1896, ii, 27; Whitney, *Abstr.*, 1896, ii, 525; Richards and Bonnet, *Abstr.*, 1904, ii, 343).—The degree of hydrolysis of the salts in question in different dilutions at 25° has been determined from measurements of the H⁺ ion concentration with a hydrogen electrode (Denham, *Trans.*, 1908, **93**, 22), and the conclusions as to the constitution of the solutions confirmed by transport and freezing-point measurements.

As regards the blue salt, the results of the measurements agree best with the assumption that the hydrolysis is represented mainly by the equation $\text{Cr}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} = 2\text{Cr}(\text{SO}_4)\cdot\text{OH} + \text{H}_2\text{SO}_4$. It therefore seems probable that the normal sulphate ionises according to the equation $\text{Cr}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{CrSO}_4^+ + \text{SO}_4^{--}$, the hydrolytic decomposition being then represented as follows: $2\text{CrSO}_4^+ + \text{OH}^- \rightleftharpoons \text{Cr}(\text{SO}_4)\cdot\text{OH}$. A 1/100 molar solution of the normal blue salt is hydrolysed to the extent of 8.3% at 25°.

In order to estimate the complexity of the green salt in solution, the freezing point of aqueous solutions of the salt and of solutions saturated with chromic hydroxide and normal with regard to sulphuric acid respectively have been determined. In all cases, the depression is smaller for the green than for the blue solution, and, although the results are not quite conclusive, they appear to show that a complex cation $[\text{Cr}_4\text{.....}]$ is present. Migration experiments show that the complexity is not due to the presence of a complex acid.

Measurements of the hydrolysis in solutions of the green salt show that, contrary to the views of Recoura and of Whitney (*loc. cit.*), the salt is not hydrolysed to a definite fraction (one-sixth), but undergoes hydrolysis in the ordinary way. On the basis of the above results and of those of Richards and Bonnet (*loc. cit.*), it is considered that, on heating the blue solution, two molecules of the salt unite to form the green salt according to the equation $2\text{Cr}_2(\text{SO}_4)_3 = [\text{Cr}_4(\text{SO}_4)_4](\text{SO}_4)_2$, the latter salt then becoming partly hydrolysed. In solutions up to 1/40 molar, hydrolysis is represented by the equation



on further dilution, more complete hydrolysis occurs, represented thus: $[\text{Cr}_4(\text{SO}_4)_4](\text{SO}_4)_2 + 4\text{H}_2\text{O} = \text{Cr}_4(\text{SO}_4)_4(\text{OH})_4 + 2\text{H}_2\text{SO}_4$. G. S.

Corrosion of Tinned Containers of Preserved Food by Acids and by the Contents. KARL B. LEHMANN (*Arch. Hygiene*, 1907, **63**, 67—122).—In the absence of oxygen, tin is not dissolved by dilute acids to any appreciable extent; solution takes place most rapidly when the tin is partly in the acid and partly in the air. The rapidity with which tin is dissolved in lacquered containers depends on the amount of oxygen in the solution and above it. When oxygen is absent, its place may be taken by nitrates, generally present in well water; the nitrates are reduced to ammonia. The solution of tin on exposure to air, after the container has been opened, is not so rapid as might be expected, owing to the protective action of grease or of sugar. The action of sugar is due to a diminution in the ionisation of (tartaric) acid. The lacquering generally protects well for three to six months.

When iron has been carelessly tinned, much iron, but not more tin, is dissolved.
G. B.

Antimonides of Iron and Cadmium. NICOLAI S. KURNAKOFF and N. S. KONSTANTINOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 227—249*).—The freezing-point curve for the alloys of antimony and iron consists of four branches representing four solid phases, there being eutectic points at 628° and 1·5% iron and 1002° and 49·5% iron respectively, and a transition point at 732° and 7·0% iron. The concentration of solid solutions of antimony in iron never exceeds 5%. At 1014° the compound Sb_2Fe_3 separates, and forms solid solutions in iron up to the composition 46·0% iron. The compound FeSb_2 at its m. p. (732°) decomposes partly, thus: $3\text{FeSb}_2 \rightleftharpoons \text{Fe}_3\text{Sb}_2 + 4\text{Sb}$. In general, the antimonides of the eighth group are somewhat inert chemically, and have a tendency to form unstable compounds. In the case of the antimonides of iron and nickel, the solid substances which have escaped reaction in the liquid state retain their composition when further cooled rapidly; thus, the alloy Sb_2Fe , when cooled at the rate of 1000—300° in one to two hours, shows a microstructure composed of three elements, and only on heating an alloy of this composition for thirty hours at a temperature of 710° could the homogeneous compound Sb_2Fe be obtained. The raw antimony obtained in the commercial extraction of antimony contains Sb_2Fe in well-formed, rhombic crystals. Compounds such as FeSAs belong to the same type, the arsenic and sulphur being united directly with one another, and the structural formulæ thus obtained are in complete accord with those deduced by other methods.

As in the case of zinc and antimony (compare Schemtchuschny, *Abstr.*, 1906, ii, 549), the freezing-point curve for cadmium and antimony takes a different form, according to the conditions of solidification, as for instance, the nature of the substance covering the metals, the stirring of the mass, the presence of corresponding crystals, &c.; the two latter conditions being necessary for the formation of stable compounds at certain concentrations. The curve corresponds with four solid phases: (1) antimony, the eutectic point being at 445° and 58·4% Sb, when crystals of the compound CdSb have been added previously, otherwise this part of the curve extends to 402° and composition 52·5% Sb. (2) The compound CdSb , which separates at 455° from liquid alloys when stirred and cooled quickly. If these alloys are allowed to cool slowly under a layer of carnalite, then the unstable compound Cd_3Sb_2 is formed. (3) The compound Cd_3Sb_2 , which commences to separate at 409°. (4) Free cadmium to the eutectic point 296° and 92·5% cadmium. The alloys containing 42—52·5% antimony, when already solidified, develop heat at 260—290°, the temperature rising suddenly 20° to 30°; this occurs most markedly for alloys containing 50% antimony, and also for those still richer in antimony if crystals are not added previously and the mass is not stirred while cooling, this sudden rise in temperature being due to the compound Cd_3Sb_2 passing into a more unstable form, thus: $\text{Cd}_3\text{Sb}_2 + \text{Sb} = 3\text{CdSb}$. These views are fully confirmed by the micro-

* and *Zeitsch. anorg. Chem.* 1908, 58, 1—22.

structure of the various alloys, photographs of which are given. At concentration 7·5—36% antimony, the compound Cd_3Sb_2 separates whatever the conditions.

The crystalline structure of FeSb_2 and of Cd_3Sb_2 have been studied in detail by Isküll (*Zeitsch. Kryst. Min.*, 1906, 42, 374). Cd_3Sb_2 belongs to the rhombic system [$a:b:c=0\cdot75909:1:0\cdot96872$]. FeSb_2 also belongs to the rhombic system [$a:b:c=0\cdot5490:1:1\cdot1212$, or $0\cdot5490:1:1\cdot1237$] (Wyruboff). Z. K.

Bismuth Subnitrate. EDWARD J. BROWN (*Pharm. J.*, 1908, [iv], 26, 378).—Heavy and light bismuth subnitrates are not chemically identical; the composition of the former corresponds with the formula $\text{BiO}\cdot\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$, and that of the latter with the formula $\text{BiO}\cdot\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$. P. H.

Reduction of Gold Chloride by Charcoal. DAVID AVERY (*J. Soc. Chem. Ind.*, 1908, 27, 255).—Using a very pure charcoal carefully prepared from cocoanut shell, the author has made quantitative estimations of the hydrogen chloride, and also of the carbon dioxide produced in this reaction. The conclusion is drawn that the reduction takes place by the decomposition of the water molecule with formation of the free acid of the salt, and oxidation of the charcoal to carbon dioxide, the reaction being hastened by heating. The equation proposed by König (*Chem. News*, 1882, 45, 215) as representing the change $4\text{AuCl}_3 + 6\text{H}_2\text{O} + 3\text{C} = 4\text{Au} + 12\text{HCl} + 3\text{CO}_2$ is substantiated. Occluded gases, such as hydrogen or carbon monoxide, will also reduce gold, and possibly other metallic salts. J. V. E.

Alloys of Platinum and Tin. N. I. PODKOPEEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 249—260. Compare Doerinelckel, *Abstr.*, 1907, ii, 785).—Platinum and tin react energetically with one another with development of much heat, the temperature of the mass reaching 1340° . The freezing-point curve consists of six branches characterised by six crystalline substances. The first branch represents the separation of tin, and falls to a eutectic point at 224° and 15 atomic % platinum; on further addition of the latter, the curve rises steeply, giving several transition points, corresponding with the compounds Sn_4Pt , 505° , Sn_3Pt_2 , 846° , possibly a polymorphous form of Sn_3Pt_2 , 746° , until it reaches a maximum at 1324° , corresponding with the compound SnPt . It then falls to the eutectic point 1065° and 66·67 at. % platinum, after which it rises to a transition point 1406° , when the compound SnPt_3 separates. None of the compounds form solid solutions in tin or platinum. Photographs of the microstructure of the various alloys are given. Z. K.

Preparation of Chloroplatinic Acid by Electrolysis of Platinum Black. H. C. P. WEBER (*J. Amer. Chem. Soc.*, 1908, 30, 29—31).—The work on the atomic weight of chlorine (Noyes and Weber, this vol., ii, 371) necessitated the preparation of large quantities of chloroplatinic acid free from nitric acid, and the following method was devised for the purpose.

The platinum is obtained in a suitable condition by dissolving spongy

or scrap platinum in nitrohydrochloric acid, removing the excess of acid by neutralisation or evaporation, and reducing the solution with alkali formate or zinc. The precipitated platinum is warmed with a little dilute hydrochloric acid in order to remove iron, and is then transferred to the electrolytic apparatus, where it is washed and afterwards covered with concentrated hydrochloric acid. The electrodes are composed of sheet platinum. The apparatus and method are described with the aid of a diagram. On concentrating the solution of chloroplatinic acid resulting from the electrolysis, a small quantity of chlorine is introduced in order to ensure the absence of platinous compounds. E. G.

Liquid Hydrosol of Palladium Hydride. CARL PAAL and JOSEF GERUM (*Ber.*, 1908, 41, 805—817. Compare Abstr., 1907, ii, 559).—The absorption of hydrogen by solutions of colloidal palladium prepared by the methods described by Paal and Amberger (Abstr., 1904, ii, 180; 1905, ii, 397) has been measured. It is found that, even with the same sample of colloidal palladium, the amount of hydrogen absorbed per unit weight of the metal varies considerably, an explanation of which cannot yet be given. Whereas palladium black was found by Mond, Ramsay, and Shields (Abstr., 1898, ii, 600) to absorb 873 times its own volume of hydrogen, colloidal palladium in solution is found to combine with 926—2952 volumes of hydrogen, after deducting the hydrogen used in combining with the oxygen present in the colloidal palladium and in the solution of the hydrosol. This great absorptivity is undoubtedly due to the very fine state of division and large absorbing surface of the metal. Paal and Amberger have shown (*loc. cit.*) that almost the whole of the hydrogen is liberated when solid palladium hydride hydrosol is heated at about 140° ; when, however, the liquid hydrosol is heated, only part of the hydrogen is evolved. Thus, in one experiment, a solution of colloidal palladium containing 0.0996 gram of the metal absorbed 14.68 c.c. of hydrogen, of which 3.88 c.c. combined with the oxygen present to form water, whilst the rest, 10.8 c.c., combined with the metal, forming the hydride; on heating, only 4.6 c.c. of hydrogen were evolved. Why all the hydrogen is not liberated cannot yet be explained. W. H. G.

Palladium Hydride. CARL PAAL and JOSEF GERUM (*Ber.*, 1908, 41, 818—819. Compare preceding abstract).—Paal and Amberger (Abstr., 1905, ii, 397) found that the hydride of palladium formed by the action of hydrogen on dry palladium black, when heated, liberated 674 vols. of hydrogen per unit volume of metal. The volume of hydrogen absorbed by palladium black suspended in water has been observed, and it is found that 1 vol. of the metal combines with 1204 vols. of hydrogen, or in the atomic proportion $\text{Pd} : \text{H} = 1 : 0.98$. Under these conditions, palladium black absorbs far more hydrogen than has hitherto been recorded. W. H. G.

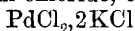
New Stage of Oxidation of Palladium. LOTHAR WÖHLER and FRIEDRICH MARTIN (*Zeitsch. anorg. Chem.*, 1908, 57, 398—413).—Hydrated palladium sesquioxide, $\text{Pd}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, and certain double

chlorides of tervalent palladium have been prepared, and their properties are described.

The sesquioxide is best prepared by electrolytic oxidation of platinous nitrate. A strong solution of the salt is cooled to 8° and electrolysed at a current density of 0.5 amp./cm^2 until the brown precipitate of the sesquioxide has settled out; the latter, after washing with ice-cold water, is quite pure. If the electrolysis is continued, the dioxide is ultimately obtained, most readily in acid solution. This is not a direct oxidation, but the sesquioxide decomposes into dioxide and monoxide, the latter then dissolving in the free acid and undergoing further oxidation. In accordance with this view, the sesquioxide is scarcely acted on when electrolysed in alkaline solution, as the monoxide is insoluble in alkali. The sesquioxide can also be obtained by the action of ozone on a solution of palladous nitrate.

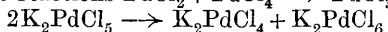
Hydrated palladium dioxide is brown in colour and unstable; both it and the dioxide decompose under an oxygen pressure of 80 atmospheres at the ordinary temperature.

The sesquioxide is easily soluble in hydrochloric acid, but the solution is very unstable. When, however, the sesquioxide is suspended in ether in the presence of rubidium or caesium chloride at the temperature of solid carbon dioxide and ether, and hydrogen chloride is led into the mixture, the double salts, $\text{PdCl}_3 \cdot 2\text{RbCl}$ and $\text{PdCl}_3 \cdot 2\text{CsCl}$, are obtained in small crystals. The rubidium double salt is greyish-green and the caesium salt, dark green. Both decompose in contact with water, and the double palladous salts, M_2PdCl_4 , are readily obtained from the solutions. When potassium chloride was used instead of rubidium or caesium chloride, only the double salts



and $\text{PdCl}_2 \cdot 4\text{KCl}$ could be isolated.

By means of the characteristic properties of the double salts, it has been shown that the trichloride is obtained both when the dichloride is oxidised by means of chlorine and when the tetrachloride is reduced (by alcohol, for example). On the other hand, the trichloride cannot be obtained by reduction of double salts of the type $\text{PdCl}_4 \cdot 2\text{MCl}$. There is therefore a difference in the behaviour of the free chlorides and those forming constituents of double salts in such a way that the free energy in the reactions $\text{PdCl}_2 + \text{PdCl}_4 \rightleftharpoons \text{PdCl}_3$ and



diminishes in the directions indicated by the arrows.

C. S.

Osmium. OSCAR MAKOWKA (*Ber.*, 1908, 41, 943—944).—A complete precipitation of metallic osmium is not effected when acetylene is passed into a dilute aqueous solution of osmium tetroxide (compare Phillips, *Abstr.*, 1894, ii, 367). On the contrary, when acetylene dissolved in acetone is used as the precipitant, a colloidal solution of osmium is obtained, from which the metal separates completely at $100\text{--}110^{\circ}$.

C. S.

Mineralogical Chemistry.

Mineral Chemistry. JOSEF LOCZKA (*Ann. Mus. Nat. Hungarici*, 1907, 5, 433—451).—A review of the position, methods, and aim of mineral chemistry.
L. J. S.

Optical Investigation of Ramanin Naphtha. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 260—276.—Compare this vol., ii, 115).—A review and criticism of previous work on this subject by other investigators is given. The fourteen samples of Ramanin naphtha studied all belong to the category of semi-transparent naphthas, and in many properties resemble the Pennsylvanian naphthas, but they have D 0.854—0.889 instead of below 0.820, and their coefficient of opacity or carbonisation constant varies between $1\frac{1}{2}$ —3%.

When distilled under similar conditions to those used in previous experiments, they behave quite normally, and the highest value for α in a 200 mm. tube that could be obtained is $+5^\circ$, Engler and others obtaining $\alpha + 20^\circ$ and above. The behaviour of the distillates towards trichloroacetic acid shows that decomposition or racemisation does not occur during distillation. The time factors in the formation of various layers of naphtha and the relation these bear to their physical and chemical properties are discussed, the conclusions drawn agreeing with those stated previously. One sample of naphtha was passed through a filter similar to those used for freeing a liquid from bacteria; thus imitating to some extent the presumed natural process, and, although the colour remained unchanged, the density changed from 0.8575 to 0.8404, and the coefficient of opacity from $1\frac{7}{8}$ %— $2\frac{1}{2}$ %.

Z. K.

The Optically Active Constituents of Mineral Oil. JULIUS MARCUSSON (*Chem. Zeit.*, 1908, 32, 377—378, 391).—The author adduces experimental evidence in support of his theory that the optical activity of mineral oils arises from cholesterol, by distilling the unsaponifiable portions of oleins obtained from wool fat and from tallow under pressure at 300—360°; he has by this means obtained a mixture which contains all the characteristic constituents of crude mineral oil, such as optically active naphtha and lubricating oil, paraffin, and asphalt.

Neuberg's view (*Abstr.*, 1906, i, 923; 1907, i, 577, 997), that the activity should be attributed to the decomposition of optically active amino-acids, is rendered improbable by experiments which show that amino-acids, even when mixed with fats or fatty acids of high molecular weight, are so soluble in water that they would most likely have been washed away by the water which was present during their formation in nature. Further, the fatty acids contained in proteins would be more likely to give hydrocarbons of low molecular weight, the activity of which is relatively low, whereas the actually observed increasing

activity with rise of boiling point and the high activity of the lubricating oils is more in agreement with the cholesterol theory. Neuberg's objection that the amount of cholesterol in animals or plants is insufficient to account for the source of the activity is met by the argument that the protein constituents are after death destroyed by putrefaction, whereas cholesterol remains unchanged.

While not entirely disputing Zaloziecki and Klarfeld's view of terpenes or resins as being, in part, responsible for the activity, the author recalls Engler's remark that, whereas terpenes and resins might be expected to yield both dextro- and laevo-rotatory oils, actually dextrorotatory oils are almost exclusively found. P. H.

Fichtelite from Borkovic, Bohemia. FRANZ PLZÁK and V. ROSICKÝ (*Zeitsch. Kryst. Min.*, 1908, 44, 332—343).—Pieces of pine wood from a peat bog at Borkovic are impregnated and encrusted with fichtelite. On the surface and in cavities are colourless to yellow, platy crystals $\frac{3}{4}$ cm. across. By extracting with ether and recrystallising from alcohol, larger (several cm.), colourless, and better crystals were obtained, but these are not so rich in faces as the natural crystals. The crystals are hemimorphic-monoclinic (there being an axis of symmetry, but no plane of symmetry), as is shown by the development of the faces and by etching figures [$a:b:c=1.4330:1:1.7563$; $\beta=126^{\circ}47\frac{1}{4}'$]. The material is very soft ($H<1$); $D\ 1.01$; $m. p. 46^{\circ}$. The mean of several analyses agrees closely with the formula $C_{18}H_{32}$. The molecular weight, determined by the cryoscopic method in benzene, is 254.2 ($C_{18}H_{32}=248.32$). Oxidation with chromic acid in an acetic acid solution yielded two acids, the silver salts of which gave the formulæ $C_{15}H_{20}O_6Ag$ and $C_3H_5O_3Ag$. The ether extract from the fichtelite-bearing wood yielded also an oil which has very nearly the same composition as fichtelite. L. J. S.

Chlormanganokalite, a New Vesuvian Mineral. HENRY J. JOHNSTON-LAVIS and LEONARD J. SPENCER (*Min. Mag.*, 1908, 15, 54—61).—The new mineral chlormanganokalite (*Nature*, 1906, 74, 103; *Abstr.*, 1906, ii, 455) was found as pale yellow, glassy, and highly deliquescent crystals in blocks ejected from Vesuvius during the eruption of April, 1906. A new analysis gave the following results, agreeing approximately with the formula $4KCl, MnCl_2$. The crystals are rhombohedral with $a:c=1.05801$; they are optically uniaxial and positive, with a refractive index of 1.59 and very low double refraction:

K.	Mn.	Cl.	Mg.	Na.	SO ₄ .	H ₂ O.	Insol.	Total.
36.34	11.52	48.13	0.04	0.38	0.81	1.52	0.71	99.45

The supposed new mineral chlornatrokalite (*Nature*, 1906, 74, 174), found associated with chlormanganokalite, is proved to consist of a mixture of halite and sylvite, which as large, well-formed cubic crystals are intimately grown together. Scalenohedral crystals of hæmatite also occur in the same ejected blocks; these on analysis gave 94.79% Fe_2O_3 , the remainder consisting mainly of insoluble rock-fragments. L. J. S.

Covellite and Enargite from Servia. S. STEVANOVIĆ (*Zeitsch. Kryst. Min.*, 1908, **44**, 349—354).—A recently discovered deposit of copper ore at Bor, in eastern Servia, consists of cupriferous iron-pyrites with a little copper-glance and covellite. The latter has the form of thin, flexible, six-sided plates of a blue colour and up to 6 mm. across. The angles and twinning of these plates prove that covellite is not hexagonal, but probably monoclinic (possibly triclinic). The apparent basal cleavage of the mineral is due to the separation of the plates along the planes of twinning. Analysis I agrees with the usual formula CuS:

	S.	Cu.	Fe.	As.	Sb.	Total.	Sp. gr.
I.	33·45	65·49	0·25	—	—	99·19	4·668
II.	33·23	49·00	—	15·88	1·54	99·65	—

Associated with the covellite are crystals of enargite (anal. II), in which some of the arsenic is replaced by antimony. L. J. S.

[**Synthesis of Huantajayite and Covellite: Recent Formation of Pyrrhotite: Blue Rock-salt.**] FELIX CORNU (*Jahrb. Min.*, 1908, ii, 22—57).—*Synthesis of Huantajayite.*—The natural mineral from Chile consists of minute, cubic crystals of sodium and silver chlorides with 3—11% AgCl. Mixed crystals containing 92·21—94·01% AgCl have been prepared by Gossner. When an ammoniacal solution of sodium and silver chlorides was evaporated, cubic crystals with 2·39% AgCl were obtained; these are strongly birefringent, and show a division into six sectors. At the same time, crystals of sodium chloride (with the same optical anomalies) and of silver chloride were obtained, and sometimes these are grouped together in parallel position. Mixed crystals of sodium and silver chlorides were prepared by fusion.

Synthesis of Covellite.—When yellow ammonium sulphide is poured on powdered malachite, the latter is blackened, and there is a development of heat. On allowing this mixture to remain for several weeks at the ordinary temperature, the malachite is wholly converted into a bluish-black powder, consisting of cupric sulphide. This, like the natural earthy covellite, is readily oxidised in the presence of water to copper sulphate.

Recent Formation of Pyrrhotite.—A bar of iron which had lain for three years in a heap of burning refuse from a coal mine in Bohemia was coated with a radiating platy layer of pyrrhotite 1·5 cm. in thickness.

Blue Rock-salt.—A detailed account is given of the literature bearing on the blue coloration of halite and sylvite. In the Austrian salt deposits, the blue and purple rock-salt is of earlier formation than that which is colourless. The colour disappears when the mineral is heated. Similar colours may be produced artificially by heating colourless rock-salt or sylvite in the vapour of an alkali metal, the resulting colour being the same, for the same salt, whatever the vapour (sodium, lithium, &c.). The naturally blue rock-salt has an alkaline reaction, and when it is dissolved in water there is an evolution of gas. Both the naturally and the artificially coloured

mineral becomes pleochroic when subjected to pressure in one direction. L. J. S.

A Remarkable Iron Ore from Bohemia. RICHARD BECK and THEODOR DÖRING (*Tsch. Min. Mitt.*, 1908, 26, 481—486).—A large block with somewhat the appearance of a mass of meteoric iron was found in a basalt quarry at Rudelsdorf, near Brüx. The material is iron-black with a sub-metallic lustre and a red streak; it has a fine-grained, crystalline structure with some lamellæ. Analysis indicates that the material is a mixture of magnetite and magnesioferrite (MgFe_2O_4) with a little hæmatite. L. J. S.

Hopeite and Other Zinc Phosphates from Rhodesia. LEONARD J. SPENCER (*Min. Mag.*, 1908, 15, 1—38).—A description is given of fifteen mineral species found in the new lead and zinc mines at Broken Hill, in North-Western Rhodesia. In addition to hopeite, two new zinc phosphates, parahopeite and tarbuttite, are described. The brilliant, water-clear crystals of hopeite occur in abundance associated with vanadinite on a bone-breccia in a cavern in the zinc and lead ore (consisting of a mixture of hemimorphite, cerussite, and limonite). They are orthorhombic [$a:b:c=0.5786:1:0.4758$], and consist of an intimate interlamination of two modifications of hopeite (α -hopeite and β -hopeite), which differ in their optical characters, specific gravity, and the rate at which water is lost with increasing temperature. Analysis I and II of α -hopeite and β -hopeite respectively agree with the formula $\text{Zn}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ previously deduced for artificial crystals:

	P_2O_5 .	ZnO .	H_2O .	Total.	Sp. gr.	Hardness.	Optical sign.
I.	31.8	52.1	16.1	100.0	3.04	$3\frac{1}{2}$	—
II.	[31.9]	51.9	16.2	100.0	3.03	$3\frac{1}{4}$	—
III.	31.6	53.0	15.6	100.2	3.31	$3\frac{3}{4}$	+
IV.	29.2	66.6	3.8	100.6	4.12	$3\frac{3}{4}$	—

Parahopeite occurs on tarbuttite as colourless, platy, anorthic crystals with a perfect cleavage in one direction. It is harder and denser than hopeite, but has the same composition (anal. III). No water is lost at 139° , whilst from hopeite 9.2% is expelled at this temperature.

Tarbuttite is of abundant occurrence, together with crystals of pyromorphite and desclowitzite, on cellular limonite. The crystals are anorthic with a perfect cleavage in one direction, and vary considerably in habit and appearance; they are colourless or pale shades of yellow, red, or green. It is a basic zinc phosphate, $\text{Zn}_3\text{P}_2\text{O}_8 \cdot \text{Zn}(\text{OH})_2$ (anal. IV), corresponding with, although not isomorphous with, the orthorhombic adamite [$\text{Zn}_3\text{As}_2\text{O}_8 \cdot \text{Zn}(\text{OH})_2$]. The water is lost only at a red heat. Pseudomorphs of tarbuttite after calamine (ZnCO_3) and desclowitzite are described.

The material of the bones in the cavern is partly replaced by zinc and lead minerals, namely, hemimorphite, tarbuttite, hopeite, and vanadinite. L. J. S.

Phosphate Minerals from Elder Rock, South Australia. DOUGLAS MAWSON and W. T. COOKE (*Trans. Roy. Soc. South Australia*, 1907, 31, 65—70).—A hard, yellow phosphate occurs on an isolated

rock which stands up in the flat, arid district near Paratoo railway siding in South Australia. It probably represents the remains of a deposit of bird-guano from which the soluble constituents have been leached out; the latter are represented by ammonium nitrate and soluble phosphates, which penetrate the rock to a considerable depth. Two types of material are distinguished: the more abundant forms yellow, encrusting masses and is optically isotropic (anal. I, after deducting 17·30% of admixed sand), and the other consists of an aggregation of small globules, which are yellowish-brown and birefringent (anal. II, after deducting 36·72% of sand). The first approximates in composition to evansite, and the second to beraunite. The new name *paratooite* is applied to these materials, although they are clearly not simple minerals:

	P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O (at 120°).	H ₂ O (ignition).	Alkalis, &c.	Total.
I.	42·59	20·70	8·20	2·49	11·11	20·49	3·20	[1·22]	100·00
II.	27·53	11·19	38·43	3·68	—	16·41	2·76	—	100·00

L. J. S.

Strüverite and its Relation to Ilmenorutile. GEORGE T. PRIOR and FERRUCCIO ZAMBONINI (*Min. Mag.*, 1908, 15, 78—89).—Details of the chemical analysis of the new mineral strüverite (Abstr., 1907, ii, 364) are now given. The zircona which the mineral was at first supposed to contain has been found on further examination to consist of columbic and tantalic acids. When a mixture of columbic and tantalic acids with titanic acid (that is, a mixture of columbite, tantalite, and rutile) is fused with potassium hydrogen sulphate and the fused mass treated with cold water, a considerable amount of the columbic and tantalic acids passes into solution, whilst with a 5% solution of sulphuric acid (as is necessary when the titanium is to be estimated colorimetrically with hydrogen peroxide) practically the whole passes into solution. The experiments suggest that columbium, tantalum, and titanium readily form complex combinations, which render their analytical separation a matter of some difficulty. The final results of the analysis of strüverite are given under I, corresponding with the formula $3\text{Fe}(\text{Ta,Cb})_2\text{O}_6, 10\text{TiO}_2$ or, approximately, $\text{FeO}, (\text{Ta,Cb})_2\text{O}_5, 4\text{TiO}_2$:

	TiO ₂ .	Cb ₂ O ₅ .	Ta ₂ O ₅ .	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
I.	41·20	23·48	23·48	11·38	trace	0·51	0·17	100·22	5·59
II.	53·04	21·73	14·70	10·56	—	trace	—	100·03	5·14
III.	54·57	32·15	—	12·29	—	0·11	trace	99·12	4·64

Crystallographically, strüverite is very similar to ilmenorutile (Abstr., 1907, ii, 884), but the published analyses of the latter show no close relationship to the analysis of strüverite. It was therefore thought that, if in the earlier analyses of ilmenorutile the titanic acid had been determined gravimetrically, the amounts given for this would be too high. The titanium was therefore estimated colorimetrically in the ilmenorutile from the Ilmen Mountains, in Russia, and from Evje, in Norway (Abstr., 1907, ii, 885), and found to amount to only 53·04% and 54·50%, instead of 66·90% and 73·78%, respectively; this

would increase correspondingly the amounts of the columbic and tantallic acids given in the old analyses. New analyses of ilmenorutile from the Ilmen Mountains and from Iveland, in Norway, are given under II and III respectively; these correspond approximately with the formula $\text{FeO}, \text{Cb}_2\text{O}_5, 5\text{TiO}_2$, with possibly some admixture of FeTiO_3 or FeTi_2O_5 .

Strüverite and ilmenorutile are very similar in crystalline form to rutile, tapiolite, and mossaite, and their composition is best expressed as solid solutions of the rutile (TiO, TiO_3) and tapiolite or mossaite ($\text{Fe}[(\text{Ta}, \text{Cb})\text{O}_3]_2$) molecules. The name strüverite is reserved for those members of the series which are rich in tantallic acid, and ilmenorutile for those in which columbic acid predominates, the two minerals being related to one another as tapiolite is to mossaite, and as blomstrandine to priorite (Abstr., 1907, ii, 885).

L. J. S.

Chemical Constitution of a Specimen of Aeschynite. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Petersburg*, 1908, 4, 389—395. Compare Rammelsberg, Trans., 1872, 203; Abstr., 1878, 944; Hidden, Abstr., 1881, 1110; Prior, Abstr., 1899, ii, 433).—The aeschynite examined came from Hitterö, and consisted of imperfectly formed prismatic crystals, mostly surrounded by felspar; in one case, however, the latter was found within a mass of aeschynite. The sample differed in some respects from the aeschynites described hitherto. Its constitution may be expressed by the formula: $2[2\text{Ce}_2\text{O}_3, 3\text{TiO}_2], 4(\text{ThO}_2, \text{TiO}_2), \text{Y}_2(\text{CbO}_3)_6, 3(\text{CaO}, \text{TiO}_2), 3(\text{FeCb}_2\text{O}_6), \text{FeTa}_2\text{O}_6, 6\text{TiO}_2$, which agrees well with the analyses made by the author and others.

The columbic acid, after having been most carefully purified, and in which it was impossible to detect any trace of titanic or tantallic acid, gives reactions differing somewhat from those of the pure acids, and resembling to some extent those described by Hermann. None of these reactions are given by the purified metallic acids isolated from other minerals obtained specially for purposes of comparison. The conclusion is therefore drawn that the columbic acid obtained from aeschynite contains some hitherto unknown substance, which could not be isolated owing to the extremely small quantity present. Z. K.

Reyerite from Greenland. O. B. BOEGGILD (*Meddelelser om Grönland*, 1908, 34, 93—114).—Under the name of gyrolite, a description is given of a scaly zeolite from Niakornat, in Greenland, but in a postscript it is recognised that the material described is identical with the reyerite of F. Cornu (Abstr., 1907, ii, 483). The crystals have the form of thin, six-sided plates with a perfect basal cleavage and pearly lustre; they are rhombohedral, with $a:c = 1:1.936$, and the etched figures on the base indicate that the symmetry is trapezohedral. The refractive indices are $\omega = 1.5645$ and $\epsilon = 1.5590$. Analysis by C. Christensen gave:

SiO_2 .	Al_2O_3 .	CaO .	Na_2O .	H_2O .	Total.	Sp. gr.
54.83	4.58	31.15	1.74	8.14	100.44	2.578

This gives the formula $2\text{CaO}, 3\text{SiO}_2, 1\frac{1}{2}\text{H}_2\text{O}$, a part of the calcium

being replaced by aluminium and sodium, or, as one-third of the water is lost at 100°, $\text{H}_2\text{Ca}_2(\text{SiO}_3)_{3\frac{1}{2}}\text{H}_2\text{O}$.

The micaceous zeolites from eight other localities in Greenland are briefly described; these have D 2·383—2·446, and are therefore to be referred to gyrolite.

L. J. S.

Artificial Production of Isomorphous Silicate Mixtures. VIKTOR PÖSCHL (*Tsch. Min. Mitt.*, 1908, 26, 413—456).—The materials employed (hedenbergite, chalybite, magnesia, calcium carbonate, and silica) were fused together in different proportions in a crucible, and the molten mass allowed to cool very slowly. Thin sections were cut from the central position of the mass, and the maximum angle ($c:c$) of optic extinction determined. Plotting the following results obtained for the diopside ($\text{CaMgSi}_2\text{O}_6$) and hedenbergite ($\text{CaFeSi}_2\text{O}_6$) series, it is seen that the physical characters (except sp. gr.) vary continuously with the composition, although the curve is not a straight line. The fall in the sp. gr. suggests that a labile modification of diopside with D 2·8 may be present in the isomorphous mixtures:

Diopside ...	100	90	80	70	60	50	40	30	0
Hedenbergite	0	10	20	30	40	50	60	70	100
Sp. gr.	3·08	2·87	2·90	2·96	2·98	3·01	3·16	3·26	3·53
M. p. *	1325°	1265°	1250°	1240°	1230°	1225°	1210°	1200°	1140°
$c:c$	32°	36°	38°	43°40'	45°50'	47°	49°20'	50°	50°30'
FeO%	0	2·40	5·00	7·03	9·98	12·57	14·87	17·07	25·00

* The higher limits only of the melting-point intervals are here quoted: for diopside, m. p. = 1300—1325°.

Enstatite (MgSiO_3) and diopside form an isodimorphous series similar to that given by magnesium sulphate and ferrous sulphate, the results falling on two parallel curves:

Diopside	100	75	60	50	40	25	0
Enstatite	0	25	40	50	60	75	100
Sp. gr.	3·08	3·04	3·25	2·98	3·05	3·12	3·2 ?
M. p.	1325°	1320°	1315°	1320°	1325°	1350°	1400°
$c:c$	32°	37°	39°	0°	0°	0°	0°

Somewhat similar results were obtained in the olivine group. Isomorphous mixtures of magnesium and iron orthosilicates are formed, but between $66\text{Mg}_2\text{SiO}_4 : 34\text{Fe}_2\text{SiO}_4$ and $3\text{Mg}_2\text{SiO}_4 : 97\text{FeSiO}_4$ there is a gap in the series. Forsterite and monticellite (Mg_2SiO_4 and Ca_2SiO_4) form an isodimorphous group of mixed crystals. Mixtures of magnesium, calcium, and iron orthosilicates were also investigated.

L. J. S.

Pilolite from the Pyrenees. GEORGES FRIEDEL (*Bull. Soc. franç. Min.*, 1907, 30, 80—83).—A white, finely-fibrous and finely-felted material occurs at the side of a vein of blende in limestone at Can Pey, near Arles-sur-Tech, Pyrénées-Orientales. Analysis gave the following results (a few grains of quartz are mixed with the fibres), agreeing approximately with the formula $5\text{SiO}_2, \text{Al}_2\text{O}_3, \text{MgO}, 3\frac{1}{2}\text{H}_2\text{O}$:

SiO_2 .	Al_2O_3 .	MgO.	CaO.	Fe_2O_3 .	Total.	H_2O at 100° ignition.	H_2O
70·28	21·64	7·56	0·24	0·38	100·10	9·96	23·66

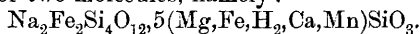
The characters and composition of this material are the same as those of "lassallite," recently described by the same author as a new mineral (Abstr., 1901, ii, 397), and it is now recognised that this is identical with Heddle's pilolite.

L. J. S.

Rhodusite from Asskys River, Siberia. WOLD. ISKÜLL (*Zeitsch. Kryst. Min.*, 1908, 44, 370—389).—A dark blue or greyish-blue fibrous mineral from the neighbourhood of the Asskys river, in the Minussinsk district, Government Yeniseisk, gave the following analyses (made on three different specimens). The material is referred to rhodusite (Abstr., 1894, ii, 461), and may be considered as a variety of glaucophane, in which the alumina is nearly all replaced by ferric oxide. It is probably identical with the mineral from the same locality recently referred to crocidolite by P. Tschirwinsky (Abstr., 1907, ii, 705):

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
54·01	trace	0·23	15·70	9·42	0·14	1·52	10·01	6·22	0·35	2·25	99·85
54·38	trace	0·28	15·12	9·21	0·11	1·23	10·54	6·86	0·31	2·16	100·20
55·06	trace	0·18	14·54	7·17	0·09	1·17	12·30	6·52	0·23	2·44	99·69

The fibres are optically negative, with a maximum extinction of 2—3°; the pleochroism is strong; D 3·12. Most of the water is expelled only above 350°. The analyses do not seem to support the amphibole formula recently proposed by Penfield and Stanley (Abstr., 1907, ii, 102). The composition is expressed as an isomorphous mixture of two molecules, namely:



Digestion with a 10% hydrochloric acid solution partly dissolves the mineral, the first of these molecules being dissolved slightly more readily than the second.

L. J. S.

Jerseyite. E. GOLDSMITH (*Chem. Zentr.*, 1908, i, 291—292; from *J. Franklin Inst.*, 1907, 164, 369—373).—The percentage composition of this supposed meteorite is found to be:

SiO ₂ .	TiO ₂ .	SnO ₂ .	Bi ₂ O ₃ .	CuO.	NiO.	Fe.	Al ₂ O ₃ .
42·80	1·90	0·49	0·22	0·26	2·00	44·36	4·18
		CaO.	K ₂ O.	Na ₂ O.	C.	S.	P.
		trace	0·92	0·80	1·84	0·34	0·12

The hardness is 6; D 3·636; and colour nearly black, but polished surface, greyish-white; it shows the Wittmanstedtian figures.

J. V. E.

Physico-chemical Investigation of the Springs of Fiuggi, near Anticoli. RAFFAELLO NASINI and MARIO G. LEVI (*Gazzetta*, 1908, 38, i, 190—216. Compare Abstr., 1906, ii, 324).—The authors discuss the therapeutic value of the waters of Fiuggi in relation to their high radioactivity, their low electrical conductivity, and their rapid catalysis of hydrogen peroxide. The rocks in the neighbourhood of the springs are all radioactive, this being more especially the case with the volcanic tufa present.

T. H. P.

Physiological Chemistry.

Resistance of Lack of Oxygen. WALES H. PACKARD (*Amer. J. Physiol.*, 1908, 21, 310—333).—Further experiments on the minnow (*Fundulus heteroclitus*) show that mannose injected intraperitoneally increases its resistance to lack of oxygen. As is the case with other sugars previously used (maltose, dextrose, lævulose), it probably acts as a depolariser in the processes of protoplasmic respiration. Galactose is apparently not absorbed from the body cavity. Alcohol and acetone are very toxic, especially the latter. They and pilocarpine decrease resistance to lack of oxygen.

W. D. H.

Distribution of the Salts in Hæmolysins. ALBERT WOELFEL (*Bio-Chem. J.*, 1908, 3, 146—154).—Stewart considered that the increased conductivity of blood after laking is not altogether due to a surrender of electrolytes by the corpuscles to the fluid, but rather that some alteration in the corpuscles, which allows ions to pass through them more freely, is caused by the laking process. Determinations of the ash in various circumstances do not yield results which are easy to interpret. On the whole, however, Stewart's view is confirmed; in formaldehyde-hardened corpuscles, which can be laked by saponin, there is no passage of electrolytes from them into the surrounding fluid, but there is nevertheless a rise of conductivity.

W. D. H.

Hæmagglutination and its Physical Basis. LUDWIG HIRSCHFELD (*Arch. Hygiene*, 1907, 63, 237—286).—The agglutination effect depends additively on the agglutinating power of the serum and on the agglutinability of the corpuscles, so that, when blood from a number of species is treated with any given serum, the order of susceptibility arrived at is maintained when these various kinds of blood are treated with any other serum. When treated with abrin, the same order is found to exist.

The differences in the agglutinability of blood corpuscles do not appear on the agglutination by colloids and salts of tervalent metals. Among the ions of bivalent metals, the less electro-positive have the greater agglutinating effect. In the case of zinc salts, the order of agglutinability of the different kinds of blood examined is the same as with sera and with abrin, but with less electro-positive metals there is no such agreement.

Agglutinability is regarded as depending on the intensities with which the electric charges are held by the colloidal corpuscles and the colloidal agglutinant substance. On this hypothesis, and with the help of Abegg and Bodländer's theory, some of the above conclusions can be arrived at theoretically.

G. B.

Hæmosozic Value of Blood-serum. D. McCAY (*Bio-Chem. J.*, 1908, 3, 97—118).—The term hæmosozic value indicates the constituents present which preserve the red corpuscles from solution. Expressed in terms of sodium chloride, it corresponds with the total salt concentration. An increase in hæmosozic value may be due to increase of salt, or due also to the presence of an anti-hæmolysin. The lowering of the hæmosozic power by the administration of certain drugs (sulphates, potassium salts, &c.) is an important factor in precipitating an attack of blackwater fever, and a rational indication for the prophylaxis and treatment of that disease is the raising of the hæmosozic power by the administration of such chlorides as those of quinine and sodium. W. D. H.

Dextrose in Cat's Saliva. ANTON J. CARLSON and J. G. RYAN (*Amer. J. Physiol.*, 1908, 21, 301—309).—Dextrose is absent from human saliva, and even in cases of diabetes the amount present is insignificant. But in the cat it is constantly present, especially in submaxillary saliva. Variations are noted for which no adequate explanation is forthcoming, but as a general rule the amount rises with an increase of dextrose in the blood. The sugar excreted is therefore in all probability not a specific product of glandular activity, but is simply passed out from the blood. W. D. H.

Investigation of Diastases. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1908, 9, 10—43).—The author's method (this vol., ii, 443) was employed in the study of diastatic ferments, and the following conclusions are drawn. The amount of ptyalin in human saliva varies very considerably, being as a rule more abundant after taking food; but this is not always so, and the kind of food taken makes no difference. Pure gastric juice of man and dog contains no diastatic ferment, but neutralised gastric juice accelerates salivary action, owing to the sodium chloride present. This action is very considerable, and it may increase the activity of ptyalin ten- or even twenty-five-fold; it is due to the chlorine ion. Other salts containing chlorine ions act similarly. The bromine ion acts in the same way; iodine is less efficacious, and fluorine prevents the action. Alkalis (except sodium carbonate) inhibit the action. Sodium phosphate, oxalate, and acetate inhibit, and sodium nitrate, nitrite and chlorate hasten, the action; sodium sulphate is indifferent. Alanine and leucine inhibit; glycine has no effect. Intestinal juice hastens the action, owing to the salts it contains. Colloidal metals (gold, silver, copper, iron), in sufficient concentration, inhibit.

The diastatic ferment of the pancreas behaves exactly like ptyalin.

The diastatic ferment of blood-serum varies very considerably in the amount in which it is present, and behaves exactly as the other two do. The diastatic action of the liver is also due to a ferment, and does not depend on the activity of the living cells. The human placenta is permeable to diastatic ferments. W. D. H.

Chemical Composition of Gastric Juice in Children. PAUL SOMMERFELD (*Biochem. Zeitsch.*, 1908, 9, 352—356).—The composition of the gastric juice produced by "mock feeding" of a child with œsophageal

and gastric fistulæ was determined. Food, varied both in quantity and character, was given, and varying quantities of juice obtained. Twenty-five experiments were carried out, and the average amount of hydrochloric acid in the juice was found to be 0.4026%. The freezing point was also determined, and the average for Δ was -0.488° .

S. B. S.

Action of Alkalis in the Protein-ferment of the Gastric Juice.

N. P. TICHOMIROFF (*Zeitsch. physiol. Chem.*, 1908, 55, 107—139).—The addition of alkali lessens and destroys to the same degree the two functions of the protein-ferment of gastric juice, namely, those relating to the milk coagulation and protein hydrolysis. By again adding acid, it is possible to make the ferment once more active to a certain extent, especially if the neutralisation by alkali has not been absolute.

W. D. H.

Action of the Enzymes of Gastric and Pancreatic Juices on Vegetable Proteins. II. ALBERT STUTZER and E. MERRES (*Biochem. Zeitsch.*, 1908, 9, 244—254).—Sheep received different fodders of known nitrogenous content, and the fæces were collected quantitatively and portions subjected to the following treatments. (i) Peptic digestion in acid solution; (ii) peptic digestion followed by tryptic digestion in 0.08% sodium carbonate solution, and (iii) peptic digestion followed by tryptic digestion in 0.20% carbonate solution. In each case, the nitrogen of the undigested protein was estimated. The results were calculated in terms of the percentage of nitrogen in the original fodder. The latter was submitted directly to the same treatments as the fæces. It was found that the percentage of undigested protein after digestion of the fæces with pepsin was nearly the same as that after directly submitting the fodder to the same treatment. A like concordance was not observed when fæces and fodder were subjected to a subsequent tryptic digestion. The action of the gastric juice affords therefore the best measure of the digestibility of a given fodder.

S. B. S.

The Effect of Alcohol on Digestion. ZITOWITSCH (*Bied. Zentr.*, 1908, 37, 287; from *Mitt. Militär. med. akad. Petersburg*).—In the dog, alcohol increases the secretion of the gastric juice, and is useful in cases of abnormal secretion, but not where secretion is normal. It continues for several days to affect the digestive processes; at first it depresses the secretion, but afterwards increases it, so that the total digestion period is prolonged. Besides increasing the amount of gastric juice, it increases the acidity and the amount of enzymes, but it decreases the activity of the juice; 1 to 2% of alcohol does not affect the enzyme action of the gastric juice.

E. J. R.

The Action of Alcohol on the Heat Relationships of the Animal Organisms. ERICH HARNACK and I. LAIBLE (*Bied. Zentr.*, 1908, 37, 287; from *Arch. internat. Pharmacodyn.*, 15—71).—Experiments on rabbits made in Harnack's calorimeter showed that small or medium doses of alcohol caused at first a fall in the total heat production and a small lowering of the body temperature. The

combustion of the alcohol in the body supplies some heat; hence during the hours in which the alcohol is acting there is a not inconsiderable sparing of combustible material. It is claimed that this action may often render alcohol useful to man. E. J. R.

Digestive Gland of the Crawfish. HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxxvi—xxxvii; *J. Biol. Chem.*, 4).—Extracts of the digestive gland of the crawfish, *Cambarus*, contain trypsin, erepsin, amyllopsin, steapsin, invertase, maltase, tyrosinase, but not pepsin, lactase, citase, or chitinase. It curdles milk. The green colour of the gland is due to biliverdin, even although hæmoglobin is absent both from blood and muscle. W. D. H.

Phosphorus Metabolism in Man. HENRY C. SHERMAN (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xli—xlii; *J. Biol. Chem.*, 4).—The data given indicate that the average amount required for the maintenance of phosphorus equilibrium in a full diet is 1.5 grams of phosphorus or 3.5 grams of phosphoric acid a day. In determining the output, both urine and fæces must be examined. W. D. H.

Effect of Castration on Metabolism. FRANCIS H. MCCRUDDEN (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xl—xli; *J. Biol. Chem.*, 4).—Castration of male and female dogs causes a greatly increased catabolism of nitrogen, sulphur, phosphorus, and magnesium. There was no effect on the metabolism of calcium. W. D. H.

Mineral Metabolism in Healthy and Rachitic Children. WALTER CRONHEIM and ERICH MÜLLER (*Biochem. Zeitsch.*, 1908, 9, 76—126).—So far as nitrogenous, fatty, and calcium metabolism are concerned, sterilised milk is not inferior to raw milk as a food. The unfavourable effect of sterilised milk is due to circumstances which it is at present impossible to specify. No difference in metabolic exchanges was noted in children suffering from rickets and in healthy children. This may have been due to the fact that convalescence had set in, or, perhaps, the slow development of the infant renders conclusions difficult where experiments are confined to short periods of time, whereas in the offspring of animals, in which development is more rapid, this disadvantage is not apparent. W. D. H.

Calcium Foods in Growing Animals. HANS ARON and KARL FRESE (*Biochem. Zeitsch.*, 1908, 9, 185—207).—Three series of metabolism experiments on growing dogs are given with full details; they led to the following conclusions: (1) that these animals are as well able to supply their need for calcium from the inorganic tricalcium phosphate, which is very slightly soluble, as from the calcium contained in milk; (2) sterilisation of milk makes no difference to its value as a supply of calcium to the body, and (3) the amount of calcium absorbed, whether in milk or inorganic salts, is very great, certainly over 80% of that administered. W. D. H.

Changes in Metabolism Due to the Action of Strontium. GIOVANNI BURGASSI (*Chem. Zentr.*, 1908, i, 145; from *Arch. Farm. sperim.*, 1907, 6, 551—568).—Strontium chloride is slightly toxic to

rabbits, much less so than barium chloride. It increases metabolism, so that the urine contains more nitrogen, sulphur, and phosphorus, and it renders intra-organic oxidation more energetic. G. B.

Action of Phosphorus on the Circulation of Calcium in Normal and Rachitic Children. MARIO FLAMINI (*Chem. Zentr.*, 1908, i, 659; from *Arch. Farm. speriment.*, 1907, 6, 653—663).—The administration of phosphorus increases the uptake of the calcium of milk by the tissues (bone and nervous tissues); this is especially marked if the children are rachitic. W. D. H.

Utilisation of Sugars by the Tissues. HUGH MCGUIGAN (*Amer. J. Physiol.*, 1908, 21, 334—350).—The living muscles of an animal when perfused with solutions of dextrose, laevulose, or galactose cause rapid oxidation of the sugars. This increases when the amount of sugar is increased, or the muscles are made to contract. It ceases when the muscles die. Little or no maltose is oxidised similarly. The perfused liver also utilises the common sugars, and probably other glandular organs act in the same way. The glycogen-storing action of the liver is lost in perfusion much sooner than the sugar-destroying function. The same holds for the muscles. The glycolysis occurring in drawn blood at 40° in two hours is very slight. W. D. H.

Glycolysis. HUGH MCGUIGAN (*Amer. J. Physiol.*, 1908, 21, 351—358).—Mixtures of muscle and pancreatic extracts are as inert in glycolysis as is the muscle extract alone. W. D. H.

Cerebro-spinal Fluid. ANASTAZY LANDAU and MIECZYSLAW HALPERN (*Biochem. Zeitsch.*, 1908, 9, 72—75).—Analyses of nitrogen and sodium chloride in various diseased cerebro-spinal fluids are given; the differences in twenty-two cases of the former substance are not very great (0.03—0.08%), and the difference in sodium chloride are still less (0.51—0.67%). A rise in one substance is usually accompanied with a fall in the other. In meningitis there is less sodium chloride than in the other diseases examined. W. D. H.

The Egg-cases of Sharks. LOUIS HUSSAKOF and WILLIAM H. WELKER (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xliv—xlv.; *J. Biol. Chem.*, 4)—The egg-cases of the skate (*Raja crinacea*) and the Port Jackson shark (*Heterodontus japonicus*) are mainly composed of a substance which resembles keratin, but is somewhat more soluble. The pigment is indiffusible, and was obtained in the form of reddish-black scales on desiccation; these are soluble in water; acid changes the colour to straw-yellow, and alkali to a dark brown. W. D. H.

Decomposition of Fat by Lung-tissue. NADINE SIEBER (*Zeitsch. physiol. Chem.*, 1908, 55, 177—206).—The lung-tissue is able to liberate fatty acids from natural and artificial fats, and the activity may be estimated by the acidity produced. This is believed to be due to complex intracellular processes, but it is lessened if previously the lung has been

washed free from blood. The activity of the same lung towards different fats varies; variations are also observed according to the animal employed. The results are given in tables. W. D. H.

Changes in the Nitrogenous Constituents of the Liver when the Kidneys are placed out of Action. G. OLIVI (*Chem. Zentr.*, 1908, i, 55; from *Arch. Farm. speriment.*, 1907, 6, 521—529).—In rabbits, the changed metabolism increases in the liver the amount of nitrogenous constituents precipitable by phosphotungstic acid.

G. B.

Post-mortem Autolysis. HOLMES C. JACKSON (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxxvii—xxxix; *J. Biol. Chem.*, 4).—Experiments on the liver show that toluene in amounts usually employed for antiseptic purposes lessens autolysis. Autolysis is greatest if the animals were well fed previously; the presence of blood in the organ makes no difference; light and darkness have no effect. The presence of disodium hydrogen phosphate or sodium dihydrogen phosphate has also no effect on the rapidity of autolysis. The latent period of two to four hours observed to occur in well fed animals by Claypon and Schryver before autolysis began was not observed. If there was any delay, it occurred in badly-nourished animals. W. D. H.

Percentage of Iron in Fats, Lipoids, and Waxes. W. GLIKIN (*Ber.*, 1908, 41, 910—915).—Nasse originally showed that iron compounds occurred in the spleen and red bone marrow of sucking animals, and it was concluded that they were iron proteins. That this is not so is shown by the fact that these iron compounds are contained in the ether extract of fats. A higher percentage of iron in bone marrow is found in young animals than in the old; thus, in a newly born pig, 1.15%, one six weeks old, 0.30%, eight weeks, 0.15%, and in old pigs, 0.03%. The decrease in the percentage of iron is almost in the same proportion as the lecithin (compare this vol., ii, 120; *Abstr.*, 1907, ii, 566).

Iron is found in all fats from organs or tissues, in plant fats, like cacao butter, and in oils, and in waxes, such as beeswax and Japanese wax.

Iron has been found in all the specimens of cholesterol and lecithin examined, and cannot be removed from the fat by dilute hydrochloric acid. W. R.

Isolation of Carnaubic Acid from Ox-kidney. EDWARD K. DUNHAM (*J. Biol. Chem.*, 1908, 4, 297—300).—Carnaubic acid from the kidney of the ox was identified by examination of the free acid (m. p. 72.5°) and analysis of its silver salt and ethyl ester. The cerebronic acid obtained by Thierfelder (*Abstr.*, 1905, i, 621) is not identical with carnaubic acid, but it is of interest that such high fatty acids should be constituents of lipoids from both brain and kidney. W. D. H.

The Antagonistic Action of Adrenaline and Choline in the Suprarenal Glands. ALFRED LOHMANN (*Pflüger's Archiv*, 1908, 122, 203—209).—That the adrenaline and choline of the suprarenal

gland are antagonistic is true, not only for blood pressure, but also for cardiac activity and intestinal peristalsis. The diabetes which adrenaline produces is not, however, prevented by choline.

W. D. H.

Extra-intestinal Origin of Hydrobilirubin. A. E. AUSTIN and MABEL D. ORDWAY (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxxii—xxxiii; *J. Biol. Chem.*, 4).—Stercobilin and urobilin are regarded as identical; apparently hydrobilirubin is regarded as the same substance, although it is not explicitly stated so in the paper. Urobilin normally originates from bilirubin by reduction and hydration in the intestine through bacterial action. The facts of disease show that, in the absence of bile in the intestine, urobilin may originate extra-intestinally by the action of the tissues and blood on bilirubin. Attempts to effect the change *in vitro*, however, failed. W. D. H.

Alleged Formation of Bile Pigments and Bile Acids by the Action of Trypsin on Hæmoglobin. FREDERICK S. HOLLIS (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxxiii—xxxv; *J. Biol. Chem.*, 4).—Croftan (*Pflüger's Archiv*, 1902, 90, 685) states that the formation of bile acids and pigments is a purely chemical process due to the action of trypsin on hæmoglobin in the presence of dextrose, and is not the result of specific hepatic action. The present experiments do not confirm this view; tests for bile acids were uniformly negative; Gmelin's test for bile pigments was, however, positive, but answered equally well if trypsin and dextrose were omitted, especially if bacterial growth had not been excluded. Blood laked by ether and allowed to stand gives a good Gmelin test. W. D. H.

Bile and Biliary Pigments. M. PIETTRE (*Compt. rend.*, 1908, 146, 786—789).—The author has studied the absorption spectra of the bile of man, of the pig, of the dog, of the fowl, and of the haddock. These differ greatly, but all possess the two green bands $\lambda 572$ and $\lambda 535$, although with varying intensity. The latter seem analogous to the α ($\lambda 575$) and β ($\lambda 535$) bands of oxyhæmoglobin. Bilirubin has no specific spectrum; biliverdin, when first prepared, shows no absorption, but after exposure to the air the band $\lambda 638$ appears.

Besides these, chloroform extracts from bile a solid substance with a reddish-brown reflex, giving a deep orange solution and having a characteristic spectrum. The spectra observed in bile must be due to the superposition of the spectra of the latter two pigments, and their variations are explained by the differences in the proportions of the two pigments present. Diagrams are given of the spectra of the various species of bile studied. E. H.

Passage of Substances into the Human System by Osmosis. LOUIS KAHLLENBERG (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxiv—xxvi; *J. Biol. Chem.*, 4).—Saturated boric acid solutions are absorbed through the skin, and boric acid appears in the urine within a few minutes. Lithium chloride diffuses through dead membranes and also through living mucous membranes more readily than boric acid, but it is not absorbed at all through the living skin. If the feet

are soaked in citric acid the acidity of the urine rises, but if hydrochloric or sulphuric acids (decinormal) are employed, the urine becomes alkaline within a few minutes.

W. D. H.

Peroxydase Reaction of Milk. JOSEPH H. KASTLE and MADISON B. PORCH (*J. Biol. Chem.*, 1908, 4, 301—320).—In general, milk which has been boiled or pasteurised at, or above, 80° does not show the peroxydase reaction, whereas raw milk does. But there are exceptions to this rule, for all raw milk does not give the reaction as ordinarily carried out. The power of milk to induce the oxidation of phenolphthalin and other leuco-compounds by hydrogen peroxide is intensified by phenol, the three cresols, and β -naphthol. If these accelerators are employed, the test is a safe criterion between raw and cooked milk. Heating at 70° for one hour or at 75° for twenty minutes destroys the reaction; heating at 60° for twenty minutes (a method of pasteurisation recommended by Rosenau because it does not destroy the biological characters of milk) intensifies it. Cow's milk exhibits great variations in peroxydase activity, but as a rule the power of human milk is less, except during the colostrous stage.

W. D. H.

Bacterial Growth and Chemical Changes in Milk Kept at Low Temperatures. MARY E. PENNINGTON (*J. Biol. Chem.*, 1908, 4, 353—394).—Bacteria in milk increase in numbers even at a little below 0°. Clean milk, containing 300 organisms per c.c., may in a few weeks contain some billions per c.c. The organisms which resist cold are principally those which form acid and act on protein. *B. formosus*, *R. solitarius*, and *B. Ravenel* are specially resistant. The caseinogen of milk is rapidly digested, caseoses, peptones, and amino-acids being formed; 50% of it may be changed into soluble compounds. The milk has a very high acid content; the formation of acid and digestion of caseinogen are far greater in cold storage than at room temperature.

W. D. H.

Efficiency of Thymol and Refrigeration for the Preservation of Urine. PHILIP B. HAWK and HARRY S. GRINDLEY (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, ix—x; *J. Biol. Chem.*, 4).—Urine to which a little thymol has been added and kept in cold storage (7—10°) shows no change in ammonia, creatinine, uric acid, urea, or total nitrogen after twenty-four hours. After ninety-six hours, the ammonia rises by 2.8% and the urea falls by 3.6%.

W. D. H.

Mechanism of Salt Glycosuria. FRANK P. UNDERHILL and ISRAEL S. KLEINER (*J. Biol. Chem.*, 1908, 4, 395—402. Compare Abstr., 1906, ii, 186, 243).—Renewed investigation has afforded no occasion to modify the views previously expressed by the authors regarding the mechanism of salt glycosuria. Under appropriate conditions in the rabbit, glycosuria due to renal permeability induced by sodium chloride injections can be inhibited by injections of calcium chloride. If calcium chloride is given, glycosuria fails to be evinced even when free sugar is injected in addition.

W. D. H.

Excretion of Hexamethylenetetramine in Bile and Pancreatic Juice. S. J. CROWE (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxxv—xxxvi; *J. Biol. Chem.*, 4).—After giving hexamethylene-tetramine (urotropine) by the mouth to dogs, it was excreted in quantity both in bile and pancreatic juice. It also passes into the cerebro-spinal fluid.
W. D. H.

Influence of Meat on the Dimethylaminobenzaldehyde Reaction of Urine. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1908, 4, 403—405).—The cherry-red coloration of the urine induced by an acid solution of Ehrlich's aldehyde is particularly strong in certain affections of the digestive tract. Bauer considers that the reaction depends on urobilinogen; it is also augmented by giving scatole, and indole-acetic acid in concentrated urine may also give the reaction. The exact mechanism of the reaction is far from clear, and the substances which produce it are probably numerous. It is always intensified both in dog's and human urine by the giving of meat, especially beef. Liebig's extract intensifies it somewhat. Feeding on blood has no effect, but the white flesh of fish, or ground beef thoroughly washed from pigments, does not induce the reaction.
W. D. H.

Indole-acetic Acid as the Chromogen of Urorosein. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1908, 4, 253—258).—A crystalline substance obtained from the urine of a patient suffering from a peculiar type of intestinal bacterial putrefaction was found to give reactions identical with those of indole-acetic acid. Both form scatole and carbon dioxide when heated, and give Nencki and Sieber's urorosein reaction. Bacteriologists who employ the nitrite reaction for indole should not confound indole-acetic acid with indole. The test for indole should never be made except in the distillate. W. D. H.

Hæmaphæic Reaction of Urines. EMILE DUFAU (*J. Pharm. Chim.*, 1908, [vi], 27, 333—336; *Bull. Soc. chim.*, 1908, [iv], 3, 460—462).—The reaction, formerly called hæmaphæic, which consists in the production of a reddish-brown colour when nitric acid is poured on urine, is due to the super-position of a yellow coloration, caused, at least in part, by urobilin, and of a red coloration, due to an unknown substance.
G. B.

Effect of Ether Anæsthesia on Nitrogen Excretion. PHILIP B. HAWK (*J. Biol. Chem.*, 1908, 4, 321—352).—Ether anæsthesia in dogs increases the output of nitrogen during the twenty-four to forty-eight hours following the narcosis; the longer the duration of the anæsthesia the greater is this increase, but the actual amount varies greatly in different animals. Even in the same animal, the effect of anæsthesia is different at different times, in some cases even leading to a decrease in nitrogen excretion. Ether-narcosis has no effect on the fæces. The practical outcome of this is that in metabolism experiments, if ether anæsthesia is employed, the figures for nitrogen output are untrustworthy; check experiments on the influence of the

anæsthesia alone are difficult, seeing how great is the variability of the result even in the same animal. W. D. H.

Fats and Lipoids of Malignant Hypernephromas. H. GIDEON WELLS (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxii; *J. Biol. Chem.*, 4).—These tumours show a high content of lecithin and cholesterol, and are probably of adrenal origin. W. D. H.

Chemo-therapeutic Trypanosome Studies. PAUL EHRLICH [in part with E. FRÄNKE] (*Chem. Zentr.*, 1908, i, 60—61; from *Berl. klin. Woch.*, 1907, 44, Nr. 9—12).—In infectious diseases, a drug can only be of use if it is taken up more readily by the parasite than by the organism, that is, if it is more bacteriotropous, or aetiotropous (Hans Meyer), than organotropous. In general, bacteria are more resistant than the organism, but many protozoa take up dyes (such as methylene-blue) more readily, so that, for instance, trypan-red (from 1 mol. tetrazotised benzidinemonosulphonic acid and 2 mols. sodium naphthylamine-3 : 6-disulphonate) is active against trypanosomes. Some amino- and hydroxy-derivatives of trypan-red are more active than the original substance.

Triphenylmethane-dyes, derived from rosaniline by alkylation of the amino-groups, are, to trypanosomes, but slightly more aetiotropous than organotropous, and hence of no therapeutic value.

Substances derived from dyes, alkaloids, phenols, &c., by the introduction of acid groups, or of phenolic hydroxyl groups, are less toxic than the parent substances, and may be without action on trypanosomes.

The action of atoxyl (sodium p-aminophenylarsinate) on trypanosomes is also discussed. G. B.

Chemical and Physiological Properties of a Solution of Hydrochloric Acid and Sodium Chloride. AMOS W. PETERS (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxviii; *J. Biol. Chem.*, 4).—The lethal concentration of hydrochloric acid for protozoa is lowered by the addition of a concentration of sodium chloride, which, in itself, is harmless. Colorimetric experiments favour the hypothesis that this is due to the increased acidity of the mixture. W. H. D.

Action of Cæsium on the Normal and Fatty Heart. VITTORIO SCAFFIDI (*Chem. Zentr.*, 1908, i, 659; from *Arch. Farm. speriment.*, 1907, 6, 631—652).—The injection of a centi-normal solution of cæsium chloride into the muscles or under the skin increases the work of the heart in frogs and tortoises. As a similar action occurs with fatty hearts, it is considered that the favouring action is not entirely on the heart muscle, but also on the nervous system. W. D. H.

Influence of Potassium Cyanide on Nitrogen Excretion in Dogs. WILLIAM H. WELKER (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxxi; *J. Biol. Chem.*, 4).—Experiments on six dogs failed to show any alteration in the partition of nitrogen among the urinary constituents after subcutaneous dosage with potassium cyanide. W. D. H.

Physiological Action of Atropine and Allied Alkaloids. W. WEBSTER (*Bio-Chem. J.*, 1908, 3, 129—145).—In dogs, atropine, hyoscine, hyoscyamine, scopolamine, and daturine produce a fall of blood pressure. This is due to action on the heart substance, leading to a lessening of the cardiac output. Some degree of immunity is produced by repeated doses. In small doses, the respiration is made quicker and deeper; large doses paralyse it. The treatment of chloroform poisoning by atropine is not recommended. Adrenaline is better, although its utility is limited. W. D. H.

The Constipating Action of Morphine. RUDOLF MAGNUS (*Pflüger's Archiv*, 1908, 122, 210—250).—The experiments were performed on cats, dogs, and rabbits by Cannon's Röntgen ray method. The constipating action of morphine or of tincture of opium is almost entirely due to the delay produced in the stomach; the emptying of the stomach is delayed from three to 7—25 hours. The passage through the cardiac orifice of the stomach is also difficult. W. D. H.

Physiological Actions of Yohimbine. On the "Fly-catching Reflex." J. A. GUNN (*Quart. J. Exp. Physiol.*, 1908, 1, 111—114). On Medullated Nerve. JOHN TAIT and J. A. GUNN (*ibid.*, 191—202).—A sub-lethal dose of yohimbine in frogs causes a hypersensitiveness of the centre involved in the snapping or fly-catching reflex, similar to that said to have been produced by the removal of the cerebrum. Its action on nerve resembles (with certain differences) that of anaesthetics, low temperature, and asphyxia. The abolition of conductivity is gradual, the refractory period is prolonged, and fatigue changes may be demonstrated; recovery from fatigue is, however, extremely rapid; a few seconds' rest abolishes it. W. D. H.

Toxicity of Silver Salts to Fishes. LUCIANO PIGORINI (*Chem. Zentr.*, 1908, i, 56; from *Arch. Farm. speriment.*, 1907, 6, 530—547).—Silver salts are toxic even at great dilution; the lethal doses of the fluoride, nitrate, and lactate are in the ratio 1 : 2 : 5. G. B.

Lead Poisoning and its Detection. P. SCHMIDT (*Arch. Hygiene*, 1907, 63, 1—22).—When per million of red blood corpuscles there are more than one hundred containing basophil granules, chronic lead poisoning may be suspected; this affords valuable assistance in diagnosis. G. B.

Antitoxic Globulin. I. EDWIN J. BANZHAF. II. E. J. BANZHAF and ROBERT H. GIBSON (*Proc. Amer. Sci. Biol. Chem.*, 1907—8, xi—xii, xii—xiv; *J. Biol. Chem.*, 4).—From a comparison of nitrated plasma and the anti-diphtheritic globulin solutions and their fractions, it appears that the antitoxic unit is not impaired by the elimination of albumins and other non-antitoxic proteins by the methods of salting-out and dialysis. The euglobulin is not increased relatively to the total globulin in horse's blood during immunisation. W. D. H.

Action of Various Chemical Reagents on the Virus of Rabies. CLAUDIO FERMI (*Arch. Hygiene*, 1907, 63, 315—330).—The virus is most susceptible to mercuric chloride, being destroyed in

half-an-hour at a concentration of 1 : 130,000 ; next come silver salts, and then copper sulphate, mineral acids, and certain aniline dyes ; phenol has only a feeble destructive action.

Cocaine and holocaine are without action on the virus, and can be used in therapeutic injections ; the virus preserves its activity in glycerol for twenty days, but not much longer. G. B.

Toxolecithides. A. MINZ (*Biochem. Zeitsch.*, 1908, 9, 357—381). —The hæmolytic action which cobra poison exerts on blood corpuscles of certain species only in the presence of lecithin is inhibited by the presence of cholesterol, and investigations were undertaken to determine whether the cholesterol acts on the cobra poison (the prolecithide), the lecithin, or the combination of the two substances (the toxolecithide). One c.c. of a warm saturated solution of cholesterol was thrown into 9 c.c. of water. The suspension thus formed was treated in different experiments with the prolecithide, the lecithin, and the toxolecithide solutions. The mixtures were then filtered, and the hæmolytic actions investigated, in the case of the prolecithide, after addition of lecithin, and in the case of lecithin, after the addition of prolecithide. It was found that cholesterol removes from solution the lecithide, the prolecithide, and, to a minor degree, lecithin itself. The combination of prolecithide with cholesterol takes place in a very short time ; after some hours, a further combination appears to take place ; the reaction does not appear to be a simple one.

The neurotoxic action of cobra poison is not influenced by cholesterol ; this substance may serve possibly, for this reason, for the separation of the neurotoxin from the hæmolysin. In the viper poison, the hæmorrhagin is not influenced by cholesterol, whereas the hæmolysin combines ; the former is, however, destroyed by hydrochloric acid, whereas the latter remains intact. These facts indicate the presence of two different components in the viper poison. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Potassium Cyanide on the Respiration of *Aspergillus niger*, with Remarks on the Mechanism of the Action of Hydrocyanic Acid. G. SCHROEDER (*Chem. Zentr.*, 1908, i, 276 ; from *Jahrb. wiss. Bot.*, 1907, 44, 409—481 ; *Naturw. Rundsch.*, 1907, 22, 600—602).—The amount of carbon dioxide given off, and of oxygen taken up, by *Aspergillus* is diminished by potassium cyanide, but, if the poison does not act for too long a time, a complete return to normal respiration can take place. The action of potassium cyanide on respiration is a primary one, unlike that of ether. G. B.

Production of Ammonia by Bacteria. BERGHAUS (*Arch. Hygiene*, 1907, 64, 1—32).—The saprophytic organisms examined

produced much more ammonia than the pathogenic species. The increase of combined ammonia in the culture fluid is especially marked after the second week, and is due to a greater production of phosphoric, carbonic, and other acids, so that less ammonia escapes; about this time, most cultures begin to form a sediment which retains much ammonia.

The greatest production of ammonia observed was 17.4% of the available nitrogen. With killed cultures, a formation of ammonia by enzymes could be demonstrated. G. B.

The Decomposition and Formation of Lactic Acid by Micro-organisms. RICHARD MEISSNER (*Bied. Zentr.*, 1908, 37, 215—216; from *Ber. k. Württemb. Weinbauversuchsanst.*, 1904).—Of the nine moulds examined, six readily consumed lactic acid, whilst the others did not; small amounts of volatile acids were formed during the process. Malic, succinic, tartaric, and citric acids can all be converted by some of the moulds, such as *Penicillium glaucum*, *Aspergillus niger*, and *Botrytis cinerea*, into lactic acid. E. J. R.

The Influence of Sterilisation on "Kalkstickstoff" Solutions. HUBERT KAPPEN (*Centr. Bakt. Par.*, 1908, ii, 20, 704—715).—It is generally assumed in investigations on the decomposition of calcium cyanamide by bacteria that the preliminary sterilisation of the solution does not cause decomposition, or only a slight production of dicyanodiamide and calcium hydroxide, thus: $(\text{CN}\cdot\text{NH})_2\text{Ca} + 2\text{H}_2\text{O} = \text{C}_2\text{N}_2(\text{NH}_2)_2 + \text{Ca}(\text{OH})_2$; this decomposition is not supposed materially to effect the observed changes, since dicyanodiamide is not acted on by bacteria. The author controverts this view, and quotes as evidence of the complexity of the effect of heat the work of Hallwachs (*Annalen*, 1870, 153, 293), showing that dicyanodiamide is decomposed by lime to form aminodicyanic acid, which again undergoes further changes. In no circumstances should "kalkstickstoff" solutions be sterilised by boiling; instead, the solid substance should be sterilised by dry heat, and the other constituents of the solution in the ordinary way. E. J. R.

The Decomposition of Calcium Cyanamide. HUBERT KAPPEN (*Bied. Zentr.*, 1908, 37, 204—205; from *Fühling's Landw. Zeit.*, 1907, Heft 4).—Lohnis has stated that a preliminary heating of calcium cyanamide favours the action of bacteria, but the author is unable to confirm this. Dicyanamide and dicyanodiamide are only very slightly, if at all, attacked by the soil organisms; cyanamide, however, is readily decomposed, apparently more so than calcium cyanamide. E. J. R.

On the Relation of Soil Bacteria to the Decomposition of Nitrogenous Organic Matter. CONRAD HOFFMANN (*Bied. Zentr.*, 1908, 37, 219—220; from *23rd Annual Report Agric. Expt. Stat. Univ. Wisconsin*, 1906, 120).—An account of some preliminary experiments on the relation between the bacterial flora of the soil and the decomposition of various added nitrogenous compounds, especially dried blood, bran, bone-meal, and peat. The rate of decomposition is

proportional to the number of bacteria present, and is therefore greater in soils containing large numbers of bacteria, such as peaty soils or loams, than in sandy soils, where the bacterial content is smaller. Formation of ammonia precedes nitrification, and distinct amounts of ammonia could always be detected in very fruitful soils. The dried blood and the bran were found to decompose more rapidly than the bone-meal or the peat. E. J. R.

Solvent Action of Soil Bacteria on the Insoluble Phosphates of Raw Bone-Meal and Natural Raw Rock Phosphate. WALTER G. SACKETT, ANDREW J. PATTEN, and CHARLES W. BROWN (*Centr. Bakt. Par.*, 1908, ii, 20, 688—703).—The authors find that numerous organisms, which are not specific acid producers, are capable of dissolving a certain amount of the phosphates present in bone, and a smaller amount of those present in mineral phosphate. The greatest effect was seen when the organisms were inoculated with a culture solution made up of sodium chloride, potassium sulphate, and ferrous sulphate, with asparagine as the source of nitrogen and containing also bone meal. When peptone was used as the source of nitrogen, less phosphoric acid was found in the solution, and a still smaller quantity was dissolved when meat extract and peptone were used.

The organisms employed were *B. subtilis*, *B. mycoides*, *B. proteus vulgaris*, and *B. coli communis*, as well as several agar cultures from garden soil. In a few cases, it was found that the culture had consumed a greater amount of phosphate than it had dissolved.

The next series of experiments was made with acid-producing organisms, *B. acidi lacti* and "mother of vinegar" being tried. When inoculated respectively into milk and into fermented wort, these yielded liquids having, as might be expected, a strong solvent action on the phosphates.

The influence of the medium was next investigated. Organisms inoculated into an agar medium containing also magnesium and ammonium sulphates did not exert any solvent action on either calcium carbonate, di- or tri-calcium phosphate, bone-meal, or mineral phosphate. When sugar was added, the phosphates were attacked, as also when meat extract was added, but the action was then much reduced.

The results are regarded as preliminary, but they tend to show that the solvent action of micro-organisms on phosphates is not entirely the result of any secretion of acid specific to the organism, although it is greatly increased when such an acid is present. The carbon dioxide liberated by the organism appears to be a factor of importance. E. J. R.

The Influence of Micro-organisms on the Utilisation of the Potassium in Leucite by Plants. SANTE DE GRAZIA and G. CAMIOLA (*Bied. Zentr.*, 1908, 37, 207; from *Staz. sperim. agrar. ital.*, 1906, 39, 829).—When leucite is introduced into a culture solution inoculated with certain moulds, it is attacked and dissolved. The amounts of potassium present in the various solutions at the end of the experiment were found to be: in the control, 0.0365; in a solution inoculated with *Aspergillus niger*, 0.0758, *Penicillium glaucum*, 0.0895, *P. brevic*, 0.0851, unknown mould, 0.0905. E. J. R.

Can Betaine be Regarded as a Source of Nitrogen for Yeast? VLADIMIR STANĚK and OLD. MIŠKOVSKÝ (*Chem. Zentr.*, 1908, i, 146; from *Zeitsch. ges. Brauwesen*, 1907, 30, 566—568).—Brewery and distillery yeasts cannot use betaine as a source of nitrogen when cultivated in inorganic nutrient solutions to which dextrose has been added. G. B.

Behaviour of Cultivated Varieties of Yeast in Composite Nutrient Solutions. WILHELM HENNEBERG (*Chem. Zentr.*, 1908, i, 56—57; from *Woch. Brauerei*, 1907, 24, 542—546, 575—579, 581—586, 596—601, 609—613, 618—620).—Seven varieties of yeast, from breweries and distilleries, were examined in solutions containing ammonium salts, asparagine, peptone, and a variety of salts. In acid solution, the cells die more rapidly than in neutral or in alkaline solution. The flocculation of top fermentation yeast is less than that of bottom fermentation yeast, but the difference is only relative. The latter kinds are less resistant. Addition of chalk, gypsum, sodium carbonate, or potassium phosphate increases the yield of alcohol; addition of calcium lactate hastens fermentation. The increase in acidity after all the sugar has been fermented increases with increase in the sugar concentration. Crystals of calcium oxalate were never observed. Morphological and other characteristics are also discussed. G. B.

The Production of Succinic Acid during Alcoholic Fermentation. FELIX EHRLICH (*Bied. Zentr.*, 1908, 37, 197; from *Zeitsch. Spiritusindustr.*, 1907, 327).—The author shows that under certain conditions glutamic acid is converted by fermentation into succinic acid; this happens when the yeast cells are insufficiently supplied with ammonia, and is apparently the result of the organisms attacking the acid for its nitrogen. The process is considered to be glutamic acid \rightarrow hydroxyglutaric acid \rightarrow formic acid and the semialdehyde of succinic acid \rightarrow succinic acid. The author suggests that the succinic acid formed during fermentation may arise in this way. E. J. R.

Anaerobic Respiration Without the Formation of Alcohol. II. S. KOSTYTSCHIEFF (*Ber. Deut. bot. Ges.*, 1908, 26a, 167—177. Compare Abstr., 1907, ii, 571).—When a current of hydrogen is passed through the juice of *Agaricus campestris*, obtained by means of a Buchner press, considerable quantities of carbon dioxide are evolved, but not a trace of alcohol; with a current of air, more carbon dioxide is evolved (about twice as much). The pressed juice contained no unbroken cells; sterility was ensured by an addition of sodium fluoride, or, preferably, of quinine hydrochloride. The pressed juice does not reduce Fehling's solution, as alcohol is not even produced on the addition of dextrose to the juice; it follows that *Agaricus* does not contain zymase, and that, in this case, anaerobic respiration has no connexion with alcoholic fermentation. G. B.

The Respiratory Pigments of Plants. WLADIMIR PALLADIN (*Ber. Deut. bot. Ges.*, 1908, 26a, 125—132; *Zeitsch. physiol. Chem.*, 1908, 55, 207—222).—During the autolysis of germinating wheat, kept under

chloroform water, a chromogen is formed, which oxidises at the surface of the liquid to a blackish-brown pigment, similar to that which gives black bread its colour, and to the black pigments formed in plant juices by laccase and by tyrosinase (compare Bertrand, Abstr., 1907, ii, 716).

It is now suggested that these pigments are formed from anaerobic precursors by oxidation with molecular oxygen during respiration, and, in order to bring out a physiological resemblance, the name *phytohaematin* is proposed for the members of this class of pigments. On this view, the process of respiration is primarily anaerobic, and results, for instance, in the production of alcohol and other substances, and of carbon dioxide and water. The absorption of oxygen is merely due to a secondary oxidation of some of the products of fission. G. B.

Chemical Processes Accompanying the Germination of Seeds. FRANCESCO SCURTI and A. PARROZZANI (*Gazzetta*, 1908, 38, i, 216—227. Compare Abstr., 1907, ii, 803).—The products of the proteolytic changes occurring in sunflower seeds digested at 30° with water containing acetic acid have been compared with the nitrogenous compounds found in the etiolated shoots of the same seeds. In both cases the following compounds were identified: xanthine, hypoxanthine, arginine, histidine, lysine, and choline, in addition to which the digested seeds contained a small proportion of tyrosine. The conclusion is drawn that in so far as the proteins are concerned, natural germination consists of an ordinary proteolysis quite analogous to that produced by the action of the isolated enzymes on the isolated proteins, and that such natural germination can be readily reproduced artificially. Further, in artificial germination, the alterations which the proteins undergo can be limited to simple hydrolytic actions, the partial or total disappearance of the products of proteolysis, such as occur in the latter stages of natural germination, being thus avoided.

In the authors' experiments, no asparagine was formed during the digestion of the sunflower seeds or during the initial period of their natural germination, although it made its appearance during the more advanced stages of the germinative process. This observation confirms Schulze's view that asparagine is not a direct product of the resolution of proteins, but is a secondary product formed by special transformations at the expense of the primary products. T. H. P.

Physiological Function of Potassium in Vegetable Organs. JULIUS STOKLASA (*Chem. Zentr.*, 1908, i, 746—747; from *Zeitsch. landw. Versuchswe. Oesterr.*, 1908, 11, 52—61).—The chlorophyll of sugar beet and barley was found to contain 0.43 and 0.57% of K₂O. The amounts of sucrose and starch produced per 1 gram of potash are 25—27 and 23—25 grams respectively. N. H. J. M.

Vegetation of Odoriferous Plants. Successive Conditions of Plant Constituents during the Normal Development of a Perennial Plant. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1908, i, 476—477; from *Wiss. industr. Ber. Roure-Bertrand Fils*, 1907, [ii], 6, 3—14. Compare Abstr., 1907, ii, 905).—In perennial plants

there is a migration of organic substances from the leaves to the flowering portions. With the approach of winter, however, there is also a migration to the roots. N. H. J. M.

Endo- and Ecto-invertase of the Date. A. E. VINSON (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxviii—xxx; *J. Biol. Chem.*, 4).—The invertase of the date cannot be extracted by solvents until the fruit ripens, although the green fruit tissues are very active when placed in a sugar solution. Tannin does not retard the action. The following theory is put forward. The endo-enzyme forms an insoluble combination with some constituent of the protoplasm without modifying its catalytic properties. This is independent of the life or death of the protoplasm. It is usually released on maturity, possibly by autolysis, but may be liberated by external, physical or chemical influences, which destroy the integrity of the cell. A similar view is advanced in relation to Buchner's zymase. W. D. H.

Chemical Examination of *Micromeria Chamissonis* (Yerba Buena). FREDERICK B. POWER and ARTHUR H. SALWAY (*J. Amer. Chem. Soc.*, 1908, 30, 251—265).—An account of the examination of the entire air-dried plant, *Micromeria Chamissonis* or Yerba Buena, which is indigenous to the Pacific Coast of the United States.

On distillation with steam, an essential oil was obtained in quantity amounting to 0.16% of the weight of the air-dried plant. This oil has a pale yellowish-brown colour, an aromatic mint-like odour, D_{20}^{20} 0.9244, and α_D^{22} 22°48' in a 100 mm. tube.

The alcoholic extract of the plant was found to contain the following substances.

Xanthomicrol, $C_{15}H_{10}O_4(OH)_2$, m. p. 225°, a phenolic compound, which forms slender, lemon-yellow needles, and yields a *diacetyl* derivative, m. p. 116°. This substance is present to the extent of 0.02% of the air-dried plant.

An alcohol, *micromerol*, $C_{33}H_{51}O_3 \cdot OH, 2H_2O$, m. p. 277°, forms colourless needles, and has $[\alpha]_D + 57^\circ$; its *acetyl* derivative, m. p. 188°, has $[\alpha]_D + 47.1^\circ$, and the *methyl ether*, $C_{33}H_{51}O_3 \cdot OMe, H_2O$, has m. p. 116—117°, or, when anhydrous, m. p. 167°. This substance forms about 0.25% of the air-dried plant.

An alcohol, *micromeritol*, $C_{30}H_{44}O_2(OH)_2, 2H_2O$, m. p. 294—296°, crystallises in colourless needles, has $[\alpha]_D + 61.4^\circ$, and corresponds with about 0.05% of the air-dried plant; its *mono-* and *di-acetyl* derivatives have m. p. 255° and 204° respectively.

Among other substances present may be mentioned hentriacontane, m. p. 66—67°, about 0.05%; a phytosterol, $C_{27}H_{46}O, H_2O$, m. p. 135°; glycerides of palmitic, arachidic, and behenic acids; free formic, acetic, and butyric acids, and dextrose.

The plant does not exert any marked physiological activity.

E. G.

Root of *Rheum Rhaponticum* and Austrian Rhubarbs. OSWALD HESSE (*J. pr. Chem.*, 1908, [ii], 77, 321—352. Compare Abstr., 1900, i, 41; Gilson, *Bull. Acad. roy. med. Belg.*, 1903; Tschirch and Christafoletti, Abstr., 1905, ii, 851).—The roots of *Rheum*

Rhaponticum, 1904, and of *R. Austriacum*, 1905, 1906, 1907, have been investigated. Each was powdered, dried, extracted with ether and then with acetone, and from these extracts various fractions were obtained. Practically the same products were obtained from each root.

The products isolated were rhapontin, anhydorrhapontigenin, chrysophanic acid and its methyl ether (?), rhabarberon, chrysaron and its methyl ether, glycochrysaron, gallic acid, and rhapontic acid. The hydrolysis of certain fractions pointed to the presence of chrysophanin and glucogallin. Tschirch and Christofolletti's chrysopontin and chrysorhapontin were not obtained. It is probable that the former was impure rhabarberon and the latter chrysophanic acid. Rhapontin, $C_{21}H_{24}O_9$, may be obtained fairly pure by crystallisation from dilute acetic acid, or quite pure by the hydrolysis of its hexa-acetyl derivative. It forms colourless needles, begins to turn brown at 215° , and decomposes between 230° and 336° , according to the rapidity with which it is heated. It does not give a coloration with ferric chloride. It yields a *penta-acetyl* derivative, $C_{21}H_{19}O_9Ac_5$, m. p. 100° and $[\alpha]_D^{15} - 11.6^\circ$, and a *hexa-acetyl* derivative, which is identical with Tschirch and Christofolletti's diacetylrhaponticin; it crystallises in brilliant colourless needles, and has m. p. 138° and $[\alpha]_D^{15} - 30.4^\circ$.

Rhapontigenin crystallises when rhapontin is boiled with sixty times its weight of 5% sulphuric acid for about thirty-five minutes and the solution allowed to cool. The other product of hydrolysis is dextrose. Rhapontigenin crystallises from dilute methyl alcohol in colourless needles having the composition $C_{14}H_{11}O_3 \cdot OMe, H_2O$, and not that stated by Tschirch and Christofolletti. It gives a green coloration with ferric chloride, and an intense red coloration with concentrated hydriodic acid. It has m. p. 188° , and yields a *triacetyl* derivative, $C_{14}H_8(OMe)(OAc)_3$, m. p. 112° , which yields unaltered rhapontigenin when hydrolysed with calcium hydroxide solution.

In one experiment, *anhydorrhapontigenin*, $C_{15}H_{12}O_3$, was obtained by the action of acetic anhydride and rhapontigenin at $89-90^\circ$. It crystallises from glacial acetic acid in glistening yellow plates, m. p. 203° .

isoRhapontigenin, $C_{14}H_{11}O_3 \cdot OMe$, crystallises from dilute acetic acid, and when moist turns brown on exposure to the air; it is not soluble in either sodium hydroxide or carbonate solutions.

Glycochrysaron, $C_{21}H_{20}O_{10} \cdot H_2O$, crystallises from alcohol in small, yellow, nodular masses, dissolving in sodium hydroxide to a purple solution. It is hydrolysed by dilute aqueous alcoholic sulphuric acid to dextrose and *chrysaron*, $C_{15}H_{10}O_5$. This latter crystallises in glistening plates, m. p. 165° , and appears to be accompanied by a small amount of a methyl ether. When reduced with hydriodic acid, it yields *chrysaranthranol*, $C_{15}H_{12}O_4$, m. p. 225° (decomp.), which crystallises from alcohol in small, yellow plates.

Chrysophanic acid has m. p. $195-196^\circ$, and is accompanied by chrysaron, from which it can be freed by conversion into its acetyl derivative and crystallisation from ethyl alcohol. *Triacetylchrysaron*, $C_{15}H_7O_5Ac_3$, forms pale yellow plates or prisms, m. p. 165° , and is also accompanied by a small amount of a methyl ester.

The last acetone fractions yield a resin from which *rhapontic acid*, $C_{20}H_{18}O_7$ or $C_{17}H_{16}O_6$, has been isolated as a brown powder soluble in alkalis to red solutions. It begins to decompose at 190° , and is completely fused at 230° . J. J. S.

Power of Sodium Nitrate and Calcium Carbonate to decrease Toxicity in Conjunction with Plants Growing in Solution Cultures. OSWALD SCHREINER and HOWARD S. REED (*J. Amer. Chem. Soc.*, 1908, 30, 85—97).—Seedlings of wheat were kept for twelve to fourteen days in solutions containing from 1 to 1000 parts per million of different organic compounds. The solutions were then made up to the original volume and used a second time with a fresh set of seedlings. The smallest amounts of each substance (in parts per million) which caused injury to the seedlings were as follows:

	Arbutin.	Coumarin.	Cinnamic acid.	Sodium cinnamate.	Vanillin.
1st crop	25	1	25	100	50
2nd crop.....	500	100	25	100	500

Whilst cinnamic acid and its sodium salt retained their original toxic properties, the toxicity of arbutin, coumarin, and vanillin was greatly reduced by contact with the roots of the first set of seedlings. The change is attributed mainly to alterations caused by the action of the roots and to a less extent to loss due to direct absorption by the root. Addition of pyrogallol was found to reduce the toxicity of coumarin; inorganic compounds, such as sodium nitrate and calcium carbonate, were found to be distinctly beneficial in decreasing the toxic effect of organic substances. N. H. J. M.

Relation between the Effects of Liming and of Nutrient Solutions containing different Amounts of Acid on the Growth of Certain Cereals. BURT L. HARTWELL and F. R. PEMBER (*20th Ann. Rep. Rhode Island Agric. Exper. Stat.*, 1906—7, 358—380).—The results of previous field experiments showed that, whilst rye was very slightly affected by liming, the yield of barley grown under similar conditions was increased 100—200% by the application of lime. Water culture experiments were therefore made to ascertain whether the plants chiefly benefited by liming are also more susceptible to injury by acids. It was found that barley seedlings are not more injured than rye.

Alkalinity which is insufficient to precipitate ordinary nutrient solutions has no material effect on the growth of seedlings of wheat, rye, barley, and oats, and the same seedlings are hardly affected by acidity equal to $N/5000$. Acidity equivalent to $N/2500$, $N/1700$, and $N/1250$ decreased the production of green substance about 20, 40, and 60% respectively. N. H. J. M.

Effect of Commercial Sodium Nitrate on Rye. SANTE DE GRAZIA (*Bied. Zentr.*, 1908, 37, 205—206; from *Staz. sperim. agrar. ital.*, 1906, 39, 529).—In a number of experiments both in 1903 and 1905, the author found that commercial sodium nitrate gave a slightly higher yield both in grain and straw than the pure salt. The com-

mercial substance contained small quantities of potassium, calcium, magnesium, and sulphuric acid, any, or all, of which might contribute to this result. E. J. R.

The Effect of the New Nitrogenous Fertilisers on Hemp. VRAT. STÖHR (*Bied. Zentr.*, 1908, 37, 229—233; from *Haspodar Moravsky*, 1907, 9, No. 20).—Trials were made on a loamy soil in large wooden vessels, each receiving 3 grams of nitrogen in addition to potash and phosphoric acid. The fertilisers tested were "nitrate of lime" (Notodden), Frank's Kalkstickstoff, and Polzenius's Stickstoffkalk, sodium nitrate, and ammonium sulphate.

"Nitrate of lime" gave substantially the same results as sodium nitrate and ammonium sulphate, the other two fertilisers being less effective. E. J. R.

Comparative Investigation of the Results of Chemical Soil Analyses and of Cultivation Experiments. K. OPITZ (*Chem. Zentr.*, 1908, i, 285; from *Landw. Jahrb.*, 1907, 36, 909—932).—Of soils examined (at Breslau), only 10—11% contained enough phosphoric acid, and 50—55% enough soluble potassium salts. A content of 0.1% P_2O_5 , soluble in 10% hydrochloric acid, may, in general, be considered sufficient. Light soils with more than 0.1% of soluble potassium salts have almost certainly enough, and heavy soils with less than 0.1% almost certainly too little. A content of 0.25% of soluble calcium salts is enough in all cases, although a much smaller amount may suffice in some. G. B.

Studies on Humus Formation. SHIGEHIRO SUZUKI (*Bul. Coll. Agric. Tokio*, 1907, 7, 419—493. Compare this vol., ii, 127).—Experiments on humification are described in which test-tubes and dishes containing clay soil with 10% of various organic substances were kept for ninety days at about 30°. Blackening occurred throughout in the case of soil containing tannin, and to a large extent in soils containing egg-albumin and starch with meat extract. Dextrose with meat extract, crude araban with meat extract, and straw blackened slightly, whilst xylan with meat extract blackened only in the lower portion of the tube. Crude araban, xylan, starch, and dextrose did not blacken in absence of meat extract, whilst cellulose and sawdust failed to blacken both with and without meat extract. N. H. J. M.

Effect of Carbon Disulphide on Soils and Plants. M. EGOROW (*J. Landw.*, 1908, 9, 91—95).—Carbon disulphide may act injuriously on soils by dissolving the resinous and fatty substances present and then depositing them on the surfaces of the particles of soil. In this manner, the power of retaining water is diminished, and the capillary rise of water rendered slower.

Both carbon disulphide and ether (0.03—0.06 per litre) were found to stimulate the growth of etiolated seedlings of *Helianthus annuus* and *Cucurbita Pepo*. N. H. J. M.

Isolation and Toxic Properties of an Organic Soil Constituent. OSWALD SCHREINER and EDMUND C. SHOREY (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxvi; *J. Biol. Chem.*, 4).—A crystalline

organic compound was separated from several unproductive soils. It melts at 98–99°, and has the composition of dihydroxystearic acid. It was found to be harmful to plant growth. W. D. H.

Toxic Substances Arising during Plant Metabolism. OSWALD SCHREINER and M. X. SULLIVAN (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxvi—xxvii; *J. Biol. Chem.*, 4).—From wheat-sick soil there was obtained by steam distillation a crystalline substance which is toxic to wheat. From cowpea-sick soil, another crystalline substance was obtained, which was toxic to cowpea, but not to wheat. If the extracts of the soils are shaken with carbon-black, the deleterious substances are removed. W. D. H.

Fertilising Value of Snow. FRANK T. SHUTT (*Trans. Roy. Soc. Canada*, 1908, [iii], 1, 35–38).—Determinations of nitrogen were made in twelve samples of snow collected just outside Ottawa from February 21 to May 4, 1908, the first sample representing the surface 1·5 inch of snow accumulated since November, 1907, whilst all subsequent samples were freshly-fallen snow. The amounts of nitrogen per million of snow are as follows:

	Nitrogen per million			
	As ammonia.	As nitrates and nitrites.	Albuminoid ammonia.	Total.
Arithmetical means	0·256	0·163	0·052	0·471
Minimum	0·082	0·024	0·033	0·180
Maximum	0·589	0·390	0·078	0·972

The percentages of nitrogen as ammonia and as nitrates in the total (excluding albuminoid ammonia) were 61·1 and 38·9 respectively. The snowfall during the winter 1907–8 amounted to 85·5 inches, or about one inch reckoned as rain; the total nitrogen, per acre, in the snow would therefore be about 1 lb. N. H. J. M.

Manurial Experiments on Pasture Land. ERIK SOLBERG (*Bied. Zentr.*, 1908, 37, 157–161; from *Beretning Statens kemiske Kontrolstation i Trondhjem*, 1903–1907).—A number of manurial trials on pasture land are recorded, and it is shown that in most cases a complete manure is most profitable. Nitrates especially were found to be valuable; even soils rich in nitrogen responded freely, so that the nitrogen content of the soil was no guide to its behaviour with nitrogenous manure. On the other hand, there was a relation between the amount of phosphoric acid or of potassium found by analysis (presumably by the Norwegian method) and the effect of phosphatic or potassic manuring, a soil poor in either of these constituents proving distinctly responsive when the deficiency was made up. E. J. R.

Swedish Manurial Trials. P. BOLIN (*Bied. Zentr.*, 1908, 37, 161–168; from *Bihang k. landbruks-akad. Stockholm*, 1907).—Oats were found to respond best to a mixture of superphosphate and sodium nitrate unless the soil was rich in humus, when superphos-

phate only was required; potatoes, however, responded to a complete manure even on rich soils. Beets also required a complete manure, but, when varying amounts of potash were used, the gain in crop due to the extra increments of potash was less than was expected. The effect of manures on grass land depended on the nature of the herbage; where grasses predominated, sodium nitrate proved most effective and potash least; where there was a large amount of clover, superphosphate gave the largest increase.

Experiments with "nitrate of lime" (the basic calcium nitrate produced in Norway) show that it was fully as useful as sodium nitrate; cyanamide also proved to be as good as sulphate of ammonia.

E. J. R.

Manurial Trials with Precipitated Calcium Phosphate.

HENRIK G. SÖDERBAUM (*Bied. Zentr.*, 1908, 37, 155—157; from *Meddelanden k. landtbruks-akad. Stockholm*, 1907, 1—10).—The author investigates the effect on barley of precipitated calcium phosphate obtained from Norwegian apatite by Palmoer's process. This process consists in electrolysing a solution of sodium chlorate or perchlorate, and allowing the chloric acid or perchloric acid from the anode to act on the mineral phosphate. By systematically arranging the extraction, a saturated solution is finally obtained; this is then mixed with the alkaline liquor from the cathode until the acid is neutralised, the whole being shaken meanwhile. A fine, granular precipitate is obtained, quite white, and almost free from foreign matter. Its composition depends on the temperature of precipitation; at the ordinary temperature, dicalcium phosphate, CaHPO_4 , is chiefly produced; at 50° , however, some tricalcium phosphate is thrown down. The former, being more soluble, is of more immediate use to the plant, and has substantially the same effect as superphosphate. The material precipitated at 50° , on the other hand, is only about half as useful as superphosphate, particularly when applied in small dressings.

E. J. R.

Relation between the Increased Yield due to Phosphatic Manure and the Amount of Phosphoric Acid in the Soil. FERDINAND PILZ (*Zeitsch. landw. Versuchswes. Oesterr.*, 1908, 11, 36—51).—Field experiments with barley showed that the increase in yield resulting from manuring with superphosphate increased with the percentage of nitrogen in the soil. Similar indications were obtained by grouping the results according to the amount of potassium in the soil; in the case of potassium, however, the relationship is less marked. When soils containing simultaneously more than 0.2% of nitrogen, phosphoric acid, and potash are compared with soil containing less than 0.2%, the crop results show that application of phosphoric acid has more effect on the former than on the latter.

N. H. J. M.

Effect of the Addition of Sodium to Deficient Amounts of Potassium on the Growth of Plants in both Water and Sand Cultures. BURT L. HARTWELL, H. J. WHEELER, and F. R. PEMBER (*20th Ann. Rep. Rhode Island Agric. Exper. Stat.*, 1906—7, 299—357).—The results of water-culture experiments with wheat indicated that

the presence of sodium does not result in increased growth in presence of an optimum amount of potassium, but may give an increase of 10% when there is a deficiency of potassium sufficient to cause a depression of about 30% in the weight of produce. The beneficial effect of sodium cannot be due to increased osmotic pressure in the solution, as no increase was caused by extra amounts of calcium, magnesium, phosphorus, or nitrogen.

Less potassium was taken up by seedlings when the potassium was supplemented by sodium.

Sand-culture experiments gave similar results.

N. H. J. M.

The Application of Leucite as Manure. E. MONACO (*Bied. Zentr.*, 1908, 37, 206; from *Staz. sperim. agrar. ital.*, 1906, 39, 340).—The mineral used contained 8.46% of potash, and was found to be sufficiently soluble in water and various other solvents to justify its use as manure.

E. J. R.

Analytical Chemistry.

Rapid Measuring Vessel and Rapid Pipette. FRIEDRICH SCHUBERT (*Chem. Zentr.*, 1908, i, 321; from *Oesterr.-ung. Zeitsch. Zuckerind. Landw.*, 1907, 36, 629—631).—A new form of self-filling measure and self-filling pipette is described, the rapid action of which is due to the replacement of the usual small hole through the tap by a groove of considerable size. J. V. E.

Modification of the Soxhlet Extractor. HORATIO C. WOOD (*Amer. J. Pharm.*, 1908, 80, 106).—The body of the apparatus consists of a wide glass tube, the lower end of which is connected by means of a tightly fitting cork with a siphon-shaped tube, and the upper end is closed with a cork into which is fitted a tube connected with a reflux apparatus. The latter tube carries a side tube which is bent downwards and into the flask containing the solvent. When the contents of the flask boil, the vapours pass up the tube into the reflux apparatus, are condensed, and fall on to the substance to be extracted, previously placed in the body of the apparatus, and the extract flows back into the flask through the siphon. W. P. S.

Apparatus for Estimations Involving Distillation. GILBERT T. MORGAN and TAYLOR COOK (*Analyst*, 1908, 33, 117—121).—The apparatus is similar to that described previously by Morgan (*Trans.*, 1904, 1001), but the stopper of the distillation flask is modified. The stem of a tapped funnel is fused into the hollow stopper, and a side tube allows a gaseous reagent to be admitted to the flask. The delivery tube of the flask fits tightly by means of a ground-in joint into the top of a vertical condenser, the lower end of the latter being

elongated so that it may dip into an absorbent liquid contained in the receiver. A duplicate flask of smaller capacity is also provided; the neck of this flask is of sufficient diameter to fit the stopper of the larger flask, but is somewhat longer than that of the latter, in order that the tube of the stopper may reach nearly to the bottom of the vessel in each case.

W. P. S.

Preparation of Alcoholic Potassium Hydroxide Solution and Apparatus for Storing the Same. A. SCHOLL (*Zeitsch. Nahr. Genussm.*, 1908, 15, 343—344).—In order to prevent the formation of a brown colour in alcoholic potassium hydroxide solution when kept for some time, the author recommends that the solution be prepared by crushing the potassium hydroxide (in the form of sticks) in an iron mortar; the powder is then transferred to a flask, and sufficient alcohol is added to produce a solution which shall not contain more than 56 grams of the alkali per litre. The solution should not be heated. After filtration, the solution is placed in a bottle, closed by a cork through which passes a tube reaching to the bottom of the bottle. The upper end of the tube ends in a measuring device for delivering a definite volume of the solution. This device consists of two bulbs; on forcing air into the bottle by means of an indiarubber bulb, the solution rises up the tube, fills the lower bulb, and any excess is then allowed to run back from the upper bulb into the bottle, a side tube on the indiarubber pipe allowing the air to escape. A small soda-lime tube is fitted on the tube between the indiarubber bulb and the bottle, and a second one is fixed to the upper bulb. A glass rod passing through the two bulbs acts as a delivery valve for the solution in the lower bulb.

W. P. S.

Gas Analyses. GEORGES DE VOLDERE and WILLEM DE SMET (*Chem. Weekblad*, 1908, 5, 171—175).—A mathematical paper. The views on the combustion of gases entertained by Anema and van Deventer (this vol., ii, 221), although rigidly correct, do not apply to all kinds of gaseous mixtures.

The authors refer to their own publications (*Rev. gen. chim. pure appl.*, 1906, 9, 365; 1907, 10, 233), where the matter is fully discussed.

L. DE K.

Analysis of High Percentage Gases. HARTWIG FRANZEN (*Zeitsch. anorg. Chem.*, 1908, 57, 395—397).—A simple arrangement is described by means of which a gas can be absorbed from a mixture containing much non-absorbable gas. The apparatus containing the mixed gases is connected through a wash-bottle with a cylindrical absorption vessel provided with a stop-cock at each end. The absorbing solution is sucked up into the absorption vessel, and when exhausted can be replaced by a fresh supply. When absorption of the gas in question is complete, a portion of the residue can readily be transferred to a Hempel burette or other apparatus for further investigation.

G. S.

Estimation of Hydrogen in Technical Gas Analysis. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1908, 6, 77—89).—A discussion of the degree of accuracy of different methods now in use. Slight modifica-

tions in the construction and manipulation of Hempel's apparatus for the absorption of hydrogen by palladium are described.

W. A. D.

Estimation of Small Amounts of Fluorine. GEORGE STEIGER (*J. Amer. Chem. Soc.*, 1908, 30, 219—225).—The powdered rock is fused with four to five times its weight of sodium potassium carbonate, the fused mass is extracted with water, and digested with ammonium carbonate. The filtrate, which is now practically free from alumina and silica, is carefully neutralised with dilute sulphuric acid, well shaken, and then fully acidified. To the solution is added titanium sulphate solution and some hydrogen peroxide, and the coloration formed is compared in a suitable colorimeter with a solution containing the same amount of titanium and hydrogen peroxide. In presence of fluorine, a perceptible fading of the colour is noticed, but this bleaching is not directly proportional to the amount of fluorine. Reference is therefore made to a curve (see original paper).

L. DE K.

Estimation of the Total Sulphur in Urine. EMIL ÖSTERBERG and CHARLES G. L. WOLF (*Biochem. Zeitsch.*, 1908, 9, 307—309).—The method suggested by Schulz (this vol., ii, 129), namely, the oxidation of organic matter with fuming nitric acid and precipitation of sulphates with barium chloride, gives results which are too low.

S. B. S.

Estimation of Tellurium. VICTOR LENHER and A. W. HOMBERGER (*J. Amer. Chem. Soc.*, 1908, 30, 387—391).—The authors have finally adopted the following process: The tellurium (about 0.2 gram), being present as a derivative of the dioxide or as a tellurate, is dissolved in hydrochloric acid of 10% strength and heated to boiling. Fifteen c.c. of strong sulphurous acid are added, then 10 c.c. of a 15% solution of hydrazine hydrochloride, and then again 25 c.c. of sulphurous acid. The boiling is continued until the precipitated tellurium has properly settled. It is then collected on a Gooch crucible, washed with hot water, then with alcohol, and finally dried at 105°.

L. DE K.

Estimation of Total Nitrogen, including Nitrates, in Presence of Chlorides. W. D. RICHARDSON (*J. Amer. Chem. Soc.*, 1908, 30, 421—422).—The nitric nitrogen is estimated by the Schloessing-Wagner method. In a second portion of the sample, the nitrogen is estimated by the Kjeldahl-Gunning method, after destroying the nitrates by boiling with dilute sulphuric acid and 10 c.c. of saturated ferrous chloride.

The sum of the two estimations equals the total nitrogen.

L. DE K.

Spiro's and Folin's Methods for Urea and Ammonia Estimations. PAUL E. HOWE and PHILIP B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, x—xi; *J. Biol. Soc.*, 4).—Spiro's method gives a

slightly higher value for ammonia than Folin's, but a considerably higher value for urea; the excess in the latter case is due to nitrogen arising from creatinine and hippuric acid. W. D. H.

Variations in the Composition of Ammonium Phosphomolybdate. Application to the Estimation of Phosphorus in Iron, Cast-Iron, and Steel. GABRIEL CHESNEAU (*Compt. rend.*, 1908, 146, 758—761).—As the discrepancies between the percentages of phosphorus in ammonium phosphomolybdate found by various authors are too large to be due entirely to the causes of error described previously (Abstr., 1907, ii, 985), the author has precipitated various weights of disodium hydrogen phosphate with solutions of ammonium molybdate containing (1) 50 grams of ammonium molybdate and 500 c.c. of nitric acid (D 1·2) per litre, and (2) the same as (1) together with 5 grams of ammonium nitrate, and finds that the composition of the precipitate varies considerably with the conditions. In each experiment, 50 c.c. of the reagent were used, and the mixture was heated at 45° for 2·5 hours. Using the first reagent, the proportion of phosphorus in the precipitate increases from 1·69% with phosphate containing 6·648 mg. of phosphorus to 2·25% with 0·277 mg. of phosphorus. In the presence of ammonium nitrate, the corresponding variation is from 1·62% to 1·28%. This variation is closely correlated with the crystalline form of the precipitates. With the first reagent, the precipitates are composed of very small, yellow crystals of the cubical system, the yellow colour becoming brighter as the content of the phosphorus increases. In the presence of the nitrate, the precipitates are not composed of crystals properly so-called, but of "crystallites" in the form of tripods resembling three edges of a cube. The crystallites have rounded edges, and apparently are composed of a large number of small grains. Like the cubical crystals, they have no action on polarised light; their yellow colour is fainter than that of the crystals, and diminishes with the proportion of phosphorus. When the latter is very small, the crystallites are ill-defined, and birefringent needles of ammonium tetramolybdate make their appearance.

The conclusion is drawn that the precipitates are mixtures (heterogeneous in the presence, homogeneous in the absence, of ammonium nitrate) of a definite compound with quantities of molybdic acid (or tetramolybdate) varying with the concentration.

Such variations readily explain the discrepancies between the percentages of phosphorus in ammonium phosphomolybdate observed by different authors.

The precipitates formed in ferric solutions exhibit precisely similar variations in composition.

The author recommends the following precautions in estimating phosphorus in iron: (1) For 1 gram of metal, 5 grams of ammonium nitrate, and 50 c.c. of a reagent containing 50 grams of crystallised ammonium molybdate, 50 c.c. of concentrated ammonia and 500 c.c. of nitric acid (D 1·2) per litre. (2) The first precipitation should occupy 1·5 hours at 65—70°. (3) The same quantity of ammonia should invariably be used to redissolve the precipitate, a further 15 c.c. of the molybdate reagent should be added after acidification, the

second precipitation should occupy two hours at 40° , and the precipitate should be washed with pure water. Under these conditions, the precipitate has a constant composition independent of the concentration of the phosphorus, and, after drying at 105° , contains 1.60% of phosphorus. If the dry precipitate is dissolved in ammonia, the solution evaporated to dryness, and the residue heated at $400-450^{\circ}$, a blue pyromolybdate containing 1.69% of phosphorus is formed.

E. H.

Loss of Phosphoric Acid in the Incineration of Cereals. SHERMAN LEAVITT and J. A. LECLERC (*J. Amer. Chem. Soc.*, 1908, **30**, 391—394).—The heat from a blast lamp or a muffle is not sufficiently strong to affect sensibly the total ash, but is nevertheless too high when an accurate estimation of the phosphoric acid is required.

The loss by volatilisation may be lessened by the addition of calcium acetate.

L. DE K.

[Volumetric Estimation of] Phosphoric Acid. VIRGIL COBLENTZ and OTTO B. MAY (*Amer. J. Pharm.*, 1908, **80**, 151—154).—The iodometric method proposed by A. Christensen was found to give trustworthy results in the estimation of phosphoric acid, the analyses recorded being carried out on a phosphoric acid solution which complied with the requirements of the U.S. Pharmacopœia. Five c.c. of a 5% solution of the sample (containing about 85% of H_3PO_4) are introduced into a stoppered 150 c.c. flask, 2 grams of potassium iodide, 5 c.c. of saturated potassium bromate, and 30 c.c. of water are added, and the flask is closed securely. The reaction proceeds according to the equation: $6\text{H}_3\text{PO}_4 + 6\text{KI} + \text{KBrO}_3 = 6\text{KH}_2\text{PO}_4 + 3\text{I}_2 + \text{KBr} + 3\text{H}_2\text{O}$, and is completed at the ordinary temperature in from 2.5 to 3 hours. The liberated iodine is then titrated in the usual way.

W. P. S.

Estimation of Phosphoric Acid by the Uranium Process. FERNAND REPITON (*Chem. Zentr.*, 1908, **1**, 295; from *Mon. Sci.*, 1907, [iv], **21**, 815—816. Compare this vol., ii, 320).—In applying the uranium process to calcium phosphates, it is advisable to check the standard uranium solution with a solution of calcium phosphate containing an accurately known amount of phosphoric oxide. In order to estimate the latter, the author recommends the iron method, in which the phosphoric acid is precipitated by a solution of ferric nitrate of known strength and the excess of the iron precipitated by boiling with ammonium acetate. The weight of the joint precipitate less the amount of iron oxide employed = P_2O_5 .

L. DE K.

A Method of Soil Analysis for Investigations in Plant Physiology. E. A. MITSCHERLICH (*Bied. Zentr.*, 1908, **37**, 145—148; from *Landw. Jahrb.*, 1907, **36**, 309).—The author uses a solution of carbon dioxide as a solvent in soil analysis, as has often been done before, because it may be supposed to have approximately the same effect on the soil constituents as the natural soil solution. Some preliminary investigations were made to determine the best quantities

to use, and the most suitable temperature of working ; finally, a method was evolved which, when applied to certain soils manured with known quantities of kainite, superphosphate, and sodium nitrate, discriminated between the added substances and the less soluble soil constituents. No experiments were made on soils of known cropping power, and it still remains to be seen whether the results yielded by this method can be correlated with crop results. E. J. R.

Estimation of Arsenic in Lead-Antimony Alloys. GEORGE M. HOWARD (*J. Amer. Chem. Soc.*, 1908, 30, 378—380).—The method is based on the insolubility of arsenious sulphide in concentrated hydrochloric acid. 0.5—2 Grams of the alloy are dissolved in 60—70 c.c. of strong hydrochloric acid with the aid of a few drops of nitric acid. When all is dissolved, a current of hydrogen sulphide is passed for about fifteen minutes, and the excess is then removed by a current of air. After adding a little tartaric acid and an equal volume of water, the solution is filtered and titrated for antimony in the usual way, with standard iodine in presence of a slight excess of sodium hydrogen carbonate. The precipitate, consisting of arsenious sulphide and sulphur, is dissolved in 20 c.c. of water with the aid of about 5 drops of 20% sodium hydroxide, and 20 c.c. of 3% hydrogen peroxide are added. After boiling down to 20 c.c., 0.1 gram of potassium iodide is added, and also 20 c.c. of hydrochloric acid. After five minutes, the iodine liberated (which represents the arsenic) is titrated with standard thiosulphate, using starch as indicator. L. DE K.

Iodometric Estimation of Arsenious Acid. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1908, 30, 31—46).—See this vol., ii, 363.

Detection of Boric Acid in Foods. CARL MANNICH and H. PRIESS (*Chem. Zeit.*, 1908, 32, 314—315).—Five grams of the substance, such as meat, are rubbed in a mortar with 0.25 c.c. of 20% sulphuric acid, and then repeatedly with small quantities of 90% alcohol until the total filtrate measures 50 c.c. Twenty c.c. of this are then mixed with 0.5 c.c. of 15% sodium hydroxide, and, after evaporating to dryness, the residue is burnt to ash. This is moistened with 2 c.c. of sulphuric acid, and then introduced into Beckmann's spectrum lamp (*Abstr.*, 1907, ii, 209). After ascertaining that the flame is colourless, the basin is rinsed with 4 c.c. of methyl alcohol, which is then also introduced into the apparatus, when a persistent green colour of the flame will show the presence of boric acid. L. DE K.

Apparatus for the Estimation of Carbide in Steel and Iron. G. MARS (*Chem. Zentr.*, 1908, i, 165 ; from *Zeitsch. Chem. Apparatenkunde*, 1907, 2, 606—607).—A flask, holding about 1 litre, is fitted at the top with a funnel and stopcock. The funnel is drawn out at the top, so that it may be connected with a gas-generating apparatus by means of a rubber tube. The bottom of the flask is fitted with a stopcock having an additional piece, to which is sealed a filtering tube. The apparatus allows of the separation, filtration, washing, and drying of any insoluble, but oxidisable, substance with exclusion of air.

Working on 1 gram of iron, and using dilute hydrochloric or sulphuric acid (1 : 10), an estimation of carbide will take from two to four hours.

L. DE K.

New Gravimetric Processes. [Estimation of Carbon Dioxide ; Nitric Acid ; Arsenic.] PAUL JANNASCH (*Chem. Zentr.*, 1908, i, 410—411; from *Verh. Naturhist.-Med. Vereins, Heidelberg*, 1907, 9, 74—86).—*Indirect Estimation of Carbon Dioxide by Fusion with Sodium Pyrotungstate.*—7.5 Grams of sodium tungstate are fused with 2.5 grams of tungstic acid, and, after cooling in a desiccator, the mass is weighed. A weighed quantity of the carbonate is sprinkled over the surface, and the mass is again fused, when the loss in weight represents the carbon dioxide.

Indirect Estimation of Nitric Acid in Nitrates.—This is effected in the same way as with carbonates.

Estimation of Carbon Dioxide by Heating with Sulphuric Acid and Collecting the Gas in Soda-Lime Tubes.—0.5 Gram of the carbonate is placed in a 200 c.c. generating flask, and treated with 20 c.c. of strong sulphuric acid, afterwards heating at 85—90°. A current of dried, purified air is then passed through the apparatus to expel the carbon dioxide completely.

[With E. HEIMANN.]—Arsenic acid may be separated from iron by heating with hydrochloric acid with addition of hydrazine sulphate. The metallic mixture is evaporated with nitric acid, and the dry residue dissolved in 200 c.c. of hydrochloric acid and 5 grams of hydrazine sulphate. After connecting the flask with the usual absorption tubes filled with water, a rapid stream of hydrogen chloride is passed for fifteen minutes, and 125—200 c.c. of the solution are then distilled off, which operation should occupy from three to five hours. The distillate contains all the arsenic.

L. DE K.

Detection of Small Quantities of Helium in Minerals. FRED. BORDAS (*Compt. rend.*, 1908, 146, 628—630).—The minerals to be examined for helium or other gases are heated in a quartz tube which is connected by suitable taps with a Plücker tube and a Dewar charcoal absorption tube. The gas evolved is examined spectroscopically, and is then exposed to the action of the cooled charcoal. These operations are several times repeated; the fact that helium is much less quickly absorbed than other gases allows of its detection by this method even when present in very minute quantities.

H. M. D.

Estimation of Potassium by the Platinichloride Method. HENRI J. F. DE VRIES (*Chem. Weekblad*, 1908, 5, 176—184. Compare Abstr., 1907, ii, 504, 719).—The paper is devoted chiefly to the analysis of samples containing much potassium (or other) sulphate. This sulphate should be converted into chloride by precipitation with the merest excess of barium chloride, but, on account of the slight solubility of barium sulphate in liquids containing free hydrochloric acid, only a few drops of this should be present in 50 c.c. of the solution. If excess of barium chloride cannot be avoided, 80% alcohol should be used to dissolve the excess of platinic chloride.

L. DE K.

Estimation of Sodium and Potassium in Silicates. J. E. THOMSEN (*J. Amer. Chem. Soc.*, 1908, 30, 420—421).—One gram of the clay, &c., is heated with sulphuric and hydrofluoric acids and evaporated to dryness. The residue is dissolved in boiling water, and powdered barium hydroxide is added until the liquid is alkaline. The filtrate is freed from barium by means of a current of carbon dioxide, evaporated to 50 c.c., and mixed with 25 c.c. of strong alcohol. The precipitate is filtered off and washed with 50% alcohol, a measured excess of *N*/10 hydrochloric acid is added, and the carbon dioxide expelled by boiling, using litmus as indicator, and the excess of acid is then titrated with *N*/10 sodium hydroxide. The solution is then evaporated to dryness and the mass gently ignited, when the residue represents potassium and sodium chlorides. After allowing for the sodium chloride introduced, all data are obtained for calculating the amount of the alkali metals in the clay. L. DE K.

Evaluation of Barium Peroxide. A. CHWALA (*Zeitsch. angew. Chem.*, 1908, 21, 589—592).—A criticism of the large number of processes proposed from time to time for the valuation of barium peroxide. The only trustworthy methods appear to be Quincke's gasometric method and Mohr's iodometric process.

In practice, it is, however, quite sufficient to titrate the peroxide with standard permanganate in presence of hydrochloric and sulphuric acids. L. DE K.

Estimation of Magnesium Oxide in Magnesites. JOSEF MAYRHOFER (*Zeitsch. angew. Chem.*, 1908, 21, 592—593).—Five grams of the finely-powdered mineral are decomposed by heating with nitrohydrochloric acid on the water-bath. The dry residue is heated at 180—200° for half an hour in order to render the silica insoluble, treated with a little more acid, and dissolved in water; the filtrate is then made up to 1 litre.

Forty c.c. of the solution (or 20 c.c. in the case of burnt magnesites) are mixed in succession with 5 c.c. of sulphuric acid, 100 c.c. of citrate solution (100 grams of citric acid and 333 c.c. of ammonia, D 0.91, made up to a litre), 20 c.c. of 10% disodium hydrogen phosphate, and 15 c.c. of ammonia. The mixture is stirred for five minutes, avoiding touching the walls of the beaker, and then left at rest for two hours. The triple phosphate is collected and ignited as usual. Calcium is not precipitated, owing to the ammonium citrate. L. DE K.

Action of Hydrogen Sulphide on Alkaline Solutions of Zinc Salts. LEROY W. MCKAY (*J. Amer. Chem. Soc.*, 1908, 30, 376—378).—Experiments proving that, when a rapid current of hydrogen sulphide is passed through a solution of zinc containing free sodium hydroxide, the hydrated zinc sulphide precipitated at first is gradually redissolved, and there is considerable danger of the zinc escaping recognition altogether. L. DE K.

Volumetric Estimation of Zinc. WM. HERBERT KEEN (*J. Amer. Chem. Soc.*, 1908, 30, 225—233).—With due precautions, satisfactory

results may be obtained by titration with standardised ferrocyanide, using the spot test with uranium acetate as indicator.

Other metals present should be removed first by suitable means.

L. DE K.

Electrolytic Analysis. ALEXANDER CLASSEN (*Zeitsch. Elektrochem.*, 1908, 14, 141—142). F. MOLLWO PERKIN (*ibid.*, 143).—A continuation of the discussion about priority with Foerster (this vol., ii, 226). Perkin remarks that rotating electrodes were first described by Gooch and Medway, Edgar Smith, and himself almost simultaneously in 1903.

T. E.

Influence of Temperature on the Electrolytic Precipitation of Copper from Nitric Acid. JAMES R. WITHROW (*J. Amer. Chem. Soc.*, 1908, 30, 381—387).—A series of experiments from which the following conclusions are drawn. The smallest amounts of nitric acid have a tendency to retard the electrolytic precipitation of copper, but its presence is nevertheless desirable on account of its beneficial effect on the character of the deposit. Whilst in general an increased temperature means an accelerated precipitation, this is not the case above 70° if a low current strength is used.

L. DE K.

Microchemical Analysis: The Silver Group. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1908, 47, 209—234).—The process is based on the characteristic microscopical appearance of the chlorides (and other compounds) of silver, lead, and mercury. The mixture of the three salts is treated with suitable solvents (ammonia, nitrohydrochloric acid, &c.), from which the compounds are then crystallised on an object glass; in some cases, sublimation is resorted to.

L. DE K.

The Estimation of Lead, Copper, and Silver in Complicated Organic Salts. M. RINDL and HUGO SIMONIS (*Ber.*, 1908, 41, 838—840).—The methods of estimating metals in salts of organic acids containing halogen, sulphur, or nitrogen have been examined critically. Lead salts are best evaporated with concentrated sulphuric acid. In compounds containing more than the equivalent of sulphur to lead, the analysis may be combined with the sulphur estimation by the Carius method; the lead is weighed as sulphate, and the excess of sulphuric acid as barium sulphate.

The methods for estimating copper as oxide by heating and continually adding ammonium nitrate or mercury oxide are very unsatisfactory; excellent results are obtained by evaporating the copper salt with concentrated sulphuric acid. Copper salts containing sulphur or nitrogen are converted quantitatively into copper oxide on ignition.

Silver may be estimated in salts containing halogen by heating in a Carius tube with fuming nitric acid in presence of potassium halide. Quicker is the method of Dupont and Freundler of evaporating with aqua regia (hydrobromic acid being used for salts containing bromine). Silver salts containing sulphur and nitrogen give metallic silver when ignited, but require a very high temperature.

E. F. A.

New Method of Estimating Mercury Vapour in Air. P. MÉNIÈRE (*Compt. rend.*, 1908, 146, 754—756).—One hundred or one thousand litres of air, according to the proportion of mercury vapour present, are aspirated by means of a water pump at the rate of one litre per minute through 125 grams of boiling nitric acid (40° Baumé) contained in a flask to which an air-cooled Lebel-Schloesing condensing worm is attached vertically. The latter is surmounted by a smaller water-cooled worm, and, after leaving this, the air is compelled to pass through a second apparatus precisely similar to the first, the flask of which, however, contains only 75 grams of acid. At the end of this operation, the total weight of the acid should be almost exactly 200 grams; if it is not, the rate of passage of the air has been incorrect, or the condensers have been insufficiently cooled.

The acid solution is very slowly evaporated at 50° until only four to five drops of liquid remain, to which 20 c.c. of water are added. Two methods are adopted for the estimation of the mercury in this solution, according as it contains (1) less than, or (2) more than, $\frac{1}{100,000}$ th of its weight of mercury. In the first case, 1 c.c. of a reagent, prepared by digesting 0.25 gram of diphenylcarbazide with 100 c.c. of alcohol at 40° for twenty-four hours and then filtering, is added to 5 c.c. of the solution, which must not contain more than 0.5% of nitric acid, contained in a graduated tube. A chart is given showing the colours produced by this reagent with solutions containing from 0.01% to 0.000025% of mercury, and the colour observed is compared with this scale, the proportion of mercury being thus deduced. If the colour produced is darker than the darkest on the chart, the second method is applied. This consists in titrating 5 c.c. of the solution with a standard solution of sodium iodide, the latter being added very slowly drop by drop, the end of the reaction being determined by the complete solution of the mercuric iodide first precipitated.

The author suggests that the method could be used for measuring the vapour pressure of mercury. E. H.

Estimation of Mercuric Chloride in Pastilles. ENRICO RIMINI (*Boll. chim. farm.*, 1908, 47, 145—147. Compare Saporette, Abstr., 1908, ii, 133).—The mercuric chloride is reduced to the metal by hydrazine; the volume of the nitrogen evolved may be measured, or the reduction may be carried out in a Geissler carbon dioxide apparatus, and the nitrogen estimated by loss of weight. More simply, for each gram of mercuric chloride in solution, about 20 c.c. of a cold saturated solution of hydrazine sulphate are added; the solution is then rendered neutral to methyl-orange, and 10 c.c. of *N*-sodium hydroxide (per gram of HgCl_2) are run in. After shaking, the mercury is filtered off and washed, and the filtrate is titrated back with *N*/10 acid. The calculation is based on the equation:

$$\text{N}_2\text{H}_4 \cdot \text{NaHSO}_4 + 2\text{HgCl}_2 + 5\text{NaOH} = 4\text{NaCl} + \text{Na}_2\text{SO}_4 + 2\text{Hg} + \text{N}_2 + 5\text{H}_2\text{O}.$$
 G. B.

Use of Ammonium Persulphate in the Separation of Manganese [from Copper] in Acid Solutions. WILLY GOTTSCHALK (*Zeitsch. anal. Chem.*, 1908, 47, 237—240).—Ammonium

persulphate may be used for the separation of manganese from copper. Forty c.c. of the liquid are mixed with 10 c.c. of a 10% solution of the reagent and gradually heated to 60°. After four hours, the temperature is raised to 70°. The manganese dioxide so obtained is free from copper if washed with water containing 2% of nitric acid. L. DE K.

Separation of Iron from Indium. FRANK C. MATHERS (*J. Amer. Chem. Soc.*, 1908, 30, 209—211).—The metals may be separated by electrolysis, but the indium so obtained still contains iron. From this, it may be freed by redissolving in acid, neutralising with ammonia, and adding an equal volume of 50% acetic acid. From this solution, the iron may now be precipitated completely by addition of nitroso- β -naphthol dissolved in 50% acetic acid. L. DE K.

A Separation of Iron from Manganese. RICHARD B. MOORE and IVY MILLER (*J. Amer. Chem. Soc.*, 1908, 30, 593—594).—The whole of the iron is precipitated when pyridine is added to a solution of the metal containing free hydrochloric acid, whilst aluminium, chromium, and zinc are only partly precipitated, and manganese, nickel, and cobalt remain in solution. This method can therefore be used to separate iron from the last three metals. In the present paper, it is shown that a fairly satisfactory separation of iron from manganese can be effected with one precipitation. The ferric hydroxide precipitate must be washed with pyridine water (1 : 500). The manganese in the filtrate cannot be completely precipitated by the addition of bromine water to the hot solution; it may, however, be estimated by boiling the solution with potassium carbonate or sodium hydroxide. W. H. G.

Detection of Nickel in Ores and Nickel-Steel. HERMANN GROSSMANN (*Chem. Zeit.*, 1908, 32, 315—316).—The solution obtained in the usual way is precipitated, if necessary, with hydrogen sulphide, and the filtrate is concentrated to a small volume. After neutralising the bulk of the free acid, 4 grams of sodium potassium tartrate are added for every gram of ore or alloy taken. A slight excess of ammonia is now added, and then 1 gram of dicyanodiamidine sulphate, followed by aqueous potassium hydroxide. The nickel is deposited immediately or after some little time in the form of a beautifully crystallised dicyanodiamidine compound. In presence of much manganese, it is advisable to add also some hydrazine sulphate to prevent oxidation, and subsequent separation of higher oxides of manganese. L. DE K.

Detection of Gold, Silver, and the Platinum Metals by means of the Metaphosphate Bead. JULIUS DONAU (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 9, 273).—As in the case of borax, certain metallic salts are reduced in metaphosphate beads, and, owing to the high viscosity of the fused mass, the ultramicroscopic particles of metal unite together so slowly that the colloidal state is evident. Continued heating causes the colour of the bead to change, and finally to disappear as the union of the metallic particles to a non-colour-producing

size proceeds. These metallic aggregates in the colourless bead can easily be seen under the microscope. Decolorised metaphosphate beads do not regain their colour when reheated, the colloidal state not being reversible as with gold ruby glass. Small quantities of foreign substances, such as alkali salts, silicic acid, or water glass, have no effect on the colour produced. As an indication of the sensitiveness of this test, beads containing 0.00003 mg. of gold, 0.0002 mg. of silver, or 0.00008 mg. of platinum show distinct colours. J. V. E.

Estimation of the Hardness, also of the Free, Semi-combined, and Combined Carbon Dioxide in Waters. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1908, 21, 640—641).—A criticism of the processes now in vogue, and a plea for uniformity in technical water analyses. L. DE K.

Estimation of Organic Carbon in Waters. NIKOLAUS POPOWSKY (*Arch. Hygiene*, 1908, 65, 1—16).—A suitable quantity of the water is acidified with sulphuric acid and evaporated to about 8 c.c. This is then submitted to the ordinary moist combustion in a current of air (heating with sulphuric acid and potassium dichromate, and passing the dried gases through a tube containing copper oxide heated to redness and lead peroxide heated at 150°), and the carbon dioxide formed is passed through a weak solution of sodium carbonate containing phenolphthalein. From the degree of bleaching as observed in a colorimeter, the amount of carbon dioxide can be ascertained, or the excess of sodium carbonate may be titrated with water containing a known amount of carbon dioxide, but this is not quite so satisfactory.

For minute working details, the original paper and the accompanying curve should be consulted. L. DE K.

Estimation of Benzene in Illuminating Gas. LOUIS M. DENNIS and ELLEN S. MCCARTHY (*J. Amer. Chem. Soc.*, 1908, 30, 233—247).—Sulphuric acid, D 1.84, cannot be recommended as an absorbent for benzene, as it also combines with varying amounts of ethylene; it also causes much inconvenience, owing to foaming. An ammoniacal solution of nickel cyanide, however, gives trustworthy results. This reagent is prepared by dissolving 50 grams of crystallised nickel sulphate in 75 c.c. of water, and adding 25 grams of potassium cyanide dissolved in 40 c.c. of water; the nickel cyanide formed is then dissolved by addition of 125 c.c. of ammonia, D 0.91.

A Hempel apparatus may be employed, filled with either water or mercury as the confining liquid. L. DE K.

Detection and Estimation of Small Quantities of Benzene in Alcohol. DAVID HOLDE and G. WINTERFELD (*Chem. Zeit.*, 1908, 32, 313).—One hundred c.c. of the spirit to be tested are diluted with so much water that the amount of real alcohol equals 24.7% by weight. The liquid is then distilled until 10 c.c. have been collected in a tube immersed in ice. The distillate is diluted with 10—20 c.c.

of water, and introduced into a narrow graduated cylinder; if the liquid remains turbid, the cylinder may be heated slightly in the water-bath. The volume of the benzene is then read off. A correction of +0.3% should be applied. L. DE K.

Estimation of Alcohol in Concentrated Ethyl Nitrite. W. A. PEARSON (*Amer. J. Pharm.*, 1908, 80, 101—105).—The method described originally by Dupré, subject to certain modifications, was found to be trustworthy. For the separation of the alcohol from the ethyl nitrite, from 25 to 30 grams of the concentrated preparation were weighed out in a flask partly filled with ice-water, and the flask was connected immediately with a series of wash-bottles containing cold water. The outlet tube of each bottle reached nearly to the bottom of the next one. The ethyl nitrite was allowed to evaporate at the ordinary temperature for three days. Instead of the wash-bottles, spiral condensers partly filled with water were also employed with good results. When the volatilisation of the ethyl nitrite was complete, the water in the flask and wash-bottles was transferred to a graduated flask and diluted, so that each 20 c.c. contained from 0.1 to 0.3 gram of alcohol. Twenty c.c. of this solution were then placed in a bottle, sufficient sulphuric acid and potassium dichromate to oxidise the remaining traces of ethyl nitrite and the alcohol were added, the bottle was closed securely, and heated for two hours in a boiling water-bath. When cold, the excess of chromic acid was reduced by the addition of zinc, the mixture was distilled, and the acetic acid determined in the distillate and calculated into alcohol. Any ethyl nitrite, or aldehyde, in the alcoholic solution was estimated separately, and an allowance was made for the quantities found. W. P. S.

Quantitative Estimation of Methoxyl- and Methylimino-groups. ALFRED KIRPAL (*Ber.*, 1908, 41, 819—822. Compare Busch, *Abstr.*, 1902, i, 501; Goldschmiedt and Hönigschmid, *Abstr.*, 1903, ii, 578; Goldschmiedt, *Abstr.*, 1907, i, 30, 894).—*3-Hydroxypyridinebetaine*, $\text{CH} \begin{smallmatrix} \diagup \text{C}(\text{OH}) \cdot \text{CH} \\ \diagdown \text{CH} = \text{CH} \end{smallmatrix} \text{N} \begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{O} \end{smallmatrix} \text{CO}$, has been prepared by the condensation of 3-hydroxypyridine with chloroacetic acid; the *methyl ether* is obtained by the action of methyl iodide on the silver salt. On carrying out methoxyl estimations with this substance by Zeisel's method, values were obtained which were always too low; this was probably due to the wandering of the methyl group from the oxygen to the nitrogen atom, similarly to the case observed by Decker and Solonina (*Abstr.*, 1902, i, 767). The method of Herzig and Meyer (*Abstr.*, 1895, ii, 296; 1896, i, 68; 1898, i, 53) for estimating methyl attached to nitrogen was therefore employed, but the values so obtained were too high. This was undoubtedly due to partial decomposition of the substance, since 3-hydroxypyridinebetaine, which does not contain any methyl group, yields methyl iodide when treated according to the Herzig-Meyer method. It is therefore evident that untrustworthy results may be obtained by the methods of Zeisel and Herzig-Meyer. This problem is under investigation, and it appears that the position

of the hydroxyl group exerts a great influence on the stability of the betaine.
W. H. G.

The Keeping Power of Fehling's Solution, and the Volumetric Process of Estimating Reducing Sugars with it. FRANCIS WATTS and HAROLD A. TEMPANY (*J. Soc. Chem. Ind.*, 1908, 27, 191—193).—The authors find that Violette's modification of Fehling's solution may be kept ready mixed for many months without fear of deterioration if light and air are not allowed to have access to it. In the estimation of reducing sugars, the indicator employed consisted of a potassium ferrocyanide solution acidified with acetic acid. When the titration was nearly completed, a drop of the copper solution was placed on a layer of three pieces of filter paper, and the lowest one was then tested with the indicator. The sugar solutions used in the titrations were prepared so as to contain approximately the same concentration of reducing sugar, and a correction was applied for the influence of sucrose on the titrations. Under the conditions of the experiments, this correction was in the proportion that 1 gram of sucrose is equal in reducing power to 0.0033 gram of invert sugar.

W. P. S.

Comparative Investigations on Various Reduction Processes for the Estimation of Dextrose. TÖSAKU KINOSHITA (*Biochem. Zeitsch.*, 1908, 9, 208—230).—The following methods were investigated: those of (1) Allihn, (2) Knapp, (3) Pavy as modified by Kumagawa and Sutō. Estimations were made with solutions of dextrose in strengths varying from 0.1% to 0.7%. The most accurate results were in all cases obtained with a dextrose solution of 0.2%. The Allihn and modified Pavy methods were found on the whole the more accurate, showing a mean error of 0.04% and 0.02% respectively, as compared with an error of 1.730% in the Knapp method. Owing to the ease with which the Pavy-Kumagawa-Sutō method can be carried out, it is recommended in preference to the others, especially for the estimation of sugar in urine.

S. B. S.

Estimation of Sugar by Allihn's and Meissl's Methods. H. SCHAUMANN (*Zeitsch. anal. Chem.*, 1908, 47, 235—237).—The troublesome handling of the hot porcelain dish in which the precipitation of the sugar by means of Fehling's solution takes place, and the continual filling of the filtering tube, may be avoided by using the author's arrangement, in which the supernatant liquid, and afterwards the precipitate also, is removed by suction.

L. DE K.

Estimation of Aldehydes by the Spectroscope. PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1907, 955—977. Compare Abstr., 1907, ii, 656).—The change in the absorption bands, which is observed when a solution of defibrinated blood, to which yellow ammonium sulphide has been added, is treated with a solution containing an aldehyde, can be employed for the quantitative estimation of aldehydes. The measurement depends on the fact that the time which elapses between the mixing of the aldehyde and blood solutions

and the appearance of the absorption band with a maximum at $\lambda = 560$ is inversely proportional to the concentration of the aldehyde.

The mode of operating, which is comparative, is illustrated by the estimation of citral in essence of lemon. The natural essence to be examined and an artificially prepared essence, in which the aldehyde originally present has been removed and in its place a known quantity added, are treated simultaneously with the solution containing defibrinated blood and yellow ammonium sulphide, and are then observed together in the spectroscope. If the absorption band ($\lambda = 560$) makes its appearance at the same moment in the two solutions, the percentage concentration of the aldehyde in the two solutions is the same. If the bands do not appear simultaneously, the amount of citral in the artificial essence is varied until this is the case.

H. M. D.

Some Colour Reactions of Organic Acids with Phenols.

HENRY J. H. FENTON and G. BARR (*Proc. Camb. Phil. Soc.*, 1908, 14, 386—387).—The authors have tabulated the colour reactions which are produced when formic, oxalic, dihydroxytartaric, pyruvic, *aa*-dimethylglutaric, lactic, saccharic, lævulic, and oxalacetic acids and their salts or esters are treated at the ordinary temperature with resorcinol, phenol, pyrogallol, or *o*-cresol in the presence of strong sulphuric acid.

P. H.

Estimation of Lactic Acid in Lactates. JOHANNES PAESSLER (*Chem. Zentr.*, 1908, i, 66; from *Collegium*, 1907, 388—392).—In the absence of other reducing substances, the process is as follows: 0.4 gram of the lactate is dissolved in water, 10 c.c. of dilute sulphuric acid are added, and the lactic acid is fully oxidised to acetic acid and carbon dioxide by boiling for an hour in a reflux apparatus with addition of 25 c.c. of $N/2$ potassium dichromate. When cold, the excess of dichromate is estimated iodometrically as usual. One c.c. of dichromate = 0.01127 gram of lactic acid. Lactic anhydride is but imperfectly oxidised, and should therefore be first digested with a slight excess of alkali hydroxide. Antimony, if present, should be removed by hydrogen sulphide, and the excess of the latter boiled off.

L. DE K.

Estimation of Lactic Acid in Musts and Saccharine Liquids. LUDWIG LEGLER (*Chem. Zentr.*, 1908, i, 299—300; from *Arb. hyg. Instituten, Dresden*, 2, 91—108).—The solution is concentrated to 10 c.c. and shaken thrice in succession with ether for five minutes. The ethereal residues are neutralised with barium hydroxide and then treated according to Möslinger (*ibid.*, 1902, ii, 1386). The result, however, is too low, but this may be remedied by multiplying by 1.11.

L. DE K.

Estimation of Benzoic Acid in Ketchup. CHARLES H. LA WALL and HENRY A. BRADSHAW (*Amer. J. Pharm.*, 1908, 80, 171—172).—Twenty grams of the ketchup are mixed thoroughly with 5 c.c. of hydrochloric acid and 25 c.c. of saturated sodium chloride solution; the mixture is then poured on a moistened filter, and the

residue is washed with saturated sodium chloride solution until the filtrate and washings amount to 100 c.c. The filtrate is shaken with three successive quantities of chloroform, and the united extracts are evaporated at the ordinary temperature. The residue, which is usually perfectly white and crystalline, is dried to constant weight over sulphuric acid. If the residue is yellow in colour and oily, it must be dissolved in dilute ammonia, and the solution again shaken with chloroform, after acidifying with sulphuric acid. The weighed residue may be dissolved in a little alcohol, and the solution titrated with $N/20$ potassium hydroxide solution, using phenolphthalein as indicator, the quantity of alkali used being then calculated into benzoic acid. If salicylic acid and "saccharin" are also present in the ketchup, they are extracted along with the benzoic acid, and must be estimated separately. W. P. S.

Estimation of Glycine in Human Fæces. FELIX VON OEFELE (*Pharm. Zentr.-h.*, 1908, 49, 203—204).—The crude glycine, obtained in the usual manner, is converted into hippuric acid by means of benzoyl chloride. The nitrogen of the hippuric acid is then estimated and calculated into glycine.

As much as 7.54% of glycine has been found in dried fæces.

L. DE K.

Estimation of Fat in Samples of Fæces and Food-stuffs by the Kumagawa-Sutō Method. RYOTARO INABA (*Biochem. Zeitsch.*, 1908, 8, 348—355).—The fat was estimated in the samples by extraction with ether and weighing the extract (Soxhlet's method). The extract was hydrolysed and the fatty acids determined, and the fat recalculated from these results. (A).—The residue, from the ether extraction, was treated with alkalis and the fatty acids (purified by petroleum as in the Kumagawa-Sutō method) determined, and, from the numbers so obtained, the fat in the residue calculated (B). Finally, the fat was determined in the whole samples by hydrolysis with alkalis by the Kumagawa-Sutō method. The determinations by the Soxhlet method were always lower than those of the direct Kumagawa-Sutō method (which did not differ much from A and B); the results generally confirm those described by Kumagawa and Sutō (this vol., ii, 331). S. B. S.

Determination of the Saponification Number. HUGO MASTBAUM (*Chem. Zeit.*, 1908, 32, 378—379).—When applying the Kötstorfer method for the determination of the saponification number of fats, it is desirable that the alcoholic potassium hydroxide should be as near as possible colourless and also keep so for a reasonable time. A serviceable solution is obtained by dissolving 30 grams of potassium hydroxide in 25 c.c. of water and diluting to a litre with 96% alcohol, which has been rectified over sodium hydroxide. If now the solution is preserved in colourless bottles and exposed to daylight, it will keep remarkably well. Solutions which have turned so yellow as to be useless, may be rendered again serviceable by exposure to sunlight. L. DE K.

Detection of Methylamines in the Presence of Ammonia. L. TSALAPATINI (*Chem. Zentr.*, 1908, i, 299; from *Bull. Soc. Stiinte Bucuresti*, 1907, 16, 167—169).—The solution of the mono-, di-, or tri-methylamine is neutralised with hydrochloric acid and evaporated to dryness. The residue is dissolved in 95% alcohol, and 5 c.c. of the solution heated at 70—75° with a few centigrams of tetrachlorobenzoquinone, when a violet coloration appears. Ammonia gives no reaction in those circumstances. L. DE K.

Volumetric Estimation of Mustard Oil. MAX KUNTZE (*Arch. Pharm.*, 1908, 246, 58—69).—The following method is recommended for the estimation of mustard oil (allylthiocarbimide) in its alcoholic solutions. Five c.c. of the solution containing about 2% of the oil are placed in a 100 c.c. flask together with 10 c.c. of ammonia and 50 c.c. of *N*/10 silver nitrate solution. The flask is then attached to a reflux apparatus, and the contents are heated for one hour by means of a boiling water-bath. After cooling, the solution is diluted with water to a volume of 100 c.c. and filtered. Fifty c.c. of the clear filtrate are then rendered slightly acid with nitric acid, 1 c.c. of ammonium ferric sulphate is added, and the excess of silver nitrate is titrated with *N*/10 ammonium thiocyanate solution. W. P. S.

[Detection and Estimation of] “Saccharin.” GIOVANNI PARMEGGIANI (*Boll. chim. farm.*, 1908, 47, 37—38).—See this vol., i, 267.

Detection of “Saccharin” (o-Benzoicsulphinide) in Fatty Oils. A. BIANCHI and E. DI NOLA (*Boll. chim. farm.*, 1908, 47, 183—185).—The authors give two methods for detecting o-benzoicsulphinide in fatty oils, the more expeditious being as follows.

The oil is saponified by heating on the water-bath with alcohol and not much more than the requisite quantity of potassium hydroxide solution, most of the alcohol being then removed by evaporation and the residual soap dissolved in water. To this solution is added concentrated magnesium chloride or sulphate solution, the liquid being separated from the insoluble magnesium compound by decantation and washing. This aqueous solution is concentrated on the water-bath, acidified with sulphuric acid, and shaken with a mixture of ether and light petroleum, the ethereal solution being separated and evaporated to dryness on a water-bath. The presence of o-benzoicsulphinide in the residue is detected by the sweet taste, and by the formation of salicylic acid on fusion with sodium hydroxide at 250°. T. H. P.

Estimation of Total Alkaloids in Coca Leaves. ANNE W. K. DE JONG (*Chem. Weekblad*, 1908, 5, 225—229. Compare Abstr., 1905, ii, 778).—A criticism of Greshoff's method (*Pharm. Weekblad*, 1905, 2, 286). The results obtained by this process show great differences from those got by the Keller-de Jong method. This is caused by loss of alkaloid, due to overheating the solutions, and also to imperfect ether extraction, owing to the emulsion formed. The process may, however, be trusted when worked as follows.

The alcoholic solution is evaporated in vacuum, the residue is dissolved in water, and then made alkaline with ammonia. Two successive shakings with ether now suffice to remove all the alkaloid. In one instance, the author's process gave 1.82% of alkaloid, whilst the Greshoff method showed but 1.60%. But when using the above modification 1.83% was obtained.

L. DE K.

Evaluation of Java Coca. MAURITS GRESHOFF (*Chem. Weekblad*, 1908, 5, 253—256).—A reply to de Jong (see preceding abstract). The author's method is intended as a guide to manufacturers, whereas de Jong's process gives results which cannot be realised in practice.

L. DE K.

Estimation of Indole in Fæces. WACŁAW VON MORACZEWSKI (*Zeitsch. physiol. Chem.*, 1908, 55, 42—47).—About 30—40 grams of the fæces, when the dry substance is about 20%, or correspondingly larger quantities with liquid fæces, are mixed with 700 c.c. of water. The mixture should be neutral or weakly alkaline. Five hundred c.c. are then distilled off, best in a Kjeldahl distillation apparatus. Of the distillate, about 150 c.c. are taken, acidified with ten drops of concentrated sulphuric acid, and well shaken with 1 gram of kieselguhr. A slight loss of indole is caused by the adsorption of the kieselguhr, but this is constant when the working conditions are always the same. The mixture is then filtered, and 100 c.c. of the clear filtrate are used for the test. To this five to ten drops of a 2% sodium nitrite solution are added, and the whole is left until the maximum colour reaction is produced, which takes about two hours. The colour is then compared with a standard in a Wolff colorimeter. The standard is made by diluting 1 c.c. of a 1% solution of pure indole to 500 c.c. Five c.c. of this diluted solution are then made up to 100 c.c., to which ten drops of concentrated sulphuric acid and five drops of 2% sodium nitrite are added. The standard solution must be freshly prepared. The distillate from the fæces is sometimes somewhat coloured; in this case, it is advisable to bring the standard to the same colour by the addition of tropæolin or dichromate solution.

S. B. S.

Iodometric Estimation of Basic Colours. LOUIS PELET-JOLIVET and V. GARATI (*Chem. Zentr.*, 1908, i, 303; from *Bull. Soc. Vaudoise Sci. Nat.*, 1907, [v], 43, 30—38).—One gram of the colouring matter is dissolved in water to a litre, and 40—100 c.c. of the solution are titrated with iodine solution containing 5 grams of iodine per litre. The end reaction is ascertained by applying the spot-test with starch solution on a porcelain plate. Satisfactory results were obtained with *magenta*, *safranin*, *methylene-blue*, and *chrysoidin*, which all give precipitates. One mol. of the dye absorbs 2 atoms of iodine.

L. DE K.

Volumetric Estimation of Dyes. LOUIS PELET-JOLIVET and V. GARATI (*Chem. Zentr.*, 1908, ii, 303; from *Bull. Soc. Vaudoise Sci. Nat.*, 1907, [v], 43, 1—29).—The process is based on the fact that

basic dyes are more or less completely precipitated by addition of acid dyes, and, if the dyes are of a different colour, the end reaction may be observed by a spot-test on filter-paper. It is best to use solutions containing 0.2—0.5% of the colouring matter. In this manner, satisfactory results are obtained in the titration of *methylene-blue* with crystal-ponceau, sodium carminate, pyramin-orange B, cotton-brown; *safranin* with helvetia-blue, naphthol-yellow S, acid-violet 6BN; *magenta* with alkali-blue, helvetia-blue, bluish-light-green SF. Reversely, the acid dyes may be titrated with the basic colours.

L. DE K.

Colour Reactions in Biochemistry. I. F. A. STEENSMA (*Biochem. Zeitsch.*, 1908, 8, 203—208).—The colour reactions employed in biological chemistry can be generally classified in groups. The first of these is designated the "aldehyde-acid" group. An aromatic or heterocyclic aldehyde in the presence of a mineral acid gives a colour with either phenols or heterocyclic compounds containing the grouping $C=CH$. The colour obtained by this reaction can be changed by the addition of nitrous acid. A general reaction is suggested to account for the colour formation in the reactions of this aldehyde-acid group, and it can be shown that a large number of the biochemical reactions are included in it. Furthermore, on the assumption that the interaction of phenols or heterocyclic compounds containing the grouping $C=CH$ with all aromatic aldehydes in the presence of mineral acids always give rise to colours, new reactions can be predicted; for example, certain new colour reactions of thiophen are described. It is proposed to consider other groups of colour reactions in a subsequent communication.

S. B. S.

Detection of the Bile Pigments. F. A. STEENSMA (*Biochem. Zeitsch.*, 1908, 8, 209).—The Salkowski-Huppert reaction often gives negative results even when bile pigments are undoubtedly present in the urine. This is due to the fact that the bilirubin is not always oxidised. The oxidation can be conveniently accomplished in this test when the result is negative, by the addition of one drop of a 0.5% sodium nitrate solution.

S. B. S.

Blood and Red Pigmented Urines. ALBERT FLORENCE (*J. Pharm. Chim.*, 1908, [vi], 27, 145—151. Compare Abstr., 1907, ii, 827).—Urobilin cannot always be detected in the urine by the ordinary method. If, however, urine is treated with hydrochloric acid, the urobilin is set free from its combination with salts, and can be extracted with ethyl acetate, which assumes a yellow colour; this solution then gives the ordinary spectrum of urobilin, but not the reaction with alcoholic zinc acetate. On keeping, it assumes an orange colour, which becomes yellow again on treatment with ammonium sulphide. The dark-coloured solution gives the zinc acetate reaction. This method of treatment is recommended for the examination of pathological urines.

S. B. S.

The Reactions for Bile Pigments in Urine. J. C. SCHIPPERS (*Biochem. Zeitsch.*, 1908, 9, 241—243).—A comparative investigation was made of the sensitiveness of the reactions of Nakayama (*Abstr.*, 1903, ii, 120), Huppert-Salkowski, and Huppert-Salkowski as modified by Bouma. The first was found to be the most sensitive. The following modification of the Huppert-Salkowski reaction was found to give equally good results. Ten c.c. of urine are neutralised with a few drops of sodium carbonate solution, and 5 drops of 20% sodium carbonate solution and then 10 drops of 20% calcium chloride are added. The precipitate, after washing, is warmed with 3 c.c. of alcohol containing hydrochloric acid, and then sodium nitrite is added. This reaction is advantageous, in that all the reagents are colourless. S. B. S.

Estimation of the Fundamental Colouring Matter of Urines.

J. BROWIŃSKI and S. DABROWSKI (*Bull. Acad. Sci. Cracow*, 1908, 139—141).—Eight hundred to one thousand c.c. of urine are defecated by means of milk of lime or else by an ammoniacal solution of the acetate of an alkaline earth metal, and the clear solution is then precipitated with copper acetate. After twenty-four hours, the urochrome-copper precipitate is collected and washed, and then decomposed by hydrogen sulphide at 50°. The filtrate is freed from excess of hydrogen sulphide by passing a current of carbon dioxide under reduced pressure, and the solution is evaporated in a vacuum to a definite volume, say, 150—200 c.c.

The liquid is now placed in a separating funnel containing carbon disulphide. Excess of iodic acid is added, and after four to six hours the iodine liberated is extracted by repeatedly shaking the contents; four extractions generally suffice. The carbon disulphide solution is then titrated for iodine in the usual manner with *N*/100 thiosulphate. 0.1319 Gram of iodine represents 1 gram of urochrome. L. DE K.

Estimation of Nitrogenous Metabolism Products in Fæces. ALBERT STUTZER, E. MERRES, and L. SEIDLER (*Biochem. Zeitsch.*, 1908, 9, 310—317).—The nitrogenous matter in the fæces, which can be rendered soluble by treatment with gastric juice, consists of nitrogenous metabolism products, which include mucin, bile, and pancreatic secretion. The amount of this matter can be determined by estimating the total nitrogen of the fæces and the nitrogen in the residue after peptic digestion in acid solution, the amount of acid being gradually increased from 0.2% to 1%. When the fæces are not investigated in a fresh, moist condition, but are kept with preservatives, the metabolism products are apt to undergo change, so that they are no longer rendered entirely soluble by peptic digestion. An investigation showed, that of the preservatives employed, carbon disulphide produced the smallest amount of change, practically the same results having been obtained with fresh fæces and with material preserved with this substance. One c.c. suffices for 100 grams of fæces. S. B. S.

Estimation of Gliadin. WALTER E. MATHEWSON (*J. Amer. Chem. Soc.*, 1908, 30, 74—81).—The extraction of gliadin from gluten by means of alcohol gives unsatisfactory results. With some flours,

8—17% more nitrogenous matter is extracted when 4 grams per 100 c.c. of 70 vol. % alcohol are used than when 16 grams of flour are taken. A previous drying in the water-oven also renders 10—20% of the gliadin insoluble, although pure gliadin is not affected. Propyl alcohol of 70% strength is no better suited than ordinary alcohol.

Anhydrous phenol (temperature 40°) dissolves a large percentage of protein from flour; this, however, is not pure gliadin but a mixture.

L. DE K.

A New Method for Estimating Diastatic Ferments. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1908, 9, 1—9).—A series of test-tubes are taken, each containing the same amount of 1% solution of starch, but different amounts of solution of a diastatic ferment; all are placed simultaneously in a warm-bath for thirty or sixty minutes, and then transferred to ice-cold water to stop further action. Each is then shaken with the same amount of a dilute iodine solution, and the one which shows no trace of blue colour, that is, the one next to the specimen which still shows a trace of blue or violet, is taken; supposing the selected tube contains 0.02 c.c. of saliva and 5 c.c. of starch solution, and the time of exposure to 40° was 30 minutes, then 1 c.c. of saliva would have caused the disappearance of the starch in 250 c.c. of solution in the same time; this is represented by the following abbreviation in a series: $D_{30/4}^{40} = 250$.

W. D. H.

Reaction Distinguishing between Galenical Preparations made from Leaves and from other Parts of Plants. A. RICHAUD and BIDOT (*J. Pharm. Chim.*, 1908, [vi], 27, 278—280).—A few drops of a tincture, or other galenical preparation made from leaves, diluted with water give on careful addition of ammonia solution a yellowish-green ring at the junction of the two liquids. Preparations made from roots, seeds, or flowers do not give this colour reaction, except in the case of *Polygala* root. The substance to which the coloration is due is probably a decomposition product of chlorophyll.

T. A. H.

General and Physical Chemistry.

Refractometric Studies of Some Derivatives of Methane in which Two or Three Atoms of Hydrogen are Replaced by Negative Radicles. ALBIN HALLER and PAUL TH. MÜLLER (*Ann. Chim. Phys.*, 1908, [viii], 14, 125—144).—A résumé of work already published (compare Abstr., 1904, ii, 221; 1905, i, 112). The specific refractions for the α -, β -, and γ -hydrogen lines and the D -sodium line of the following substances have been determined: ethyl cyanoformate, D_D^{20} 1.0034, n_D^{20} 1.3821; methyl cyanoglyoxylate, n_D^{25} 1.4916; ethyl α -cyano- β -ethoxycrotonate, n_D^{25} 1.4936. A table is given of the molecular refractions for the different rays, and of the molecular dispersions between the α and γ lines. The values obtained are compared with those calculated from Brühl's data for the M_α and dispersion, and with Conrady's for M_D . It is pointed out that, whilst the optical constants for ethyl cyanoacetate, ethyl malonate, and malononitrile are not affected by solution in absolute alcohol, this solvent increases the molecular refractions by approximately one unit in the case of ethyl cyanomalonate and ethyl cyanoethylacetoacetate. This is considered to be due to increased enolisation of these substances.

W. O. W.

Regularities in the Structure of Spectra. F. STÄHLI (*Chem. Zentr.*, 1908, i, 591—592; from *Apoth. Zeit.*, 1908, 23, 51—53).—A theoretical paper, in which an explanation is given of the division of alkali and alkaline-earth metal spectra into primary and secondary series. The carrier of the primary series is considered to be the electrically neutral atoms, whilst the secondary series is dependent on those atoms which through loss of one or more electrons are positively charged. The connexion between the spectra of different, but closely related, elements is also discussed.

J. V. E.

Spectra of the Alkali [Metals]. W. RITZ (*Physikal. Zeitsch.*, 1908, 9, 244—245).—A criticism of Runge's conclusions (this vol., ii, 78) relative to the nature of the new series of lines discovered by Bergmann (this vol., ii, 242) in the red and ultra-red regions of the spectra of the alkali metals. The differences between the vibration frequencies of the several lines in a series are very approximately constant; this indicates that the new series are subsidiary series. This view agrees with the observed fact that the lines in these series shift towards the red end of the spectrum as the atomic weight of the alkali metal increases. Formulæ of the Rydberg type are given which represent the several lines of the series for potassium, rubidium, and caesium.

H. M. D.

Flame Spectra of Iron. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1908, 146, 859—862. Compare this vol., ii, 336).—The spectra of iron, obtained by passing one of the

gases supplied to the burner over electrodes of the metal between which an arc or sparks are passing, have been compared with the spectra obtained when the flame is fed with the spray from a solution of an iron salt. The spectra are the same for a given flame, but very considerable differences are found in the spectra when different combustible mixtures are used. Between the limits represented by $\lambda = 2250$ and $\lambda = 5000$, 750 lines were found in the iron spectrum, using coal gas and air; with coal gas and oxygen the number was 250, and with hydrogen and oxygen (or air), 210. H. M. D.

Ultra-violet Spark Spectrum of Dysprosium and Some Remarkable Magnetic Properties of this Element. GEORGES URBAIN (*Compt. rend.*, 1908, 146, 922—925).—The original contains a list of ninety-two prominent lines in the spark spectrum of dysprosium between the values 2872 and 4221.3. By means of the Curie and Chéneveau magnetic balance, the coefficient of magnetic susceptibility of the oxide, Dy_2O_3 , obtained from six consecutive terms of one of the fractions (Abstr., 1906, ii, 359) was determined; the mean value for $\chi \cdot 10^{-6}$ was $290 \cdot 10^{-6}$, the limiting values being $286 \cdot 9 \cdot 10^{-6}$ and $291 \cdot 7 \cdot 10^{-6}$. Dysprosium therefore stands first in the list of paramagnetic elements, its oxide, Dy_2O_3 , being 12.8 times more magnetic than the oxide of iron, Fe_2O_3 ; in view of this fact, the author suggests that the high values obtained by Meyer (*Sitzungsber. K. Akad. Wien.*, 110, 492—541) for the magnetic susceptibility of rare earths fractionated by Cleve and Nilson, and containing yttrium, erbium, and holmium oxides, were probably due to the presence of dysprosium. M. A. W.

Magnetic Changes in the Spectrum of Silicon Fluoride Observed Parallel to the Field. A. DUFOUR (*Compt. rend.*, 1908, 146, 810—811).—Chautard showed that the spectrum of silicon fluoride given by a Geissler tube containing this gas exhibits new rays on placing the tube in a magnetic field, and Cotton observed that the new rays persist after the action of the field, being probably due to chemical action, since the glass is attacked. The author has studied the Zeeman effect for the primitive spectrum of silicon fluoride under the conditions described previously (this vol., ii, 138), a large dispersion being employed. The spectrum is markedly sensitive to the magnetic field, and its structure is well shown by this means. The spectrum consists of diffuse rays accompanied at the red end by a background of varying intensity, the latter being often resolved into more or less widely-spaced channels. Examination of the magnetic changes parallel to the field shows that the lines may be separated into three principal groups, of which the frequencies in each group obey Deslandre's formula $N = A - (Bm + C)^2$. In the first two groups, the Zeeman effect is abnormal, and in the third group, normal. E. H.

Fluorescence, Luminescence, and Chemical Constitution. ARTHUR HANTZSCH (*Ber.*, 1908, 41, 1214—1216. Compare Abstr., 1907, ii, 834).—Largely polemical in reply to Kauffmann (this vol., ii, 5). Although aqueous solutions of potassium quinoldisulphonate do exhibit a very slight violet fluorescence when examined with the aid

of Kauffmann's apparatus, still this fact in no way affects the main points at issue between these authors.

W. H. G.

Unchangeability of the Colour of Acids of Unchangeable Constitution during the Formation of Alkali Salts and Ions. ARTHUR HANTZSCH [and, in part, ROBERT CLARK and KURT MEYER] (*Ber.*, 1908, 41, 1216—1227).—An investigation of the intensities of solutions of hydrogen platinichloride and sodium platinichloride of widely varying concentrations and in various solvents. These substances were chosen as objects for investigation because they contain the completely saturated complex PtCl_6 , and are consequently not affected by the solvent. It is found that equivalent solutions of the acid and of the salt in the same solvent are optically identical, that is, show the same absorption spectrum, and that the molecular absorption is independent of the degree of ionisation. The light absorption of the acid and of the salt is also unaffected by changes of temperature. The solvent does not appear to exercise any influence on the absorption in the blue and violet parts of the spectrum, but does so to a very slight extent in the green and ultra-violet.

From these results, and of work not yet published, it follows that : (1) salts, acids, or bases with completely saturated coloured complexes are optically unchangeable, no matter whether they be ionised, non-ionised, or with what colourless cation (H,M) or anion (X) they may be connected; examples : $(\text{PtCl}_6)(\text{H}_2\text{M}_2)$; $\text{MnO}_4(\text{H,M})$; $\text{Cr}_2\text{O}_7(\text{H}_2\text{M}_2)$; $(\text{CrO}_4)\text{M}_2$; $[\text{Cu}(\text{OH}_2)_4]\text{X}_2$; $[\text{Cu}(\text{NH}_3)_4]\text{X}_2$.

(2) Unsaturated substances, such as anhydrous salts, which become saturated on the addition of a definite number of molecules of water (or ammonia), forming a saturated coloured complex, undergo a marked alteration in colour during this change; directly the complex is completely formed, further addition of the substance combining to form the complex produces no further effect; examples : $\text{CuSO}_4 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ or $[\text{Cu}(\text{OH}_2)_4]\text{SO}_4$.

W. H. G.

Characterisation of Auxochromic Actions. ARTHUR HANTZSCH and FRIEDRICH STAIGER (*Ber.*, 1908, 41, 1204—1213).—The auxochromic effect of various solvents on nitroquinol dimethyl ether has been investigated; further, with the object of ascertaining the influence of the so-called chromophoric nitro-group on the colour intensity, the mono-, di-, and tri-nitro-derivatives of quinol dimethyl ether, also a mono- and di-nitro-derivative of toluene, have been compared in the same solvent. The effect of isomerism on colour was also studied, nitroveratrole being compared with nitroquinol dimethyl ether, and 2:3-dinitroquinol dimethyl ether with the corresponding 2:5-dinitro-compound. In this case, it is found that the introduction of a nitro-group into various parts of the benzene nucleus is accompanied by a variable change in intensity, but the extent of the change varies with the compound.

The presence of halogens in solvents which do not contain oxygen increases the intensity of the solution, bromine and iodine, as a rule, more than chlorine; in solvents containing oxygen, this rule no longer applies; for instance, the intensities of solutions of nitroquinol

dimethyl ether in ethyl chloro-, dichloro-, and trichloro-acetate decreases in the order given. With the exception of the most indifferent solvents, the effect of dissolving nitroquinol dimethyl ether is to increase its molecular intensity.

The result of introducing a second nitro-group into nitrotoluene is to increase the intensity, but the change of nitroquinol dimethyl ether into the corresponding di- and tri-nitro-derivatives is accompanied by a decrease in the colour intensity, except in the case of the solutions in methylene chloride and ethyl acetate.

From the results obtained, it is evident that the effect of solvents and substituents on the colour of substances varies considerably; in fact, the lack of laws of general applicability might be said to be characteristic of auxochromic actions.

W. H. G.

Electrochemistry of Light. I. WILDER D. BANCROFT (*J. Physical Chem.*, 1908, 12, 209—278).—Evidence is adduced in favour of the suggestion of Grotthuss that the chemical action of light is analogous to that of a voltaic cell. The available data as to the action of light on salts, and its effect in promoting the oxidation of organic compounds, quoted in the form of long extracts from the writings of Eder, Vogel, Herschel, and others, are considered from this point of view. The presence of a depolariser increases or makes possible the action of light, and it is shown that in certain cases of oxidation by gaseous oxygen, the latter acts as the depolariser, whilst for reactions in which the halogens are concerned, it is usually the latter which are rendered active by light. When two substances react under the influence of light, a determination of the active rays will usually show which of the two is rendered active, and which is the depolariser.

G. S.

Action of Potassium Salts on Photographic Plates. MAX LEVIN and RUDOLF RUER (*Physikal. Zeitsch.*, 1908, 9, 248—250).—The photographic activity of a series of potassium salts (chloride, sulphate, carbonate) obtained from different sources has been examined. All the salts examined were found to be active, the intensity of the action being equal for the various preparations. The intensity of the radiation is approximately 1/1000 of the intensity of the β -radiation of uranium oxide. Control experiments were made with sodium sulphate, lead hydroxide, and metallic lead. The sodium sulphate was found to be quite inactive; the metallic lead produced about the same effect as the various potassium salts, whereas that due to the lead hydroxide was very much smaller, and could only be recognised when the image was intensified.

H. M. D

Energy of Radium. W. A. BORODOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 460—465).—A discursive paper giving no new results.

T. H. P.

Atomic Weight of Radium. THOMAS E. THORPE (*Proc. Roy. Soc.*, 1908, 80, A, 298—309).—From 500 kilos. of pitchblende residues of radioactivity 2.5 compared with uranium, 413 grams of barium chloride

of activity 560 were obtained. The radium chloride in this material was concentrated by 9400 fractional crystallisations, first from water and later from increasingly strong hydrochloric acid, as described by Mme. Curie. The acid employed had been distilled in a platinum retort, and the later crystallisations were carried out in vessels of fused rock crystal. It was found necessary to remove a trace of lead from the radium chloride towards the end of the series of crystallisations. Finally, 64 milligrams of radium chloride were obtained, with which two determinations were made. These 64 milligrams were supplemented by 24 milligrams of material purchased in Cambridge, and the whole was recrystallised to give 78.4 milligrams of material, with which a third determination was carried out.

The radium chloride was weighed to 0.1 milligram in a small glass vessel with a conical base and a hollow ground-in stopper. A similar vessel was used as a counterpoise, both being dried over phosphoric oxide. The chloride was dissolved in 2 c.c. of distilled water, acidified with dilute nitric acid, warmed, and mixed with slight excess of silver nitrate solution. The precipitate was washed at least six times with hot water, and the supernatant liquid siphoned off through a fine capillary tube. The washed silver chloride was dried at 100°, heated at 160°, and kept over phosphoric oxide before weighing.

The method was tested by five determinations with barium chloride, the results deviating less than 0.5% from the accepted atomic weight. Barium bromide and also barium chloride and bromide recovered from the filtrates gave similar results.

The radium chloride was recrystallised until successive crystallisations gave approximately constant atomic weights. It was then repeatedly crystallised from pure strong hydrochloric acid. Spectroscopic tests made by Sir William Huggins showed that the material contained only a trace of barium.

Two determinations of the atomic weight of radium in this chloride gave the values 226.8, 225.7, whilst the above mentioned 78.4 milligrams of material gave 227.7. The mean value, 226.7, is in close agreement with Mme. Curie's number, 226.2 (*Abstr.*, 1907, ii, 728).

Incidentally, the author states that when radium chloride is exposed to perfectly dry air, it gains in weight, a substance with the properties of ozone is produced, and the chloride itself appears to be slightly oxidised. The quartz vessels employed in recrystallisation were gradually turned a deep purplish-black.

R. J. C.

Decay of Radium *B* and *C* at High Temperatures. WALTER MAKOWER and SYDNEY RUSS (*Physikal. Zeitsch.*, 1908, 9, 250—251. Compare *Abstr.*, 1907, ii, 421; H. W. Schmidt, this vol., ii, 141).—The authors maintain the accuracy of their previous experimental observations, and consider that the results, from which Schmidt has drawn the conclusion that the rate of decay of radium *C* is independent of the temperature up to 1300°, are not inconsistent with a variation in the activity of from 5 to 10%.

H. M. D.

Occurrence of Radium *D*, *E*, *F* in Ordinary Lead. JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1908, 9, 289—294).—Experiments are described which indicate that the radioactivity of

lead is due to the presence of radium *F*. The active substance may be conveniently isolated from "pure" lead acetate or chloride. The acetate is dissolved in water containing a little acetic acid, and the lead precipitated by addition of sulphuric acid; the filtered liquid is then treated with hydrogen sulphide, the precipitate dissolved in fuming nitric acid, and the solution evaporated to dryness after the addition of hydrochloric acid. After the residue has been treated with a little water, a copper plate is left in contact with the solution, and the radioactive substance after twenty-four hours is found to have been almost entirely deposited on the copper. The activity of the substance separated in this manner falls to half value in one hundred and forty-three days, which corresponds with the decay constant for radium *F*. The substance emits α -particles, and measurements of the range of these particles by different methods have given values slightly less than 4 cm., which is the range of the particles from radium *F*. The proof that the activity of lead is due to the presence of traces of a foreign substance is regarded as a strong argument against the assumption that all kinds of matter are more or less radioactive. H. M. D.

Influence of Radium on the Decomposition of Hydriodic Acid. H. JERMAIN M. CREIGHTON and A. STANLEY MACKENZIE (*Amer. Chem. J.*, 1908, 39, 474—493).—In investigating the effect of light on the decomposition of hydriodic acid, Pinnow (*Abstr.*, 1901, ii, 634) used solutions of potassium iodide acidified with sulphuric acid, and found that the best results were obtained when the potassium iodide had a concentration of 1 gram per litre. A solution of the same strength was used in the experiments now described.

Radium bromide (5 mg.) of activity about 1,000,000 was enclosed in a small glass tube, from which the β - and γ -rays were allowed to pass into the solution for a given time. The amount of decomposition was then compared with that which had taken place in a similar solution not acted on by radium. The following results were obtained.

A solution prepared with pure water of conductivity 1.6×10^{-6} at 18° decomposes in the dark, an equilibrium point being reached in sixty hours at 12° , twenty-three hours at 24° , and six hours at 36° . When ordinary distilled water is used, the decomposition is accelerated, owing to the catalytic action of some impurity which introduces a second reaction; in this case, the amount of iodine liberated reaches a certain maximum and then gradually decreases. At temperatures up to 24° , the amount of iodine set free in any given time from a solution of hydriodic acid in the dark is increased by exposure to radium rays. At 36° , however, in presence of radium rays, the amount of free iodine reaches a maximum in twenty-two hours and then decreases indefinitely, whereas in the absence of radium an equilibrium value is attained. This is accounted for by the supposition that at 36° radium causes the formation of the same product as is produced at lower temperatures by some impurity in the water. In general, a rise of temperature causes an increased liberation of iodine both in presence and absence of radium. The amount of iodine present at any time depends on an accelerating factor, obtained from the rate of decomposition of the

hydrogen iodide into hydrogen and iodine, and two retarding factors, one depending on the rate at which the hydrogen and iodine re-unite, and the other, on the rate at which the hydrogen iodide enters into some other reaction. The rate of decomposition of the hydrogen iodide is increased by the presence of radium, but the effect is relatively smaller the higher the temperature. The constant of the larger of the two retarding factors increases with the temperature and to a greater extent than does the accelerating constant, and at the lower temperatures is very slightly affected by the presence of radium. Whereas at 12° and 24° the presence of radium increases the rate both of the accelerating and of the retarding action, at 36° it introduces a new retarding reaction, and simultaneously diminishes the retarding action already existing. It has been found that at 24° the γ -rays alone effect the liberation of more iodine than do the β - and γ -rays together. In the absence of oxygen, the hydriodic acid solution is not decomposed either by sunlight or by radium rays.

E. G.

The Influence of Radium on the Electrolytic Conductivity of Colloidal Solutions. LADISLAS ŻŁOBICKI (*Bull. Acad. Sci. Cracow*, 1907, 1009—1016).—The author states that the electrolytic conductivity of colloidal metal solutions prepared by Svedberg's method differs from that of the solvent, that the conductivity is considerably affected by radium, and that it undergoes variation from day to day. Colloidal solutions of silver, copper, and gold in water, ether, alcohol, and xylene were examined.

Radium diminishes the conductivity of the solutions in alcohol, ether, and water, but increases it with xylene as solvent. The change of conductivity is complete about half an hour after the solution is first exposed to the radium, and a like period elapses after removal of the radium before the original conductivity is restored.

Radium has no influence on the conductivity of Bredig's hydrosols, or of aqueous colloidal solutions of such substances as gum-arabic and egg-albumin.

A. J. W.

Kinetics of the Transformations of Radioactive Compounds. PHILIPPE A. GUYE (*J. Chim. phys.*, 1908, 6, 294—306).—It is pointed out that the constant for the rate of decay of radioactivity with time is simply the velocity constant of the chemical reaction of the first order which the transformation follows. Further, simultaneous or successive radioactive transformations follow the law of the coexistence of chemical reactions.

In contrast with ordinary chemical reactions, the temperature-coefficient of atomic disintegration is small. Reasons are given for the view that in the familiar equation, rate of chemical action = driving force/resistance, the alteration of the "driving force" with temperature is small, and that the large temperature-coefficient for the rate of ordinary chemical reactions is due almost entirely to diminution of the resistance with temperature. It may be anticipated, however, that the resistance to atomic disintegration will remain nearly constant with change of temperature, and therefore the

rate of disintegration will be nearly independent of the temperature, in accordance with the experimental facts. G. S.

Absorption of β -Rays of Radioactive Elements. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1908, 9, 321—333).—With the object of determining whether the absorption of β -rays takes place according to an exponential formula, the absorbing action of aluminium has been examined for a number of radioactive substances. Thorium and its transformation products emit three distinct kinds of β -rays, which are due respectively to thorium 1 + 2 (meso-thorium), to thorium A, and to thorium B + C. The last two types of rays are absorbed exponentially, but the β -rays from thorium 1 + 2, the penetrating power of which is intermediate between that of thorium A and thorium B + C, deviate considerably from the requirements of the exponential formula. The β -rays of uranium X and radium E₂ are also found to be absorbed exponentially, and the general conclusion is drawn that exponential absorption curves correspond with homogeneous β -ray products. On the other hand, when the absorption-coefficient decreases with increasing thickness of the absorbing layer, the active substance is a mixture of β -ray products. Increase of the absorption-coefficient with the thickness of the absorbing medium is a phenomenon which probably depends on the special conditions of the experiment.

Concerning the β -rays emitted by the active deposit from thorium collected on a negatively charged wire, it has been found by two independent methods that 43% of the total ionisation is due to the β -radiation from thorium A. H. M. D.

Amount of Radioactive Emanation in Air from the Soil. ALBERT GÖCKEL (*Physikal. Zeitsch.*, 1908, 9, 304—306).—The author has examined the quantity of emanation in air extracted from soil at a depth of one metre below the earth's surface under various meteorological conditions. The variations of 1:4 which have been observed are traced to changes in the absorptive power of the upper layers of the earth's surface, and to changes in barometric pressure. Rain and frost increase the absorptive power, resulting in an increase of the emanation content of the air below the surface. The highest observed value of the emanation concentration was at the end of a protracted period of frosty weather. H. M. D.

Relative Quantities of Ions Produced in the Atmosphere at Rome by the Solid Transformation Products of Radium and of Thorium, and the Quantity of Thorium in the Earth in that Neighbourhood. GIAN A. BLANC (*Physikal. Zeitsch.*, 1908, 9, 294—304).—It has been found that negatively charged substances exposed in the open air at Rome acquire induced activity of the thorium type. The relative proportions of this and of the simultaneously acquired induced activity of the radium type have been measured.

The ionisation of the air near the earth's surface is due to the action of (a) radioactive emanations, (b) solid transformation products of the emanations floating in the air, and (c) transformation products

deposited on substances exposed to the air. On account of the relatively rapid decay of thorium emanation, the ionising action of this is only effective under normal conditions in close proximity to the earth's surface. At a height of 6 metres above the surface, the author found that from 5 to 10% of the ions in the air are to be referred to the activity of thorium products ($B + C$). Experiments with a wire negatively charged to a potential of about 500 volts indicate that, after sufficiently long exposure, from 40 to 75% of the active deposit consists of induced activity of the thorium type. With shorter periods of exposure, the proportion of thorium-induced activity is smaller, corresponding with the smaller value of the decay constant of thorium A compared with that of radium C .

It is probable that under the influence of the earth's electric field, the greater part of the induced thorium activity is deposited on the earth's surface. This is due to the rapid decay of the emanation, and special experiments have shown that the observed quantity of thorium emanation which escapes from the surface corresponds with the presence of 0.0000145 gram of thorium hydroxide in each gram of earth substance. This large proportion of thorium would result in the heat development associated with the processes of disintegration of thorium compounds, being of much greater importance than that resulting from the disintegration of radium compounds so far as the magnitude of geo-thermal gradients is concerned. H. M. D.

Constituents of Atmospheric Radioactivity. H. M. DADOURIAN (*Amer. J. Sci.*, 1908, [iv], 25, 335—342; *Physikal. Zeitsch.*, 1908, 9, 333—337. Compare Abstr., 1905, ii, 132).—The relative amounts of radium and thorium emanation in the air of New Haven and of Rome have been determined, in the latter case from the observations of Blanc (*Phil. Mag.*, 1907, [vi], 13, 378; this vol., ii, 248). For a negatively charged wire which had been exposed to underground air (air which had filtered through the soil) for three hours, about 5% of the initial activity was found to be due to the products of thorium emanation, the remainder to those of radium emanation, whilst for a negatively charged wire exposed in the open air for four days, 20—30% of the total initial ionisation was due to thorium products, the remainder to radium products. From the last observation it is calculated that the amount of radium emanation in the air at New Haven is 30,000—50,000 times that of the thorium emanation, whilst the corresponding ratio at Rome is 20,000—30,000 : 1. G. S.

Radioactivity of Roumanian Petroleums. DRAGOMIR HURMUZESCU (*Ann. Sci. Univ. Jassy*, 1908, 5, 1—31).—The radioactivity was measured by the electrical conductivity of air which had been bubbled through the samples of petroleum. The activity of petroleum from Câmpina-Bustenari (Prahova) and from Câmpeni-Parjol-Moinesti (Bacau) is of the same order of magnitude as that of an average mineral or thermal spring water. The activity falls to half value in a little more than three days, which is only slightly different from the time corresponding with the decay constant of radium emanation. Samples from different borings in the same

neighbourhood differ somewhat in regard to their radioactivity. This depends on the nature of the geological formation of the immediate surroundings of the boring, and also on the density of the petroleum, the lighter petroleum being the more active.

The gases disengaged from a particular boring are less active than the petroleum itself, and the associated water and argillaceous mud are still less so. The radioactivity of the petroleum from a new boring is greater than that found after the boring has been worked for some time.

H. M. D.

Radioactivity of Uranium Minerals. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1908, [iv], 25, 269—298. Compare McCoy and Ross, this vol., ii, 80, 81).—The relative activities of the various products contained in a uranium mineral (uraninite) have been determined. The methods of separation, or partial separation, of the various products are fully described. The results are as follows, the activity of uranium itself (obtained from experiments with the oxide) being taken as unity: ionium, 0.34; radium, 0.45; radium emanation, 0.62; radium *A*, 0.54; radium *B*, 0.04 (?); radium *C*, 0.91; radium *F* (polonium), 0.46, actinium products 0.28. The total activity of the mineral is thus 4.64 times that of the uranium contained in it, whilst the average value for the same ratio, obtained directly from experiments with 10 specimens of uranium minerals, is 4.69, in good agreement with the above number. The results are not absolute, as the above ratios for uranium and its disintegration products depend to some extent on the conditions of the experiment. From the above ratio and the proportion of radium in the mineral, it is calculated that one gram of radium, free from all products, has about the same activity as 1,300,000 grams of uranium. There is evidence that the amount of actinium present is proportional to the quantity of uranium, so that actinium is probably a disintegration product of uranium.

G. S.

Nomenclature of Thorium Compounds. OTTO HAHN (*Physikal. Zeitsch.*, 1908, 9, 245). **Short-lived Intermediate Product between Mesothorium and Radiothorium.** OTTO HAHN (*ibid.*, 246—248. Compare Abstr., 1907, ii, 359).—Further examination of mesothorium has shown that it represents two substances. The first (mesothorium 1) emits no rays, and has a period of decay equal to 5.5 years. By the disintegration of this substance, mesothorium 2 is formed; this emits β -rays, and its period of decay is 6.20 hours.

The two substances can be separated by adding a small quantity of zirconium chloride to the solution of "mesothorium," and precipitating by the addition of ammonia. Mesothorium 2 is precipitated with the zirconium, whilst mesothorium 1 is left in solution.

For mesothorium 1, mesothorium 2, and radiothorium, the names thorium 1, 2, and 3 respectively are suggested.

H. M. D.

Polonium. WILLY MARCKWALD (*Ber.*, 1908, 41, 1378—1379).—Most of the reactions of polonium described by Giesel (this vol., ii, 342) have been observed previously by the author.

J. J. S.

Ionium, a New Radioactive Element. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1908, [iv], 25, 365—381).—Further experiments have shown the correctness of the earlier conclusion (Abstr., 1907, ii, 836), that uranium minerals contain a previously unidentified radioactive element. Methods are described for obtaining highly active preparations of ionium from carnotite, pitchblende, gunmite, and uranophane. One of these consists in treating carnotite with hydrochloric acid and adding several grams of the chlorides of the cerite earths. The earths are then separated as oxalates, converted into chlorides, and the solution of the chlorides precipitated by sodium thiosulphate. The substance which separates is purified by repeated precipitation with sodium thiosulphate, and the resulting product has an activity several thousand times as great as that of an equal weight of pure uranium. The range of the α -particles emitted by ionium is 2.8 cm. in air at 760 mm. pressure; indications have been obtained that β -rays are also emitted. The opinion expressed previously, that ionium is the immediate parent of radium, is maintained. The rate of production of radium indicates that the life of ionium is at least as long as that of radium if it is assumed that no other product having a slow rate of change occurs between uranium X and ionium. The data now available point to the view that Debierne's actinium, as originally prepared, consisted of a mixture of ionium and Giesel's emanium.

H. M. D.

Supposed Connexion between Dielectric Constant and Isomerising Power of Organic Solvents in Keto-Enol Desmotropy. ARTHUR MICHAEL and HAROLD HIBBERT (*Ber.*, 1908, 41, 1080—1091. Compare Brühl, Abstr., 1899, ii, 735; 1900, ii, 11; Dimroth, 1905, i, 98, 383).—From an extended series of experiments with dibenzoylacetylmethane both in its enolic and ketonic modifications, and ethyl diacetylsuccinate in hydrogen cyanide, nitromethane, acetonitrile, methyl alcohol, propionitrile, acetaldehyde, acetone, ethyl nitrate, bromide, iodide, formate and acetate, chloroform, methylal, carbon disulphide, and benzene, the authors draw the following conclusions: (1) there is no simple relationship existing between the dielectric constant, dissociating power, association factor, heat of vaporisation, medial energy of an organic solvent, and the velocity of isodynamic change; (2) the velocity and the equilibrium constant in organic solvents are independent of one another, and the latter does not stand in any simple relation to the above physical constants; (3) the isomerising power of organic solvents is not a constant property, but is dependent on the chemical nature of the compound. In some cases, the solvent produces the ketonic, in others the same solvent promotes formation of the enolic, modification.

W. R.

Electrode Potential in Liquid Ammonia. F. M. G. JOHNSON and NORMAN T. M. WILSMORE (*Chem. Zentr.*, 1908, i, 1135; from *Elektrochem. Zeitsch.*, 1908, 14, 203—206).—The authors regard C in Nernst's equation $C_o = RT/nF$ as better expressed by "electrolytic potentiality" than by "potential," and C_o as the affinity constant of the elements; the latter they have determined in liquid ammonia.

Cadmium in a saturated solution of cadmium nitrate was chosen as normal electrode, and a slow current of hydrogen saturated with ammonia was passed through the solution so as to avoid salt formation with the atmospheric carbon dioxide. All measurements were made at -33.5° , the b. p. of liquid ammonia, and to avoid as far as possible contact-potential between the solutions a $N/2$ solution of potassium nitrate in ammonia was used as solvent. It was found better to use a concentrated solution of lithium chloride than calcium chloride solution for rendering the quartz thread of the Dolezalek electrometer conductive.

The following metals and salts have been investigated: AgNO_3 and AgI with fine silver and electrolytic silver; HgI_2 with mercury; $\text{Pb}(\text{NO}_3)_2$ with lead; $\text{Zn}(\text{NO}_3)_2$ with pure zinc; MgI_2 with magnesium; $\text{Ni}(\text{NO}_3)_2$ with electrolytic nickel; $\text{Cu}(\text{NO}_3)_2$ with electrolytic copper; calcium with $\text{Ca}(\text{NO}_3)_2$; ammonium amalgam with NH_4NO_3 ; sodium with NaNO_3 and NaCl ; potassium with KI . With one platinum electrode in a blue solution of alkali metal, the same *E.M.F.* was observed as with solid alkali metal electrodes, which shows that the blue colour is due to the colloidal state of the metal present. Zinc and cadmium gave the most constant values, although zinc and also magnesium blackened after a time, whilst the *E.M.F.* of nickel at first decreased, then became constant. So as to be able to compare the results with those obtained with water solutions, measurements were made with the $\text{KCl} \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}'$ electrode; inasmuch as the temperature rose about 50° , a concentrated water solution of ammonia ($D\ 0.880$) was used. Referred to the hydrogen electrode, the results obtained for the *E.M.F.* are:

$\text{Cd} \mid \text{Cd}(\text{NO}_3)_2, 4\text{H}_2\text{O} \text{ saturated} \mid \text{NH}_4\text{OH} \mid \text{KCl } N/10 = 1.041 \text{ volts.}$

$\text{Zn} \mid \text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O } N/10 \mid \text{NH}_4\text{OH} \mid \text{KCl } N/10 = 1.403 \text{ volts.}$

$\text{Hg} \mid \text{HgI}_2, N/10 \mid \text{NH}_4\text{OH} \mid \text{KCl } N/10 = +0.164 \text{ volts.}$

Assuming the *E.M.F.* of the half element $\text{Cd} \mid \text{Cd}(\text{NO}_3)_2, 4\text{H}_2\text{O}$ saturated to be 1.048 volts, the various potentials have been calculated and compared with the potential for normal ion concentrations in water solution, and it is found that the order of the series of potentials is the same in both solvents. The potential was higher throughout in ammonia than in water, and this is possibly due to a heat potential and a relatively smaller ion concentration in ammonia solution. A definite interpretation of the results is, however, not yet possible.

J. V. E.

Variation of the Electromotive Force of Liquid Chains by Polarisation of Interposed Diaphragms. PIERRE GIRARD (*Compt. rend.*, 1908, 146, 927—929).—When a diaphragm of chromium chloride or calcined alumina is placed between a liquid couple composed of two solutions of an acid or basic electrolyte of different concentrations, the final difference of potential (p') is less than that of the original couple (p), and the difference, $p - p'$, is diminished by the addition to the solutions of salts providing multivalent ions. Thus the interposition of a diaphragm of chromium chloride in the system $N/10\text{HCl} \mid N/500\text{HCl}$ gave $p - p' = 0.036$ volt, and the addition of $N/100$ and $N/5000\text{K}_3\text{Fe}(\text{CN})_6$ respectively to the acid solutions gave $p - p' = 0.006$ volt. The author concludes that the variations in the voltage

of liquid couples caused by diaphragms or membranes are not to be attributed to variation in the mobility of the ions in the interposed media, but are due to phenomena of contact electrification of the diaphragm (compare Perrin, Abstr., 1905, ii, 138). M. A. W.

The Decomposition Tension of Fused Calcium Chloride. KURT ARNDT and KURT WILLNER (*Zeitsch. Elektrochem.*, 1908, 14, 216—218).—The *E.M.F.* of the cell $\text{Ca} \mid \text{fused CaCl}_2 \mid \text{Cl}_2$ is determined directly and also by measuring the polarisation in the electrolysis of calcium chloride. The final results obtained in the two ways agree together and give 3.24 volts at 800°. The temperature-coefficient is -0.004 . The corresponding value for strontium chloride is 3.40 volts at 880°; the highest value for barium chloride observed was 3.3 volts, but this is probably too low, owing to the difficulty of avoiding depolarisation. T. E.

Electrical Conductivity in Systems containing Zinc Sulphate, Ammonia, and Water. S. SHUMAKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 476—479. Compare Kuriloff, Abstr., 1906, ii, 343; Zubkowskaia, Abstr., 1907, ii, 940).—The specific conductivities were determined for the liquid phases of the systems $\text{ZnSO}_4\text{--NH}_3\text{--H}_2\text{O}$ in equilibrium with compounds of the first and second classes and also with colloidal compounds (compare Kuriloff, Abstr., 1906, ii, 349). Eleven different solutions were examined, comprising the region of increasing precipitate, the region of transition, and the region of diminishing precipitate.

Separate measurements were made of the conductivities of aqueous solutions of zinc sulphate, ammonium sulphate, and ammonia of concentrations similar to those in which they exist in the systems examined. The data obtained show that, from the moment of transition from a system containing compounds of the first class to a system in which exist compounds of the second class and colloidal compounds, the latter exert an influence on the change of the conductivity. T. H. P.

Cathodic Pulverisation of Metals in Attenuated Gases. VOLKMAR KOHLSCHÜTTER and TH. GOLDSCHMIDT (*Zeitsch. Elektrochem.*, 1908, 14, 221—235. Compare Abstr., 1907, ii, 7).—The investigation of Kohlschütter and Müller (Abstr., 1906, ii, 418) has been continued with improved apparatus and methods. The loss of weight of cathodes of aluminium, iron, copper, silver, gold, and platinum in hydrogen, nitrogen, oxygen, helium, and argon at about 1 mm. pressure was studied. Great care was taken to use pure materials. The current used was produced by an induction coil, but discharges in one direction only passed through the gas. The cathodic volatilisation resembles the analogous phenomenon with a heated wire, but it is not, like the latter, appreciably affected by the admixture of small quantities of oxygen with the gas. It is not caused by the escape of occluded gases; platinum cathodes charged with hydrogen or oxygen did not volatilise any more than uncharged cathodes. When intermittent current is used (with a circular disk cathode), the loss of metal

is greatest from a ring between the edge of the disk and its centre. The pressure of the gas in the tube either remains constant (helium and argon) or decreases, owing to the formation of compounds of gas and metal. When the metals are arranged in the order of their volatility (loss of weight for the same number of coulombs passed), it is found that the order is the same for all gases, and the losses are proportional to the equivalents of the metals. The quantity of metal volatilised depends also on the nature of the gas, the greater volatility being always found in the gas of higher atomic weight. The authors ascribe the volatilisation to the formation of volatile, endothermic compounds of metal and gas, which decompose on cooling. Helium and argon compounds may therefore exist under the conditions of the discharge.

T. E.

Velocity of Transport of the Ions H, Cl, OH in the Electrolysis of Solutions of Hydrogen Chloride. EMMANUEL DOUMER (*Compt. rend.*, 1908, 146, 894—896. Compare this vol., ii, 252, 349).—When a solution of hydrogen chloride is electrolysed, part of the current may be employed in electrolysing the water.

Assuming that this is the case, the transport numbers for $\overset{+}{\text{H}}$ and $\overset{-}{\text{Cl}}$ will differ from those obtained without taking this into account. Dilute solutions of hydrogen chloride were electrolysed by currents of 0.005 to 0.02 amperes, and the evolved hydrogen measured. The diminution in concentration of the acid was also determined and found to be the same at each electrode. Thus in one experiment 48.15 c.c. of hydrogen were liberated, corresponding with an equivalent weight of 0.158 gram of hydrogen chloride; the loss of acid at the negative pole was 0.027 gram, and at the positive pole 0.027 gram. Assuming the water to have been ionised, the loss at each pole should have been $P/3 - p = 0.026$ gram, where $P/3$ represents the weight of acid electrolysed, and p the loss of acid at the negative pole. If the electrolysis of water does not come into play, the loss should have been $P - p = 0.131$ gram. The conclusion is drawn, therefore, that the ionisation of water plays an important part in the electrolysis of hydrogen chloride solutions, and that the transport velocity of the H and Cl ions is the same for each ion.

W. O. W.

Electrical Transport of Inorganic Colloids. ANDRÉ MAYER and EDOUARD SALLES (*Compt. rend.*, 1908, 146, 826—829).—As a result of experiments made with colloidal arsenic trisulphide (dialysed during several weeks and having about the same conductivity as distilled water), the authors find that the transport of the colloid is not uniform. When a column of the colloid contained in a U-tube and separated from the electrodes by layers of distilled water is submitted to the action of an electric current, the velocity with which one meniscus recedes from the electrode having the same sign as the colloid is greater than that with which the other meniscus approaches the electrode of opposite sign, thus producing a contraction of the column, and the first velocity increases (to a limit), whilst the second diminishes, as the action progresses. When the transport has lasted

some time, that extremity of the colloid column which approaches the electrode of opposite sign becomes more and more opaque, whilst the other extremity becomes more and more clear. On reversing the current, all these phenomena proceed in exactly the reverse manner. The intensity of the current increases as the experiment proceeds, indicating that the conductivity of the colloid is increasing, and this is found to be the case. From these facts it is deduced that (1) the electrical transport requires a certain amount of preparation; (2) the action producing this transport increases up to a certain limit; (3) the colloidal granules seem to increase in size and decrease in velocity at the extremity of the column near the electrode of opposite sign, and to diminish in size and increase in velocity at the other extremity; and (4) these phenomena are correlated with a liberation of electrolytes.

The authors advance the hypothesis that the transport of the colloid depends on that of the ions of these electrolytes, which in a pure dialysed inorganic colloid are not pre-existent, but are formed by the passage of the current, the colloid gradually decomposing into its crystalloid elements, with the ultimate production of a large number of positive and negative ions at the ends of the colloid column. This would explain (compare this vol., ii, 24) the respective aggregation and disintegration of the colloid granules. This hypothesis is supported by the observations that, whilst the field increases from 100 to 1000 volts, the maximum velocity of the colloid increases more rapidly, and that addition of potassium chloride considerably enhances all the effects described.

The conclusion is drawn that the transport of inorganic colloids, like that of organic colloids and of powders, depends on the ions adsorbed by the colloid granules. E. H.

The Electrolysis of Solutions of Hydrochloric Acid. TH. GUILLOZ (*Compt. rend.*, 1908, 146, 581—582).—The author criticises adversely the recent conclusion of Doumer (this vol., ii, 252), that in the electrolysis of hydrochloric acid solutions part of the current is employed in the electrolysis of the solvent itself, and must be allowed for in determining the transport numbers of H^+ and Cl^- . The regularity of the values obtained by Noyes and Sammet for the mobility of the ions H^+ and Cl^- in various dilute solutions (Abstr., 1903, ii, 126) is held to constitute an experimental proof that the ions of water do not play any part in the conduction. R. J. C.

Dulong and Petit's Law. PAUL ROHLAND (*Physikal. Zeitsch.*, 1908, 9, 318—319).—Polemical against Wigand (this vol., ii, 13). The fact that the atomic heat has the value required by the law only within certain temperature limits is attributed to variations in the mutual action between the atoms and the ether with the temperature. H. M. D.

Specific Heat and Osmotic Pressure of Solutions. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 339—360).—The specific heat of a dissolved substance is expressed by the equation

$C^1 = C(1 + m_o) - C_o m_o$, where C and C_o are the specific heats of the solution and solvent respectively, and m_o the weight of solvent per unit weight of solute. The equation given by Bertrand (*Thermodynamique*, 1887, 109) becomes, in this case, $dC^1/dV = T.d^2P/dT^2$, that is, the change of the specific heat of a dissolved substance with change of volume of the solution is proportional to the second differential coefficient of the osmotic pressure with respect to temperature. The following three cases are discussed and applied experimentally: (1) $dC^1/dV = 0$, that is, the specific heat of the solute is constant, and does not change with the concentration of the solution; as d^2P/dT^2 is also zero, the osmotic pressure must, in this case, be either a linear function of, or independent of, the temperature, both of which relations are practically possible. (2) dC^1/dV is greater than zero, that is, the specific heat of the solute increases with dilution of the solution. As, also, d^2P/dT^2 is greater than zero, the osmotic pressure is not a linear function of, but increases more rapidly than, the temperature. There are many solutions exhibiting this property, notably aqueous solutions of organic hydroxylic compounds. (3) dC^1/dV is less than zero, that is, the specific heat of the solute diminishes with dilution of the solution, and the osmotic pressure consequently increases in less than linear relation with the temperature. This behaviour is characteristic of dilute solutions of electrolytes, and stands in intimate relation to their electrical conductivity. T. H. P.

Changes of Specific Heat of Ethyl Alcohol Dissolved in Liquid Hydrocarbons. IVAN SHREDER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 360—367).—The author has determined the specific heat of solutions of various concentrations of ethyl alcohol in naphtha, benzene, or chloroform, and of methyl alcohol in benzene, toluene, or chloroform. The values of the specific heat of alcohol in the various solutions have been calculated on the basis of the law of mixtures. It is found that the specific heat of the alcohol increases towards a definite limiting value as the concentration of the alcohol in the solution diminishes. Further, the specific heats of alcohol in solutions of equivalent concentration in benzene and naphtha are identical. The numbers thus calculated for the specific heat of alcohol in solution are regarded by the author as the specific heats of alcohol which has undergone change during solution, the values representing the measures of such change. At any given moment a solution must be looked on as a mixture of dissociated and associated products, and it is probable that every liquid is really a solution in this sense of the term. T. H. P.

Latent Heat of Vaporisation and Specific Heat of Methyl Silicate. LOUIS KAHLENBERG and ROBERT KOENIG (*J. Physical Chem.*, 1908, 12, 290—292).—The latent heat of vaporisation of silicon tetrachloride is 36.1, and its average specific heat between 20° and 40° is 0.1904, which confirms Regnault's value; the heat of vaporisation of methyl silicate, $\text{Si}(\text{OMe})_4$, is 46.5, and its average specific heat between 23° and 115° is 0.5011. G. S.

Evaporation of Water and Solutions of Sulphuric Acid. P. VAILLANT (*Compt. rend.*, 1908, 146, 811—814).—It has been

shown previously (*ibid.*, 582) that if the ratio of the weight of water evaporated (p) to the fall of the vapour tension ($F-f$) is constant, its value may be obtained from the expression $B = (p - p')/(F - F')$, in which p and p' are the weights evaporated in the same time from pure water (vapour tension, F) and a sulphuric acid solution (vapour tension, F'), B being independent of the concentration of the solution. The value 0.610 mg. per hour and per sq. cm. was obtained for B at 16° and 745 mm., the surface of the liquid being 5.5 mm. below the edge of the containing vessel.

Repetition of the former experiments, using a larger quantity of liquid, the surface of which was only 3 mm. below the rim of the vessel, gave the value 0.745 mg. for B at 21°. That the difference between the two results is mainly due to the smaller depth of the liquid surface below the vessel's edge in the second case is shown by the fact that with pure sulphuric acid, B increases from 0.652 mg. when this depth is 4.8 mm. to 0.891 mg. when it is 1.2 mm., the temperature being practically constant. These experiments being made on a balance pan refer only to the first instants of the evaporation, when the influence of the distance of the liquid surface from the rim of the vessel would be expected to be greatest, but experiments lasting two hours, made with solutions containing from 100% to 24.25% of sulphuric acid, also give a value for B which, except for the 100% acid, is practically constant, the mean value being 0.701 mg. (depth of surface 3.9 mm.). A similar concordance is observed when the liquid surface is only 0.5 mm. from the vessel's edge, although B has now increased to 0.931 mg.

If, however, the evaporation vessels are surrounded by cylinders 25 cm. high, B is no longer independent of the concentration of the acid, but increases from 0.396 mg. with 73.13% acid to 0.733 mg. with 24.25% acid, and the evaporation is no longer proportional to the fall of tension. This case is shown to be fairly well expressed by the equation $p = B_1(F - f) + B_2(F - f)^2$, the extreme values of B being 0.362 mg. and 0.321 mg., and of B_2 , 0.0317 mg. and 0.0288 mg.

E. H.

Apparatus for Fractional Distillation under Reduced Pressure. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1908, [iv], 3, 411).—This is a modification of Brühl's apparatus designed to permit of the separation of the fractions obtained during fractional distillation under reduced pressure without stoppage of the distillation. The receiver is a cylindrical glass vessel, 20 cm. high and 7—8 cm. wide, containing test-tubes arranged vertically round the walls and having near its base an aperture by which it may be exhausted, and provided with a bell-shaped glass cover which fits air-tight to the receiver by means of ground-glass flanges in the usual manner. An adapter ground along part of its length to fit an aperture in the cover of the receiver conveys the distillate from the condenser tube to a test-tube in the receiver, and by rotating the latter a fresh test-tube can at any desired stage in the distillation be brought under the adapter.

T. A. H.

Receiver for Fractional Distillation under Reduced Pressure. HENRI VIGREUX (*Bull. Soc. chim.*, 1908, [iv], 3, 479—481).—The apparatus consists of a short upright condenser, the outer chamber of which serves as a receiver and is provided with (a) a side tube connecting it to the distilling flask, (b) a side tube by which it can be evacuated, and (c) an opening at the base elongated into a tube provided with a stopcock, which gradually widens into a globular receptacle. This receptacle is provided near its upper end with two side stopcocks by means of which communication can be established with the atmosphere or with a pump, and terminates in a third stopcock by which fractions can be drawn off. The apparatus can be used with one or two pumps. With one pump, three fractions can be collected without interrupting the distillation, and with two pumps the operation need not be interrupted until the distillation is completed. The apparatus is figured in the original.

T. A. H.

Internal Energy of Dissolved Substances. A. SCHÜKAREFF (*Zeitsch. physikal. Chem.*, 1908, 62, 601—606).—The author has extended his study of the change of energy exhibited by gaseous-liquid systems in the neighbourhood of the critical temperature (see Abstr., 1903, ii, 710; 1906, ii, 271) to the case of partly miscible liquids in the neighbourhood of the critical solution temperature. Experiments were carried out in which homogeneous mixtures of phenol and water were cooled from temperatures at and above the critical solution temperature (T_c) to the ordinary temperature, and the heat effects determined. In supplementary experiments, the heat liberated in the crystallisation and cooling of pure phenol from 46° to 20° was found to be 39.5 cal. for each gram of phenol. Further, the heat liberated on mixing 1 gram of liquid phenol at 46° with various quantities of water was found to be 8.5 cal.

The internal energy E of dissolved phenol at 20° is estimated as the sum of (1) the heat of separation at T° of a homogeneous solution into pure phenol and water, and (2) the heat liberated in cooling pure phenol from T° to 20° . When E is plotted against concentration, curves are obtained which at temperatures above T_c are concave to the concentration axis. The curvature diminishes as this temperature is approached, until for T_c the curve becomes a straight line. At this temperature, therefore, the heat effect of mixing variously concentrated phenol solutions is zero.

J. C. P.

Condition of Substances in Absolute Sulphuric Acid. ARTHUR HANTZSCH (*Zeitsch. physikal. Chem.*, 1908, 62, 626—630. Compare this vol., ii, 14).—A reply to Oddo and Scandola (this vol., ii, 353). The author criticises the use of hygroscopic substances, like phosphoryl chloride and sulphuryl chloride, in finding the molecular depression of the freezing point for sulphuric acid. It is shown that when perfectly dry pyridine, quinoline, and acridine are taken as solutes, figures are obtained for the molecular weights which are about two-thirds of the normal values. Oddo and Scandola's values

for the molecular weights of pyridine and quinoline are too low, on account of the presence of moisture. J. C. P.

Combustion without Flame, and its Application to Lighting with Incandescent Mantles. JEAN MEUNIER (*Compt. rend.*, 1908, 146, 864—866. Compare this vol., ii, 276).—The author supposes that the temperature of the mantle is very much higher than that of the flame surrounding it. The action of the mantle consists in causing combustion to take place by incandescence as distinguished from combustion by flame, each particle of oxide acting as the centre of such a local combustion. The combustion of a gas in the manner indicated, lowers the inferior limit of inflammability of a gas mixture.

H. M. D.

Calculation of Thermochemical Constants. H. STANLEY REDGROVE (*Chem. News*, 1908, 97, 183—185. Compare Abstr., 1907, ii, 604).—It is evident from a consideration of the molecular heats of combustion and molecular heats of formation of the hydrocarbons (Abstr., 1907, ii, 929) that, in general, the former are more suitable for the calculation of constants than the latter, and constitute better criteria for the examination of any hypotheses on the subject. It is observed that the effect on the molecular heat of combustion (1) of replacing a hydrogen atom in any hydrocarbon by a chlorine atom is constant; similarly with bromine and iodine; (2) replacing in turn one, two, or three hydrogen atoms in any hydrocarbon by chlorine is constant; (3) the mere position of the halogen has no effect on the molecular heat of combustion. Molecular heats of combustion have been calculated for a number of organic halogen compounds, using the author's "fundamental molecular heat of combustion halogen constant," and are compared with the values found by Thomsen. The molecular heats of formation of the substances have been calculated in a similar manner, and compared with the experimental values.

J. V. E.

Changes in the Viscosity of Liquid Sulphur. LÉON ROTINJANZ (*Zeitsch. physikal. Chem.*, 1908, 62, 609—621. Compare Smith, Abstr., 1905, ii, 382; Smith, Holmes, and Hall, *ibid.*, 580).—The viscosity of liquid sulphur has been determined at various temperatures. With sulphur, the temperature of which has been raised gradually at the rate of 0.27° to 1.0° per minute, the maximum viscosity (52,000 relatively to water) is found at 187° . If the rate of heating has been greater, the maximum occurs at higher temperatures. With sulphur, the temperature of which has been lowered gradually, the maximum value of the viscosity and the temperature at which it occurs depend on the temperature to which the sulphur has been raised previously. The higher the temperature to which the sulphur has been heated the lower is the maximum value of the viscosity, and the higher is the temperature at which it is found.

Sulphur through which a current of ammonia has been passed has a maximum viscosity of 19,000 at 180° ; sulphur containing 0.02% iodine has a maximum viscosity of 5600 at 225° , whilst with a

content of 0.77% iodine the maximum viscosity is only 300 at 265°. The relation of the viscosity curve obtained with rising temperature to that obtained with falling temperature is very much the same for these samples of sulphur as for pure sulphur. In the case of sulphur which has been treated with ammonia, there is a break in the falling branch of the viscosity curve at 210°, marked also by a change of colour similar to what is observed in the case of pure sulphur at higher temperatures.

The author draws the conclusion from his experiments that the changes of viscosity exhibited by liquid sulphur are not to be attributed to the presence of amorphous insoluble sulphur.

J. C. P.

Study of the Solutions of Some Salts Exhibiting Negative Viscosity. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1908, 30, 721—737).—Determinations of the viscosities of some solutions of potassium salts having lower viscosities than that of the solvent (Getman, Abstr., 1907, ii, 517) showed that in every case the viscosity-concentration curve passed through a minimum, and it was suggested that this abnormal behaviour was due to the combined action of the ions and the non-dissociated molecule, the potassium ion appearing to lower the viscosity of the solvent, whilst the anions and non-dissociated molecules tended to increase it. Jones and Veazey (Abstr., 1907, ii, 438) have found that the solutions which diminish the viscosity of water are those which have cations with large atomic volumes.

A study has now been made of the viscosities of aqueous solutions of ammonium chloride, bromide, and nitrate, and rubidium iodide. The results, which are tabulated and plotted as curves, appear to confirm the theory suggested by the author. In accordance with the view of Jones and Veazey, it would be expected, for a series of salts having the same anion, that the lowering of the viscosity would vary directly with the atomic volume of the cation. It is found that rubidium iodide lowers the viscosity to a greater extent than potassium iodide, whilst the lowering produced by ammonium iodide is slightly less than that produced by rubidium iodide.

It was observed that the negative viscosity was in all cases greater at the lower temperatures. This cannot be explained by differences in the degree of dissociation at different temperatures, but it is probable that at the lower temperatures, molecular complexes are formed which, owing to greater volume and smaller surface, cause a diminution in the viscosity (compare Dunstan, Trans., 1904, 85, 817).

Slotte's empirical formula for calculating viscosities at various temperatures has been found applicable to the solutions studied between 15° and 20°. On Wiedemann's theory that the migration velocity varies inversely with the viscosity for a fixed potential gradient, the product of viscosity and conductivity should be a constant. This relation has been found to be only approximately true for the solutions investigated.

E. G.

The Internal Friction of Colloidal Solutions. H. W. WOODSTRA (*Chem. Weekblad*, 1908, 5, 303—312).—I. *The Internal*

Friction of Colloidal Silver Solution.—The viscosity has not a constant value, but diminishes with lapse of time. The presence of metallic salts diminishes the viscosity, the effect of salts of multivalent metals being greater than that of salts of univalent metals.

A. J. W.

Osmotic Pressure of Concentrated Solutions, and the Laws of the Perfect Solution. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1908, 30, 668—687).—The simple laws which are applicable to infinitely dilute solutions are not valid in the case of solutions of finite concentration, Raoult's law being the only one which ever holds in concentrated solutions. This law is re-stated as follows: "At constant pressure and temperature, the activity of the solvent in a perfect solution is proportional to its mol. fraction" (the number of mols. of solvent in one mol. altogether of solvent and solute). Several solutions are mentioned which behave as perfect solutions over the whole range of concentrations from 0% to 100% solute.

The indirect methods of determining osmotic pressure are discussed, and an exact relation between the osmotic pressure and the depression of the f. p. of an aqueous solution is given. It is also shown that the osmotic pressure at one temperature may be obtained from that at any other when the heat of dilution is known, and that, by the aid of thermodynamics alone, an equation can be obtained connecting the osmotic pressure and the concentration of a perfect solution which permits the exact calculation of osmotic pressures in perfect solutions up to 100 atmospheres. In comparatively dilute solutions, the pressures thus obtained are practically identical with those given by van't Hoff's equation as modified by Morse and Frazer, but at high concentrations the divergence is very great. An exact form is given for the mass law in concentrated perfect solutions.

E. G.

Apparatus for [the Study of] Diffusion in Solid Media. MICHEL YÉGOUNOFF (*Arch. sci. phys. nat.*, 1908, [iv], 25, 350—359).—Several pieces of apparatus which the author has used in the investigation of the rate of diffusion of substances in gelatin are described.

H. M. D.

Apparatus for Continuous Dialysis. SAMUEL B. SCHRYVER (*Proc. physiol. Soc.*, 1908, xxiii—xxiv.; *J. Physiol.*, 37).—This is essentially a modification of the Soxhlet apparatus, for continuous dialysis against distilled water or other liquids. Chiffon soaked in collodion is used for the membrane.

W. D. H.

Conditions of Possibility of Certain Reactions Forming Monovariant Systems. CAMILLE MATIGNON (*Ann. Chim. Phys.*, 1908, [viii], 14, 5—125).—After summarising the work of previous investigators in this field, the author proceeds to discuss in fuller detail the proposition relating to variation of entropy in monovariant systems undergoing dissociation which he has enunciated in former communications (compare Abstr., 1899, ii, 273; 1905, ii, 235).

Dealing with over fifty illustrative examples, the law is shown to hold true in the following cases: (1) in monovariant systems containing any number of solids, as, for example, $\text{Na}_2\text{SO}_{4\text{sol.}} + \text{HCl}_{\text{gas}} \rightleftharpoons \text{NaHSO}_{4\text{sol.}} + \text{NaCl}_{\text{sol.}} + Q \text{ cal.}$; (2) in systems which yield several gases on dissociation, for example, $\text{NH}_{3\text{gas}} + \text{H}_2\text{S}_{\text{gas}} \rightleftharpoons \text{NH}_4\text{HS}_{\text{sol.}} + Q \text{ cal.}$; (3) systems containing a gas and a liquid, one in the initial, the other in the final, stage, that is, systems conforming to the general type $\text{A}_{\text{gas}} + \text{B}_{\text{sol.}} + \dots + \text{C}_{\text{sol.}} \rightleftharpoons \text{A}'_{\text{liq.}} + \text{B}'_{\text{sol.}} + \dots + \text{C}'_{\text{sol.}}$; (4) systems dissociating into both liquid and gas, conforming to the type $\text{A}_{\text{gas}} + \text{B}_{\text{liq.}} + \text{C}_{\text{sol.}} + \dots + \text{D}_{\text{sol.}} \rightleftharpoons \text{A}'_{\text{sol.}} + \text{B}'_{\text{sol.}} + \dots + \text{D}'_{\text{sol.}}$. W. O. W.

Deduction of Gibb's Phase Rule. JOSEPH A. MULLER (*Compt. rend.*, 1908, 146, 866—867).—A simple method of deducing the relationship between the number of substances and phases of a system in equilibrium is given in which thermodynamical considerations are not involved. H. M. D.

[Vapour Pressure of Dry and of Ordinary Sal Ammoniac.] RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1908, 62, 607—608. Compare this vol., ii, 157; also Johnson, *ibid.*).—The author maintains, in opposition to van Laar (this vol., ii, 353), that the theory of heterogeneous equilibrium is applicable to the vaporisation of dry ammonium chloride, since the equilibrium can be reached from both sides. Two suggestions are made by way of explanation: (1) the heat of formation of undissociated gaseous ammonium chloride from solid ammonium chloride may be equal to the heat of dissociation of gaseous ammonium chloride into ammonia and hydrogen chloride, or (2) the molecular weights of the products of vaporisation of sal ammoniac may not be the same in the moist and the dry states. J. C. P.

Two New Methods for the Determination of the Secondary Ionisation Constants of Dibasic Acids. HERBERT N. MCCOY (*J. Amer. Chem. Soc.*, 1908, 30, 688—694).—The ionisation of a dibasic acid, H_2X , takes place in the two following stages: (1) $\text{H}\cdot\text{HX} = k_1\text{H}_2\text{X}$; (2) $\text{H}\cdot\text{X} = k_2\text{HX}$, where k_1 and k_2 are the ionisation constants, and the formulæ represent the molar or ionic concentrations of the corresponding substances. The state of equilibrium is found by combining these two equations, which gives $\text{HX}^2/\text{H}_2\text{X}\cdot\text{X} = k_1/k_2$. The author has shown previously (*Abstr.*, 1903, ii, 413) that the equilibrium in solution of the sodium carbonates is accurately represented thus: $\text{NaHCO}_3^2/\text{H}_2\text{CO}_3 \times \text{Na}_2\text{CO}_3 = \text{a constant}$. For a fixed concentration of total sodium, a good constant was found for all proportions of carbonate, hydrogen carbonate, and carbonic acid. The same principle may be applied to the study of solutions of salts of all the non-volatile acids, provided that they are sufficiently soluble in water and in some inert solvent which is immiscible with water. The aqueous solution is shaken, until equilibrium is reached, with a solvent in which the acid is soluble, but the salts insoluble. The concentration of the non-ionised free acid in the aqueous layer is directly proportional to the concentration of the same substance in the immiscible solvent, the proportionality factor being the partition

coefficient of the free acid alone, for the two solvents. A simple analysis of the aqueous solution gives the remaining data for the calculation of the concentrations HX and X . Experiments on these lines have been carried out with succinic acid and its sodium salts.

A method is described for the calculation of the secondary ionisation constant, k_2 , of a dibasic acid from the conductivities of dilute solutions of the acid and neutral sodium salts. E. G.

Ionisation Constants of the Secondary Hydrogen Ion of Dibasic Acids. E. E. CHANDLER (*J. Amer. Chem. Soc.*, 1908, 30, 694—713).—The methods described by McCoy (preceding abstract) for determining the secondary ionisation constants of dibasic acids, and applied by him to the sodium salts of succinic acids, have been extended to the salts of oxalic, malonic, pimelic, glutaric, suberic, azelaic, sebacic, phthalic, isophthalic, camphoric, itaconic, maleic, fumaric, and mono- and di-bromosuccinic acids. Determinations have been made of the partition coefficients of the acids between water and ether, the equilibrium constants, and the conductivities of the salt solutions. The results are tabulated.

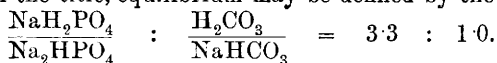
With regard to the partition experiments, the degree of ionisation, α , of an acid was calculated from the primary ionisation constant, k_1 , by means of the equation $\alpha^2/(1-\alpha)V=k_1$. The results are expressed as p , the ratio of the concentration of an aqueous solution of the acid to that of the corresponding ethereal solution, and as P , the true partition coefficient, the ratio of the concentration of the non-ionised acid in the two solvents. In the case of oxalic acid, the value of p varies very greatly with the concentration, whilst the value of P is constant within the limits of experimental error. In its change of ionisation with concentration, oxalic acid does not follow exactly Ostwald's dilution law, and in this respect resembles salts and the strong acids and bases.

It has been found that for constant concentrations of the total base, the value of k_1/k_2 is independent of the ratio of base to acid. The value increases, however, with decreasing concentration of the total base. The constant k_1/k_2 for dibromosuccinic acid does not differ much from that for succinic acid, although both k_1 and k_2 are very much greater, whence it is evident that the substitution of the halogen affects the dissociation of the two hydrogen atoms almost equally.

The determinations of the secondary ionisation constant by the conductivity method led to the conclusion that the conductivities of the HX ions were in all cases approximately equal to those of the corresponding X ions. The values of k_2 found by this method agree closely with those obtained from the partition experiments. E. G.

Equilibrium between Carbon Dioxide, Sodium Hydrogen Carbonate, Monosodium Phosphate, and Disodium Phosphate at Body Temperature. LAWRENCE J. HENDERSON and OTIS F. BLACK. **Theory of Neutrality Regulation in the Animal Organism.** L. J. HENDERSON (*Amer. J. Physiol.*, 1908, 21, 420—426, 427—448).—The first paper deals with solutions, and a

method is described for saturating them at constant temperature with carbon dioxide of known tension. In solutions containing the substances mentioned in the title, equilibrium may be defined by the proportion



This relationship corresponds with the requirements of the concentration law. These facts serve to define the most important equilibria of neutrality regulation in the aqueous solutions of the body, and the physiological factors involved in this regulation and a theory founded on the observations are discussed in the second paper. W. D. H.

Free Energy of Nickel Chloride. M. DEKAY THOMPSON and M. W. SAGE (*J. Amer. Chem. Soc.*, 1908, 30, 714—721).—Calculations of the free energy have been made by Thompson (Abstr., 1906, ii, 517) from potential measurements of all compounds for which the necessary data existed.

The free energy, ΔF , of nickel chloride has now been determined by measuring the *E.M.F.* of the cell: nickel | saturated solution of NiCl_2 | $\text{Pt} + \text{Cl}_2$. A formula has been deduced for ΔF involving the potential of this cell and the vapour pressure of the saturated solution of the systems $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ — $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ — NiCl_2 , the pressure of the latter system being obtained both by direct and indirect measurement. The value of ΔF was found to be -74.4 Cal. The free energy and total energy of nickel chloride were found to be approximately equal. E. G.

Conditions of Equilibrium in the Systems Ferric Chloride—Potassium Ferrocyanide—Water. V. VOLSCHIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 480—485).—The author has studied the formation of insoluble or soluble Prussian blue in aqueous solutions containing ferric chloride and potassium ferrocyanide in varying proportions and concentrations. The concentration of ferric chloride in the initial solution in gram-equivalents per litre is expressed by C , the ratio of the corresponding concentration of the potassium ferrocyanide to C being denoted by k .

When C is constant and has the value 0.06—0.07, variation of the concentration of the ferrocyanide reveals the existence of a "critical" point; mixtures for which k is less than 1 give precipitates, whilst those for which k is greater than 1 appear to be real solutions. Observations of various of these solutions show that, in time, certain of them undergo complete precipitation, the liquid becoming absolutely free from Prussian blue. The time, t , required for this coagulation depends on both C and k ; when the former is constant, t increases as k diminishes, and when k is constant, it increases as C diminishes. Investigation of the relation between C and t shows that, when C is sufficiently large, all the mixtures should undergo coagulation, no matter whether k is less or greater than 1. This is confirmed by experiment, for when $C=0.1$ the most stable solution coagulates in a few minutes, whilst when $C=0.2$, all mixtures coagulate rapidly, the more so as the critical point becomes more remote. Hence the conclusion is drawn that no mixture containing

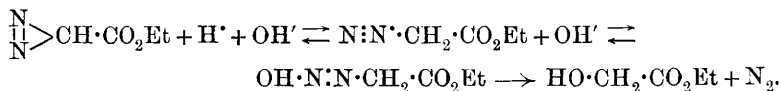
FeCl_3 , K_4FeCy_6 , and H_2O gives a stable solution, and that a soluble Prussian blue (in the ordinary meaning of the term soluble) does not exist. When C is small and k only slightly greater than 1, k may be practically infinite. The value of k corresponding with the critical point is not constant, but increases from 0.9353 to 1.0921 as C is increased from 0.00261 to 0.04828.

T. H. P.

Equilibrium in the System: Silver Nitrate and Pyridine.
LOUIS KAHLENBERG and ROBERT K. BREWER (*J. Physical Chem.*, 1908, 12, 283—289).—The complete solubility curve for silver nitrate in pyridine has been determined from the melting point of the latter to 110° . Pyridine melts at -48.5° , and its eutectic point with the compound $\text{AgNO}_3 \cdot 6\text{Py}$ is at -65° . From -65° to -24° , the solution is in equilibrium with the compound $\text{AgNO}_3 \cdot 6\text{Py}$, which was not previously known; from -24° to $+48.5^\circ$ with the compound $\text{AgNO}_3 \cdot 3\text{Py}$; from 48.5° to 79° with the compound $\text{AgNO}_3 \cdot 2\text{Py}$, and above the latter temperature with silver nitrate. The dipyridine compound melts without decomposition at 87° . The di- and tri-pyridine compounds have already been described by Jørgensen (*J. pr. Chem.*, 1886, 33, 501).

G. S.

Kinetics of Ethyl Diazoacetate and the Dilution Law.
OTTO MUMM (*Zeitsch. physikal. Chem.*, 1908, 62, 589—600).—The author supposes that as regards decomposition with evolution of nitrogen there is complete analogy between aromatic and aliphatic diazo-compounds, and that the decomposition of ethyl diazoacetate may be represented as follows:



On this basis, the experimental results obtained by Fraenkel (Abstr., 1907, ii, 746) and by Bredig and Ripley (Abstr., 1907, ii, 941), especially as these bear on the secondary formation of ethyl chloroacetate in presence of hydrochloric acid, are discussed. The following conclusions are deduced: (1) the concentration of the undissociated portion of diazo-chloride is directly proportional to the concentration of the diazo-ion; (2) the concentration of the undissociated portion of diazo-chloride is nearly proportional to the cube root of the concentration of the chlorine ion.

It appears therefore that the experiments carried out by Bredig and his pupils throw light on the question how the concentration of the undissociated part of a strong electrolyte alters when the concentration of one ion only changes. The author thus arrives at the following formulation of the dilution law: $Kc = c_1^{4/3}$, which is similar to those suggested by van't Hoff and by Bancroft (see Abstr., 1900, ii, 186). The fact that in the case of diazo-chloride the concentration of the undissociated portion varies proportionally to the cube root of the anion concentration is interpreted by the assumption that in solution three anions are united to form a complex (compare Morgan and

Kanolt Abstr., 1904, ii, 535). The bearing of such an assumption on the behaviour of strong electrolytes generally is discussed.

J. C. P.

Physicochemical Investigation of Amylase and Maltase. MLEE. CH. PHILOCHE (*J. Chim. phys.*, 1908, 6, 212—293).—The action of maltase on maltose, and of amylase (diastase) on starch and on glycogen, has been systematically investigated, but the present paper only contains part of the results obtained with the latter enzyme.

Maltase and Maltose (compare Terroine, Abstr., 1904, ii, 317).—Maltase from Taka-diastase (Merck) was allowed to act on maltose at 39° and 40° in various dilutions, and the reaction was followed mainly with the polarimeter. The question of the stability of the enzyme and of the influence of the products of reaction on the velocity has already been discussed (Abstr., 1904, i, 839; ii, 318). The velocity of the reaction is proportional to the enzyme concentration, but when more than 2% of maltose is present, it is independent of the concentration of the latter. The initial velocity, v , for different maltose concentrations is represented satisfactorily by the formula $v = Ka/(1 + ma)$, where a is the maltose concentration, and K and m are constants. As regards the whole course of the reaction, the velocity is greater than the logarithmic law would indicate, but is represented satisfactorily by the empirical formula $2K_1 = 1/t \log(a + x)/(a - x)$ (where x/a is the proportion of maltose decomposed at the time t), which also holds for the hydrolysis of sucrose by invertin (Henri, Abstr., 1902, ii, 127).

Amylase on Starch and Glycogen (compare Brown and Glendinning, Trans., 1902, 81, 388).—Three specimens of amylase from Taka-diastase, from "absolute diastase" (Merck) obtained from malt, and from pancreatic juice respectively were employed. These were allowed to act on soluble starch at 31.5°, and at definite intervals part of the mixture was removed, the reaction stopped by adding hot water, and the maltose estimated by Fehling's solution.

Up to 2½% of starch, the velocity of the reaction depends on the starch concentration, but for solutions containing more than the above proportion of starch the rate is independent of the concentration of the latter. On the other hand, the rate of appearance of maltose increases with the glycogen concentration at least up to 5% of the latter.

When the concentration of the substance acted on is constant, the rate of formation of maltose increases less rapidly than the concentration of amylase, both for the hydrolysis of starch and glycogen. In the case of starch, the velocity is represented by the linear equation $x = Bc - Ac^2$, where c is the concentration of the diastase and x the quantity of maltose formed, and A and B are constants, but in glycogen solutions, the relation appears to be more complicated. G. S.

Relation between Rotatory Power and Chemical Constitution. D. HARDIN and S. SIKORSKY (*J. Chim. phys.*, 1908, 6, 179—211).—A number of amyl derivatives have been prepared, and the specific rotations determined at intervals of 10° to 15° from the ordinary temperature to within a few degrees of the respective

boiling points. The data thus obtained are employed to test certain theoretical deductions as to the relation between rotatory power and chemical constitution.

It is assumed that in the cases dealt with, the centres of gravity of the side chains lie on the axes of the asymmetric carbon atom at different distances from it, and that the distances of the atoms in a molecule depend only on their nature and not on their arrangement. The formula connecting the product of asymmetry (Guye) and the angle of rotation, deduced on the above assumptions, contains only one unknown quantity, c , which is a function of the distance between the carbon atoms. From the experimental data, it is shown that for the simplest amyl derivatives containing not more than four atoms of carbon, c has the same numerical value, but the arrangement of the atoms in the group C_3H_{11} and higher groups must be different from that generally assumed. It is further shown that the product of the distance between an atom of a given element and an atom of carbon by the atomic weight of the element depends on the position of the latter in the periodic table, and on certain constants referring to carbon chains. For certain other deductions, more particularly as to the sign of the rotation, the original paper should be consulted.

The amyl derivatives examined were prepared from *l*-amyl alcohol (Kahlbaum), but, as the latter contained only 95% of the pure compound, the products were not quite pure. For γ -methylhexane (Marckwald, Abstr., 1904, i, 362), $[\alpha]_D$ varies only very little between 15° and 85° . β -Dimethylheptane (Guye and Amaral, Abstr., 1895, ii, 472) has D^{16} 0.7154, $[\alpha]_D^{16} + 9.48^\circ$, D^{25} 0.6334, $[\alpha]_D^{25} + 8.71^\circ$, n_D^{16} 1.40713. γ -Methyloctane was prepared by the action of metallic sodium on a mixture of *n*-butyl iodide and amyl iodide and repeated fractionation. The fraction boiling at 142.4 — 143.4 has D^{17} 0.7206, $[\alpha]_D^{17} + 9.38^\circ$, D^{40} 0.6192, $[\alpha]_D^{40} + 8.48^\circ$, n_D^{40} 1.4092. Diisomyl (Guye and Amaral, *loc. cit.*) was prepared by fractionation from the higher boiling portion of the mixture of hydrocarbons obtained as above. The fraction boiling at 159.8 — 160.8° has D^{13} 0.7348, $[\alpha]_D^{13} + 16.85^\circ$, $D^{45.5}$ 0.6343, $[\alpha]_D^{45.5} + 16.32^\circ$. Active amyl chloride (β -methylbutyl chloride), b. p. 97.6 — 99° , has $D^{17.5}$ 0.8812, $[\alpha]_D^{17.5} + 1.38^\circ$, D^{24} 0.8055, $[\alpha]_D^{24} + 0.86^\circ$; the bromide, b. p. 121 — 121.4° , has $D^{31.5}$ 1.2072, $[\alpha]_D^{31.5} + 3.69^\circ$, D^{115} 1.0973, $[\alpha]_D^{115} + 2.71^\circ$. For the corresponding amyl amine, $[\alpha]_D$ (-5.86° , according to Marckwald, *loc. cit.*) scarcely alters between 18° and 85° ; the acetate, b. p. 141.2 — 142° , has $D^{12.5}$ 0.8803, $[\alpha]_D^{12.5} + 3.35^\circ$, D^{35} 0.7609, $[\alpha]_D^{35} + 3.36^\circ$; the mercaptan, $C_5H_{11} \cdot SH$, b. p. 117.4 — 117.6° , has D^{13} 0.8483, $[\alpha]_D^{13} + 3.49^\circ$, D^{117} 0.7565, $[\alpha]_D^{117} + 2.04^\circ$. The acetal, $CHMe(OC_5H_{11})_2$, was prepared by passing hydrogen chloride into a mixture of acetaldehyde and active amyl alcohol at 0° and allowing it to remain at 0° for twenty-four hours. The fraction boiling at 207 — 209° has D^{21} 0.8255, $[\alpha]_D^{21} + 1.55^\circ$, D^{200} 0.6712, $[\alpha]_D^{200} + 3.50^\circ$; the cyanide (β -methylbutyronitrile), b. p. 151.4 — $152.6^\circ/743$ mm., has D^{10} 0.8395, $[\alpha]_D^{10} + 7.22^\circ$, D^{45} 0.7272, $[\alpha]_D^{45} + 6.29^\circ$ at 145° . β -Methylbutyric acid, prepared by hydrolysis of the nitrile, has b. p. 197.4 — 198° , D^{75} 0.8866, $[\alpha]_D^{75} + 6.43^\circ$, D^{49} 0.7178, $[\alpha]_D^{49} + 5.22^\circ$. The methyl ester has b. p. 141 — 142° , D^{65} 0.8885, $[\alpha]_D^{65} + 6.97^\circ$, D^{137} 0.7727, $[\alpha]_D^{137} + 5.22^\circ$.

G. S.

Catalysis. III. The Theories of Esterification and Saponification. JULIUS STIEGLITZ (*Amer. Chem. J.*, 1908, 39, 402—431).—Polemical. A reply to Acree (this vol., ii, 169).

R. J. C.

Catalysis. VIII. Theories of Catalysis. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, 39, 513—527).—Polemical. A reply to Stieglitz (preceding abstract).

E. G.

Pulsating Catalysis of Hydrogen Peroxide by Mercury. I—III. A. VON ANTROPOFF (*Zeitsch. physikal. Chem.*, 1908, 62, 513—588).—A continuation of earlier work on this subject (see Bredig and Weinmayr, *Abstr.*, 1903, ii, 279; Bredig and Wilke, *Abstr.*, 1905, ii, 151).—The periodic changes in the rate of gas evolution and in the potential difference at the electrode $\text{Hg} | \text{H}_2\text{O}_2$ have been recorded simultaneously by self-registering apparatus (compare Ostwald, *Abstr.*, 1901, ii, 24; Brauer, *ibid.*, 635). A large number of the curves obtained are appended to the paper, and these are discussed in detail, more especially in reference to the effect of various dissolved substances on the character of the reaction.

The potential difference of the calomel electrode being taken as -0.56 volt, the potential difference for $\text{Hg} | \text{H}_2\text{O}_2$ was found in different experiments to lie between -0.73 and -0.84 for the active condition, and between -0.84 and -0.97 for the inactive condition. Addition of alkali makes the potential of the solution more negative, whilst the addition of acid has the opposite effect.

The changes taking place at the mercury surface have been observed under the microscope, and it is found that the catalysis occurs only in the presence of the surface film referred to in the earlier paper (*loc. cit.*). The evolution of oxygen occurs only at the edges of this film, the periodic disappearances of which are due to its dissolution. For the initiation of the active stage in the pulsating reaction, a rupture of the surface film is necessary.

A closer study of the recorded curves shows that the rate of oxygen evolution is approximately proportional to the length of the boundary between the film and the bright mercury surface, whilst the potential rises and falls proportionally to the extent of the bright mercury surface.

The author regards the film as due to the formation of a precipitate (probably mercurous peroxide) after sufficient mercury ions have gone into solution. The film once formed is ruptured mechanically, and its subsequent dissolution is due to local electrical currents produced at the boundary between film and bright mercury surface. The pulsating catalysis of hydrogen peroxide by mercury is accordingly described as an intermittent electrolysis of hydrogen peroxide.

J. C. P.

Catalytic Reactions at High Temperatures and Pressures. XXI. The Decomposition of Alcohols in Presence of Metallic Oxides. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 508—513. Compare this vol., ii, 266).—The author has studied the catalytic decomposition of isobutyl alcohol by Cr_2O_3 , MnO_2 , Ni_2O_3 ,

Cu_2O , ZnO , SnO , SnO_2 , UO_2 , and Ag_2O , the resulting products being compared with those obtained by using the corresponding metals as catalysts.

If a metal acts as a catalyst in the aldehydic decomposition of alcohols, its oxide generally exhibits the same property, even although it is incapable of undergoing complete reduction to metal. Thus zinc oxide acts as an excellent catalyst in this reaction, although it is not appreciably reduced. It may be that intermediate reduction of zinc oxide and oxidation of the reduced product take place to an inappreciable extent, as a small quantity of zinc oxide is always formed during the catalysis of alcohol by metallic zinc. The conclusion is drawn that water and metallic oxide play a part in these catalytic decompositions of alcohol.

The effectiveness of the metals and their oxides as catalysts is related to the position of the metals in the periodic system of the elements. Arrangement of the metals in the order of the amounts of aldehyde formed in their action on alcohol gives the series: chromium, manganese, iron, cobalt, nickel, copper, zinc; chromium yields the least, and zinc the most, aldehyde. The capacity of manganese, iron, cobalt, and nickel for decomposing the aldehyde formed into hydrocarbon and carbon monoxide increases in the order in which these metals occur in the periodic arrangement of the elements. Metals having high atomic weights and their oxides produce a two-fold decomposition of alcohols, namely, into aldehydes and into ethylene hydrocarbons. The best metallic catalyst for the production of aldehydes and ketones from alcohols is zinc, the catalytic properties of which are not impaired by the passage of the alcohol through it. On the other hand, the catalytic activity of reduced copper, which never gives rise to such a high yield of aldehyde as does zinc, becomes gradually weakened.

The best catalysts for preparing ethylene hydrocarbons are alumina and kaolin.

When alcohol vapour is passed through magnesium oxide or barium oxide heated at $450\text{--}500^\circ$, no catalytic decomposition of the alcohol occurs.

The work of Senderens (Abstr., 1907, i, 577) is discussed.

T. H. P.

Theory of Solutions. OSCAR SCARPA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 362—369).—The author's experiments were made with a view to confirming van't Hoff's law stating that the temperature-coefficients of the pressure of a gas and of the osmotic pressure of a dissolved substance are numerically identical.

Two communicating vessels containing a salt solution were maintained at different constant temperatures until a condition of osmotic equilibrium had been attained, after which the concentrations of the salt in the two vessels were determined. Three different solutions were employed, one of sodium chloride, and two, of different concentrations, of potassium chloride. The results were, in all cases, found to be in satisfactory agreement with the equation: $\Theta/T = \gamma_2\{1 + a(\Theta - T)\}(1 + a_2)/\gamma_1(1 + a_1)$, where Θ and T are the

temperatures of the two vessels, α the coefficient of thermal expansion of the solution, γ_1 and γ_2 the molecular concentrations, and a_1 and a_2 the degrees of dissociation of the salt in the two solutions. The observations are hence in accord with van't Hoff's law.

T. H. P.

The Effect of One Salt on the Hydrating Power of Another Salt Present in the Same Solution. XX. HARRY C. JONES and CHARLES M. STINE (*Amer. Chem. J.*, 1908, 39, 313—402. Compare this vol., ii, 19).—When two salts which form solution hydrates are dissolved together in water, each will diminish the extent to which the other becomes hydrated. The authors have endeavoured to estimate the amount of this mutual interference of two salts by measurements of the conductivity and freezing points of the mixed solutions.

The pairs of salts studied always contained an ion in common, so that the retrogression of the degree of ionisation of the salts due to the presence of each other could be roughly estimated by assuming a simple mass action relation to exist between the salts and their ions. The disturbing effect of the varying amounts of combined water on this equilibrium was neglected. The viscosity of the mixtures differing considerably from that of the unmixed solutions, and the aqueous atmosphere about each ion being smaller in the mixed solutions, the resistance to ionic motion must also be different in the mixtures. The authors recognise that the conductivity of their concentrated solutions is not an accurate measure of the dissociation on account of these complications, and their theoretical deductions are somewhat vitiated thereby.

Measurements made on potassium chloride solutions lead to the conclusion that this salt is not hydrated (compare, however, Biltz, *Abstr.*, 1904, ii, 710; Caldwell, *Abstr.*, 1907, ii, 14; Philip, *Trans.*, 1907, 91, 711; Bousfield, *Abstr.*, 1905, ii, 369). On the other hand, the experimental values are not in accord with the assumption that potassium chloride is also without influence on the hydration of calcium chloride. A formula is devised to calculate the degree of hydration of calcium chloride in presence of potassium chloride. The values obtained by this means are from 2 to 4 molecules of water less than those deduced from measurements with pure calcium chloride solutions. This effect is attributed to the fact that volume-normal solutions were employed, so that there is somewhat less water per equivalent of calcium chloride in those solutions which also contain potassium chloride.

Measurements were made with the following pairs of salts: CaCl_2 — MgCl_2 , SrCl_2 — CaCl_2 , $\text{Mg}(\text{NO}_3)_2$ — $\text{Sr}(\text{NO}_3)_2$, LiBr — NaBr , $\text{Ca}(\text{NO}_3)_2$ — $\text{Mg}(\text{NO}_3)_2$, AlCl_3 — FeCl_3 , $\text{Ca}(\text{NO}_3)_2$ — CaCl_2 . The lowering of the freezing point by the mixed salts is always less than the sum of the depressions in the single solutions. It is pointed out that the hydration of each salt is necessarily diminished by the presence of the other, for otherwise some of the concentrated mixtures would contain no free water at all.

The method employed by the authors to calculate the degree of

hydration of each salt in the mixture is based on the assumption that in the competition for water each salt loses a part which is inversely proportional to its total water of hydration. The values obtained are of the nature expected, namely, that the hydration of each salt is in general somewhat diminished by the other. Deviations from this behaviour are explained by the hypothesis that the molecules of some salts may have greater hydrating power than the ions. That is, in these cases retrogression of the ionisation might lead to increase in the degree of hydration.

The diminution in molecular conductivity when solutions of potassium and ammonium chlorides are mixed is much greater at 25° than at 0°. This is contrary to expectation on the simple ionic dis-ociation hypothesis. The authors claim that it proves that conductivity does not give an accurate measure of the degree of ionisation of salts even when they may be supposed to be anhydrous in solution.

R. J. C.

Rate of Growth and Solution of Crystals. IWAN IW. ANDRÉEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 397—444. Compare Abstr., 1907, i, 336).—The results of the author's investigations lead to the following conclusions.

The rate of growth and of solution of a crystal face is given by the expression $dx/dt = kF(C - c)$, where dx/dt is the quantity of substance deposited on, or dissolved from the face in unit time, F the area of the face, C the concentration of the supersaturated or unsaturated solution, c the concentration of a solution saturated with respect to the particular face considered, and k a constant independent of the nature of the face. The relative rate of growth of any two faces varies with the concentration. In highly supersaturated solutions, the faces grow at nearly the same rate, but differences in the rates of growth appear as the solution approaches the state of saturation. By continued dilution of the solution, a point may be attained at which one face begins to dissolve, whilst another continues to grow. When etched faces appear, owing to variations in the solubility of the crystal in different directions, different faces assume almost the same rate of solution. As crystals continue to grow, the most readily soluble faces disappear, owing to the more rapid growth of the other faces.

T. H. P.

Helical Structures. PAUL GAUBERT (*Compt. rend.*, 1908, 146, 829—831. Compare Abstr., 1907, ii, 939).—When a layer of fused cholesterol, pressed between a microscopic slide and cover-glass, is repeatedly allowed to solidify and remelted, it crystallises entirely in spherulites. The latter consists of two kinds, in the first the crystalline particles possessing the same optical orientation are arranged in concentric rings, and the scrolls, habitually left-handed, are formed round the obtuse bisectrix parallel to the direction of the fibres, whilst in the second, the helical scrolls are similar, but the crystalline particles having the same orientation are arranged in the form of a spiral (a photomicrograph of this is reproduced in the paper), usually left-, but sometimes right-handed.

Since samples of cholesterol from different sources differ in the readiness with which they give spherulites having helical scrolls, the author suggests that the origin of the latter is to be explained by the presence of foreign substances in these cholesterolols in varying quantities or of diverse kinds. This view is supported by Jaeger's failure to obtain spherulites from cholesterol, whilst obtaining them easily with phytosterol.

Cholesterol melted with santonin gives a product which also forms spherulites having helical scrolls, and the greater the velocity of the formation of the spherulites, that is, the nearer the temperature is to the m. p., the greater is the pitch of the helix. The latter also depends on the proportion of santonin (compare Wallerant, *Abstr.*, 1906, ii, 838).
E. H.

Colloids and their Adsorption Compounds. WILHELM BILTZ (*Chem. Zentr.*, 1908, i, 915; from *Med.-naturwiss. Arch.*, 1907, 1, 267—299).—The author briefly sketches the preparation, structure, behaviour, and the adsorptive powers of colloids, and treats of the process of dyeing: also the purification of sewage and the retention of albumins.
J. V. E.

Gelatose as Colloid Producer. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 307).—The addition of gelatose to a jelly of gelatin containing dissolved potassium dichromate prevents the crystallisation of the salt on drying (compare *Abstr.*, 1906, ii, 273). Further, when a solution of 20 grams of gelatin in 100 grams of water is boiled for several days (gelatose being thus produced), ice no longer separates, even on prolonged exposure to a temperature of -10° .
G. S.

The Process of Gelatinisation. S. A. LEVITES (*Chem. Zentr.*, 1908, i, 700—701; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 161—170, 208—215. Compare this vol., ii, 161).—*Velocity of Gelatinisation.*—A minimum coagulation concentration for glutin is found to be 0.25 gram in 100 c.c. of water at 0° ; for δ -galactan, 0.1—0.15 gram. From results obtained, the author deduces the general rule that aqueous solutions of salts of monobasic acids, except alkali formates and acetates, retard the coagulation of gelatin; salts of di- and tri-basic acids, polyhydric alcohols, and sugars increase the rate of coagulation; monohydric alcohols retard the process more as their molecular weight increases.

Agar-agar coagulation is hastened by the presence of chlorides, bromides, cyanides, formates, acetates, and salts of polybasic acids; salts of the remaining monobasic acids retard coagulation. The velocity of coagulation is dependent on the solubility of the colloid; the greater the solubility the more slowly gelatinisation proceeds. Only the introduction of substances which alter the solubility has any influence on the coagulation, a decrease of solubility increasing the rate of coagulation. A mixed solution of gelatin and agar-agar, although depositing a small quantity of agar-agar at first,

gelatinises as a whole, the velocity being nearly equal to the mean of the coagulation velocities of the two components.

J. V. E.

Inclusion of Soluble Substances by Certain Precipitates. PAUL FRION (*Compt. rend.*, 1908, 146, 925—926).—Measurements of the quantities of lanthanum and magnesium contained in barium sulphate which has been precipitated from solutions containing a salt of one of these metals show that the amount of included soluble substance is greater when the precipitation takes place in a basic than in neutral solution, and much greater in a neutral than in an acid solution; that it increases with the concentration and with the valency of the included ion, and also with the dilution of the original solution. Assuming that the precipitate consists of granules electrically charged by contact with $+H$ or $-OH$ ions (compare Perrin, *Abstr.*, 1904, ii, 8; 1905, ii, 138), this charge is diminished by the presence of oppositely charged multivalent ions. M. A. W.

Principle of Evolution in Chemistry. BASIL B. KURILOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 471—476. Compare *Abstr.*, 1906, ii, 343, 349).—The author discusses the gradual change of properties exhibited by successive elements in a group of the periodic system, and supposes that similar gradual changes are to be met with, not only among what are termed definite chemical compounds, but also in any class of natural or artificial substances. Basic compounds (*loc. cit.*) are discussed in this connexion.

T. H. P.

Indestructibility of Matter and the Absence of Exact Relations Among the Atomic Weights. DANIEL F. COMSTOCK (*J. Amer. Chem. Soc.*, 1908, 30, 683—688).—According to the electrical theory of matter, the mass of a piece of matter is determined solely by, and is proportional to, the amount of electromagnetic energy which it contains. It follows that inertia or mass is really a property of the energy stored up in the structure which defines the space relations of a piece of matter and is not a property of the structure itself. Hence the law of the conservation of mass, which there is reason to believe is only approximate, is in reality a corollary to the law of the conservation of energy, and thus the latter law is closely related to the "indestructibility of matter."

It therefore follows that any loss of energy must involve a decrease in mass, and hence a decrease in weight. Thus when a chemical action takes place in which heat is developed, when a substance is cooled, or when by a process of radioactivity a substance loses energy and is transformed into another substance, a loss in weight must occur. In the first two cases, the change is too small to be detected, but in the last case the change should be appreciable and affords an explanation of the irregularities which occur in the table of atomic weights.

It is pointed out that, since gravity is proportional to mass,
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gravitation must be considered as acting between quantities of confined energy and not between masses in any other sense.

E. G.

The Atomic Hypothesis and the Energetic Theory of the Universe. LEO PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 444—451).—A discussion of the views of Ostwald and others regarding the constitution of matter.

T. H. P.

Energy of the Elements. NIKOLAI N. BEKETOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 451—457).—A discursive paper containing no new results.

T. H. P.

New Conception of the Element. ALDO MIELI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 374—378, 420—424).—The author criticises previous definitions of an element, which he defines as follows. He considers a given system of substances and a given field of physical conditions. The components of the system, in the sense of the phase rule, are found, and by considering these in any sub-system, and under any sub-field of conditions, the components of these components are then obtained. By repetition of this process, a group of components is obtained ultimately which are incapable of further decomposition, and which are the elements of the given system in the given field. The advantages of this definition are discussed.

T. H. P.

Electron Theory and Valency. HUGO KAUFFMANN (*Physikal. Zeitsch.*, 1908, 9, 311—314. Compare Stark, this vol., ii, 138).—A theoretical paper dealing with the conception of valency from the standpoint of the electron theory. The greater reactivity of unsaturated carbon compounds compared with the corresponding saturated compounds is explainable by the greater spacial extension of the electric fields which are associated with the electrons, each one of which corresponds with a valency unit.

The idea of partial valencies, as put forward by Thiele, is a direct consequence of the electronic conception of valency. The author interprets Thiele's benzene formula in terms of the electron theory, and discusses the possibility of the greater freedom of electrons which are associated with more than two atoms in giving rise to fluorescence phenomena.

H. M. D.

New Views on Chemical Processes. FRANZ WALD (*Chem. Zentr.*, 1908, i, 914; from *Oesterr. Chem. Zeit.*, 1908, 11, 50—51).—The possibility of treating experimental facts in a manner free from any hypothesis, and based on thermodynamic principles, is discussed.

J. V. E.

New Reflux Condenser for Extraction Apparatus. EDUARD MERKEL (*Zeitsch. angew. Chem.*, 1908, 21, 976).—A pear-shaped form of Liebig condenser is described, which enters some way into the extraction apparatus and is found effective.

J. V. E.

Cylinder for Micro-hydrometers. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1908, 47, 306).—A cylinder for use with tube-shaped micro-hydrometers is described. It consists of a thick-walled piece of glass tubing from 1 to 1.25 cm. in diameter; the lower end is closed by a glass stopper, which is ground into the tube and serves as a foot for the apparatus. As the cylinder holds only about 15 c.c. of liquid, it is useful for taking the density of small quantities of urine, serum, &c. W. P. S.

Constant Head of Water for Laboratories. HENRI MURAOUR (*Chem. Zentr.*, 1908, i, 1017; from *Rev. gén. Chimie*, 1907, 10, 359—360).—A simple arrangement is described for maintaining a constant head of water by running the feed-water into a small auxiliary reservoir connected by a siphon to the main tank. The small reservoir may be adjusted to any height, and the excess of feed-water is carried away from it by a side tube. J. V. E.

Inorganic Chemistry.

Temperatures of Maximum Density of Aqueous Hydrogen Chloride Solutions and the Expansion of the Latter on Heating. N. A. SCHERNAY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 518—536).—The author has measured (1) the temperatures of maximum density; (2) the expansion and (3) the freezing points of solutions of hydrogen chloride of different concentrations, and has examined the manner in which these magnitudes vary with the amount of hydrogen chloride in the solution.

The following values of D_4^{15} were obtained by the author, the numbers in brackets being those calculated from Mendeléeff's formula: 0.41 gram-mol. HCl per 1000 grams of water, 1.00616 (1.00654); 0.94, 1.01533 (1.01552); 1.71, 1.02807 (1.02837); 2.01, 1.03237 (1.03288); 2.99, 1.04759 (1.04823).

The coefficients of expansion at 20° are as follows: HCl + 139H₂O, 0.00021; HCl + 100H₂O, 0.00022 (Marignac); HCl + 59H₂O, 0.00023; HCl + 50H₂O, 0.00024 (Marignac); HCl + 32.5H₂O, 0.00025; HCl + 28H₂O, 0.00025; HCl + 25H₂O, 0.00028 (Marignac).

In the following table, M represents the number of gram-mols. of HCl per 1000 grams H₂O, T the temperature of maximum density, and D the depression of the temperature of maximum density of water by the hydrogen chloride:

M .	T .	D .	D/M .	$(D+7)/M$.
0.41	+1.19°	2.81°	6.85	24.00
0.94	-2.16	6.16	6.54	14.00
1.71	-10.64	14.64	8.56	12.65
2.01	-14.45	18.45	9.17	12.66
2.99	-26.25	30.25	10.11	11.70

The approximate equality of the first two values of D/M and of the last three values of $(D+7)/M$ shows that the relation between the amount of hydrogen chloride present and the depression of the temperature of maximum density caused by it is represented by two intersecting straight lines. A similar result was obtained by Depretz (*Ann. Chim. Phys.*, 1893) for solutions of calcium chloride.

Determinations of the freezing points (t) of hydrogen chloride solutions give values the relationship of which to the concentration is expressed by two straight lines. For values of M up to 1.26, the ratio t/M has the value -3.9 , whilst for higher values this ratio gradually increases up to -5.27 for $M=2.99$; for values of M from about 1.3 to 2.99, the ratio $(t+2)/M$ has a constant value of about -5.6 .

T. H. P.

Apparatus for Demonstrating the Synthesis of Water.

RICHARD KEMPF (*Chem. Zentr.*, 1908, i, 704; from *Zeitsch. phys.-chem. Unter.*, 1908, 21, 35—37).—Around the point of a water-cooled, funnel-shaped copper vessel a number of gas flames are arranged so that the condensed water runs to the point and drops into a receiver. The carbon dioxide produced can be collected from under a deep rim situated on the top edge of the copper vessel.

J. V. E.

Formation of Hydrogen Peroxide by the Silent Electric Discharge. WALTHER LÖB (*Ber.*, 1908, 41, 1517—1518. Compare Fischer and Ringe, this vol., ii, 370).—The author draws attention to his work on this subject (*Abstr.*, 1906, ii, 324).

G. Y.

The Decomposition of Ozone by Heat. EDGAR P. PERMAN and RICHARD HENRY GREAVES (*Proc. Roy. Soc.*, 1908, 80, A, 353—369).—The rate of decomposition of ozone in presence of various solid and gaseous substances has been determined at 40° , 60° , 80° , 100° , and 120° . A globe containing about 350 c.c. of dry, ozonised oxygen was heated in a bath of calcium chloride solution at the desired temperature, and the rate of increase of pressure over that in a similar globe containing air was measured by means of a sulphuric acid manometer. The amount of ozone decomposed was calculated from the pressure developed. The ozone was found to be completely decomposed by heating the bottom of the globe to about 300° with a Bunsen burner.

Great difficulty was experienced in obtaining concordant results, especially as a glass globe usually gave a greater velocity when new than after some use. The experimental values cannot be exactly expressed either as a reaction of the first or second order. In the case of glass and platinum surfaces, and also in presence of water vapour, an equation of the second order is to be preferred. In presence of porous pipeclay, copper oxide, magnesium oxide, manganese dioxide, lead peroxide, nickel foil, and nitric oxide, the unimolecular equation gives the better constant.

It was found that the rate of decomposition is largely dependent on the amount of glass surface. When the globe was packed with pieces of glass tubing, increasing the area about six-fold, the velocity at 80°

was increased sixty-fold. Glass wool, loosely packed into the globe, increased the velocity 129 times at 40°.

A few grams of porous pipeclay, granulated CuO, MgO, or MnO₂ in small lumps, produced an enormous acceleration in the rate of decomposition, but purified lead peroxide had comparatively little effect. Consistent results with metallic surfaces were obtained when the metal had been previously heated in ozone. Platinum and nickel foil produce a slight retardation of the change, but platinum black a noticeable acceleration. Silver foil becomes oxidised to silver peroxide.

The small amount of water ordinarily adhering to the glass surfaces was without appreciable effect on the rate of decomposition, but the introduction of larger amounts of water vapour into the globe produced a quickening which was proportional to the mass of water vapour present. In the case of one globe which gave a velocity constant $10^{-6} \cdot 122$ with dry ozone at 119.5°, the velocity in presence of *m*-milligrams of water was $10^{-6} \cdot (122 + 135 \cdot 1 m)$. A small quantity of nitric oxide (0.2 c.c.) increased the velocity about 1000-fold at 119.1°, but at 10° the oxide appeared to be condensed to liquid nitrogen tetroxide, and induced no decomposition.

The authors argue that if the decomposition takes place instantaneously at the surface of the glass, the velocity of the change is determined by the rate of diffusion of the ozone, and should be proportional to the square root of the absolute temperature. Actually the effect of temperature on the velocity constant is in agreement with the equation $\log k = a + b/t$, which takes no account of diffusion towards the surface. The decomposition is much more regular, however, when the surface exposed is large, and it is supposed that this may be due to the increased rapidity and shorter range of the reaction.

Water is said to accelerate the change by favouring the condensation of ozone on the glass, but nitric oxide probably functions chemically by conveying oxygen to the ozone molecules. The metallic peroxides cannot be supposed to act in the same manner, since lead peroxide is almost without effect, whilst copper and magnesium oxides have a great effect. Since a good unimolecular constant is obtained in these cases, it is supposed that the determining factor is the rate of absorption or condensation of ozone on the surface of the oxide.

The velocity of decomposition is increased on reducing the pressure of the oxygen, and to a greater extent on reducing the partial pressure of the oxygen by diluting with nitrogen. This effect cannot be traced to the reversibility of the decomposition, since the authors have shown that the reverse action, although demonstrable at 100°, is so small as to be without influence. The results obtained are not in accord with Jahn's hypothesis (Abstr., 1906, ii, 225) that a second reaction takes place, $O_3 + O = 2O_2$, and the authors prefer to suppose that variation of the oxygen pressure produces a difference in the gas-film at the surface of the glass. The conclusion is drawn that pressure measurements give no indication of the number of molecules interacting.

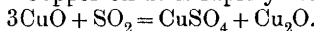
R. J. C.

The Iron Oxide Contact Process. GUSTAV KEPPELER (with JEAN D'ANS, IVAR SUNDELL, FRANZ KAISER) (*Zeitsch. angew. Chem.*, 1908, 21, 532—546, 577—589).—A long paper in which the mechanism of the reaction between sulphur dioxide and oxygen in presence of oxides of iron is discussed. In the process in question, the mixture of sulphur dioxide, oxygen, and nitrogen is first passed over burnt pyrites at about 700°, the sulphur trioxide is absorbed, and the residual gases, which contain relatively more oxygen than the original mixture, are then passed over platinum at 450° to 500°. By means of the known equilibrium constants of the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$, it is shown that the yields obtainable in this way are better than those given by one treatment with platinum at the lower temperature.

The equilibrium $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$ is studied between 638° and 721°, the sulphur trioxide, of course, dissociates partially. The partial pressures of sulphur trioxide are given by the equation $\log p = -44720/2T + 11.8626$.

At higher temperatures, iron oxide brings about the combination of sulphur dioxide and oxygen in the same way as platinum; the partial pressure of sulphur trioxide increases as the temperature falls, until a point is reached at which it is equal to the dissociation pressure of ferric sulphate; at lower temperatures it is absorbed by the catalyst, and the yield therefore falls off; there is thus a temperature of maximum yield. For pyrites-burner gases containing 7, 4, and 2% of sulphur dioxide, these temperatures of maximum yields are 665°, 650°, and 628° respectively, and the possible yields are 53.2, 65.0, and 72.5%. A comparison with the results of manufacturing practice shows that the process is carried on slightly above the temperature of maximum yield, and that the loss of sulphur by absorption is very small.

The catalytic action of ferric oxide has been ascribed to an alternate reduction and oxidation: $3\text{Fe}_2\text{O}_3 + \text{SO}_2 = 2\text{Fe}_3\text{O}_4 + \text{SO}_3$ and $4\text{Fe}_3\text{O}_4 + \text{O}_2 = 6\text{Fe}_2\text{O}_3$. It is found, however, that sulphur dioxide has no action on ferric oxide below 600°, and the reaction is extremely slow at higher temperatures. Copper oxide is rapidly reduced, thus:



A second possibility is that sulphur dioxide and oxygen combine with ferric oxide, and the ferric sulphate produced then dissociates, yielding sulphur trioxide. It is found that the absorption of sulphur dioxide and oxygen begins about 230°. A number of experiments in which a mixture of sulphur dioxide, oxygen, and nitrogen is passed over ferric oxide at 500° shows that equilibrium in the gaseous phase is reached rapidly, whilst the concentration of the sulphur trioxide is always much higher than that corresponding with equilibrium with ferric sulphate, that is, sulphur trioxide is first formed and then combines with ferric oxide.

Another set of measurements shows that sulphur dioxide is adsorbed by ferric oxide, the adsorption being of the same order of magnitude as that observed with platinum; the author draws the conclusion that the catalysis is due to a condensation of gases on the surface of the catalyst.

The absorption of arsenic by burnt pyrites, which is the most important technical advantage of their use, is shown to be due to the

formation of arsenic acid. This is reduced to arsenious acid (which volatilises) by sulphur dioxide alone, but not by a mixture containing oxygen. T. E.

Selenium. WILLIAM OECHSNER DE CONINCK and RAYNAUD (*Bull. Acad. roy. Belg.*, 1908, 57. Compare Abstr., 1907, ii, 613).—The crystalline and amorphous varieties of selenium, obtained by the action of sulphurous acid on selenious acid, when exposed to light during seven months undergo condensation. The first becomes compact, develops a metallic lustre, and shows a crystalline structure on fracture. The second forms slaty, amorphous leaflets devoid of lustre. T. A. H.

Atomic Weight of Tellurium. H. BRERETON BAKER (*Chem. News*, 1908, 97, 209—210. Compare Trans., 1907, 91, 1849).—A criticism of the use of crystallised telluric acid as the starting point for the determination of the atomic weight of tellurium. The impracticability of obtaining telluric acid, which contains water in the exact proportion required by the formula $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, is shown to be the probable cause of the low value for the atomic weight obtained by Marckwald (this vol., ii, 33). The phenomenon described by Bettel (this vol., ii, 372) cannot be ascribed to the presence of a new element in tellurium. When pure silver tellurate is reduced to telluride by heating in hydrogen, and the telluride is cupelled with lead, spreading of the silver bead takes place. When pure tellurium is added to silver and cupellation carried out in the same way, the spreading is very much smaller, but this is shown to be due to the fact that most of the tellurium volatilises before combination with the silver has set in. The phenomenon of spreading can therefore be observed with the purest tellurium, and the probable explanation is that silver telluride has a lower surface tension than pure silver. H. M. D.

Homogeneity of Tellurium. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1908, 30, 741—747).—Mendeléeff (Trans., 1889, 55, 649) and Brauner (Trans., 1889, 55, 411) have expressed the opinion that tellurium is not a single element, but probably a mixture of "true" tellurium with an element of higher atomic weight. Norris, Fay, and Edgerley (Abstr., 1900, ii, 272) and Baker and Bennett (Trans., 1907, 91, 1849), however, consider that tellurium is homogeneous.

It has been shown (following abstract) that, by the action of certain liquid anhydrous chlorides on tellurium or its dioxide, tellurium tetrachloride or a double chloride is formed. The mother liquors from these reactions contain the excess of the anhydrous chloride together with some tellurium. When this tellurium is separated from the mother liquors and purified, it always gives the same value for the ratio $\text{Te} : \text{TeO}_2$ as does that contained in the crystalline reaction product, corresponding with the atomic weight 127.5. Similarly, the fractions obtained by partial precipitation of solutions of tellurium tetrachloride with ferrous salts all show the same atomic weight.

Experiments have also been made on the action of hydrochloric

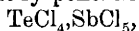
acid on tellurium in presence of air, and it is found that the dissolved and undissolved portions of the element are identical in characters and atomic weight. These results, therefore, support the view that tellurium is a true element. E. G.

Action of Various Anhydrous Chlorides on Tellurium and on Tellurium Dioxide. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1908, 30, 737—741).—In an earlier paper (Abstr., 1902, ii, 316), it has been shown that when tellurium is treated with excess of sulphur monochloride, tellurium tetrachloride and sulphur are produced. Krafft and Steiner (Abstr., 1901, ii, 235), however, have found that, when an excess of tellurium is heated with sulphur monochloride, tellurium dichloride is formed.

When tellurium dioxide is treated with excess of sulphur monochloride, tellurium tetrachloride is formed in accordance with the equation: $\text{TeO}_2 + 2\text{S}_2\text{Cl}_2 = \text{TeCl}_4 + \text{SO}_2 + 3\text{S}$. If, however, an excess of tellurium dioxide is heated with the reagent, the dichloride is produced, thus: $\text{TeO}_2 + \text{S}_2\text{Cl}_2 = \text{TeCl}_2 + \text{S} + \text{SO}_2$.

[With C. W. HILL.]—Thionyl chloride reacts with both tellurium and its dioxide, forming the tetrachloride when the reagent is in excess, and the dichloride when the element or oxide is in excess. Sulphuryl chloride reacts with tellurium to form the tetrachloride, but when the element is in excess, the dichloride is produced. Tellurium dioxide is not affected by sulphuryl chloride in the cold, but on heating the mixture in a sealed tube, crystalline *products* are formed which vary in composition, thus: $3\text{TeO}_2, 4\text{SO}_2\text{Cl}_2$; $5\text{TeO}_2, 9\text{SO}_2\text{Cl}_2$; $\text{TeO}_2, 2\text{SO}_2\text{Cl}_2$; $2\text{TeO}_2, 5\text{SO}_2\text{Cl}_2$.

Arsenic and antimony trichlorides react with tellurium dioxide with formation of tellurium tetrachloride and arsenic or antimony trioxide. Lead tetrachloride converts both the element and the oxide into tellurium tetrachloride. Phosphorus trichloride is without action on tellurium, but reduces its oxide to the element. Carbon tetrachloride does not react with either the element or the oxide. When tellurium dioxide is treated with antimony pentachloride, the *compound*,



is produced, which forms white, tabular crystals, and is readily decomposed by water. Similarly, phosphoryl chloride reacts with the oxide to form the *compound*, $\text{TeCl}_4, \text{POCl}_3$, which crystallises in deliquescent, monoclinic plates, and is decomposed by water. E. G.

Metallic Nitrides and their Magnetic Properties. I. I. SHUKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 457—459).—The author has investigated the absorption of nitrogen by finely-divided magnesium, calcium, aluminium, titanium, vanadium, chromium, manganese, iron, copper, molybdenum, and tungsten. The metal was placed in a porcelain tube, which was exhausted, connected with a nitrogen supply, and heated in an electric furnace. The tube was connected with a manometer, and the temperatures at which absorption of nitrogen by the metal commenced were measured by a pyrometer. Vanadium, iron, copper, and tungsten do not absorb

nitrogen at temperatures below 1250° , whilst molybdenum absorbs only traces. The rest of the metals named absorb nitrogen rapidly. The temperatures at which this absorption begins are as follows: magnesium, $780-800^{\circ}$; calcium, $780-800^{\circ}$; aluminium, $800-825^{\circ}$; titanium, $900-925^{\circ}$; chromium, $800-820^{\circ}$; manganese, $850-875^{\circ}$. In no case does the metal melt, although in several instances the temperatures at which absorption of the gas apparently begins are considerably above the melting points of the metals; it is probable that a slight amount of absorption proceeds at lower temperatures than those given above.

The products formed consist, in the cases of magnesium, calcium, and aluminium, of the definite compounds Mg_3N_2 , Ca_3N_2 , and AlN . Manganese absorbs 12%, chromium 8%, and titanium 21% of nitrogen, the products in these instances consisting either of solid solutions of nitrogen in the metals or of solutions of definite nitrogen compounds in excess of the various metals.

The manganese product, containing 12% of nitrogen, exhibits magnetic properties almost as intense as those of iron, and the chromium and titanium products are also distinctly magnetic.

T. H. P.

Behaviour of Metals when Heated in Ammonia.
GEORGE G. HENDERSON and J. C. GALLETLY (*J. Soc. Chem. Ind.*, 1908, 27, 387—389. Compare Fowler, *Trans.*, 1901, 79, 285; White and Kirschbaum, *Abstr.*, 1906, ii, 853).—Beilby and Henderson found (*Trans.*, 1901, 79, 1245) that when heated in a current of dry ammonia, certain metals are more or less completely converted into nitrides, or, if the conditions are such that the nitrides are not stable, undergo marked change in their physical properties, whilst other metals do not in any case yield nitrides, but undergo similar physical changes, which are probably caused by continuous formation and decomposition of an unstable nitride. In all cases, the ammonia undergoes decomposition into its elements to an extent varying with the nature of the metal and the temperature of the experiment. The work has now been extended to a number of other metals, and similar results have been obtained.

At 800° , finely-powdered manganese is almost completely converted into a dull black *nitride*, Mn_3N_2 , whilst at 850° chromium yields a similar product, which is probably the *nitride*, Cr_3N_2 , containing small amounts of unchanged metal. The resistance of the members of the chromium group to the action of ammonia, or the instability of the nitride, increases with the atomic weight: at 850° , molybdenum yields a product containing only 2.4% to 3.1% of nitrogen, whilst tungsten is only slightly altered in appearance and contains not more than traces of a nitride.

The action of ammonia on titanium at 800° leads to the formation of a dull bronze product containing 5% to 6.8% of nitrogen. Tin does not yield a nitride under any conditions, but at an incipient red-heat decomposes a large proportion of the ammonia passed over it, the rate of decomposition diminishing with the temperature; the metal

becomes frosted in appearance, showing under the microscope a number of minute bubbles. Lead behaves in a similar manner.

The behaviour of cadmium is similar to that of zinc. The powdered metal is partly converted into a green nitride; with cadmium foil, little or no nitride could be detected, but the appearance of the metal underwent the usual change.

Palladium does not yield a nitride, but decomposes large amounts of ammonia, and forms a number of rounded particles, which have the appearance of having been partly fused.

The nitrides described are decomposed when heated in air; they differ to a considerable extent in their stabilities towards water, acids, and hydrogen at red-heat.

G. Y.

Solution of Metals in Non-metallic Solvents. II. Formation of Compounds between Metals and Ammonia. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1908, 30, 653—668).—In an earlier paper (Abstr., 1907, ii, 935), an account was given of the general properties of solutions of metals in liquid ammonia and other non-metallic solvents.

Joannis (Abstr., 1890, 209, 560) separated substances formed by potassium and sodium with ammonia, and assigned to them the composition KNH_3 and NaNH_3 . Similarly, Moissan (Abstr., 1899, i, 410; ii, 152) obtained the products LiNH_3 , $\text{Ca}(\text{NH}_3)_4$, and LiNH_2Me . Ruff and Geisel (Abstr., 1906, ii, 228) expressed the opinion that these substances are not definite compounds, but mixtures of the metal with its saturated solution in ammonia.

Joannis (*loc. cit.*) has investigated the pressure of the sodium-ammonium and potassium-ammonium systems. An examination of his results by the application of the phase rule has led to the conclusion that the compounds NaNH_3 and KNH_3 do not exist. It is also found from the pressure relations that the substance LiNH_3 has no existence, and it is shown independently that, in a system containing lithium and a small quantity of ammonia, a saturated solution of the metal in ammonia is produced.

Calcium yields a solid compound, $\text{Ca}(\text{NH}_3)_6$, analogous to the barium and strontium compounds described by Mentrel (Abstr., 1903, ii, 77) and Roederer (Abstr., 1905, ii, 455). This substance has optical and electrical properties identical with those of its saturated solution.

The vapour pressures of saturated solutions of lithium and of the compound $\text{Ca}(\text{NH}_3)_6$ in ammonia, and the dissociation pressure of the calcium compound, have been determined. The heat of combination of calcium with gaseous ammonia to form the compound $\text{Ca}(\text{NH}_3)_6$ has been calculated and found to be 10.23 Cal., whilst the heat of solution of the compound by ammonia is 5.46 Cal. per gram-mol. The heat of solution of lithium is 8.70 Cal. per gram-mol. of gaseous ammonia.

The constitution of the compound $\text{Ca}(\text{NH}_3)_6$ is discussed, and it is considered probable that the ammonia is combined in the same manner as it is in the ammonio-salts. It is therefore proposed to call the compound calcium hexa-ammoniate.

E. G.

Solubility of Nitric Oxide in Aqueous Solutions of Ferrous Sulphate, Nickel Sulphate, Cobalt Sulphate, and Manganese Chloride. FRANCIS L. USHER (*Zeitsch. physikal. Chem.*, 1908, 62, 622—625. Compare Manchot and Zechentmayer, *Abstr.*, 1907, ii, 93; Hüfner, *Abstr.*, 1907, ii, 552).—It was hoped that the nature of the compound formed when nitric oxide is dissolved in ferrous sulphate might be elucidated by a study of the freezing point of the solution, but it was found that, owing apparently to chemical interaction, neither the pressure of the nitric oxide nor the freezing point of the solution remained constant. After the removal of the nitric oxide from the solution, a small quantity of ferric hydroxide was actually detected. That nitric oxide is reduced by ferrous sulphate solutions is shown also by the fact that the volume of the gas absorbed gradually increases as time goes on.

The author, in disagreement with Hüfner (*loc. cit.*), finds that nickel sulphate, cobalt sulphate, and manganese chlorido behave like other salts, and diminish the solubility of nitric oxide in water. Comparable results for the absorption-coefficient in the various salt solutions are obtained only by redetermining the solubility in water for each sample of the gas prepared. Attention is drawn to the fact (see Emich, *Abstr.*, 1892, 940) that nitric oxide is decomposed by potash, and that for nitric oxide, washed by passing through concentrated sulphuric acid, a smaller absorption-coefficient is obtained than for nitric oxide washed by passing through potash. J. C. P.

Preparation of Nitrogen Peroxide. PAUL WINANS (D.R.-P. 193696).—When the mixture of nitric oxide and nitrogen peroxide, evolved by acid from a nitrite, reacts with nitrogen pentoxide, the following change occurs: $\text{NO} + \text{NO}_2 + \text{N}_2\text{O}_5 = 4\text{NO}_2$, and pure nitrogen peroxide is produced.

An intimate mixture of alkali nitrite and nitrate is treated with fuming sulphuric acid, and the production of the pure peroxide occurs in accordance with the equation: $\text{NaNO}_3 + \text{NaNO}_2 + \text{H}_2\text{S}_2\text{O}_7 = 2\text{NaHSO}_4 + 2\text{NO}_2$. Sufficient of the hydrogen sulphate from an earlier operation is added to fix any excess of sulphur trioxide: $2\text{NaHSO}_4 + \text{SO}_3 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{SO}_4$. The homogeneous mixture of the two salts is ensured either by using the salts in the molten condition or by pouring the fused mixture into carbon tetrachloride or into a saturated aqueous solution of the salts themselves. G. T. M.

Production of Nitric Acid during Electric Discharge in Air. GUSTAV MEYER (*Chem. Zentr.*, 1908, i, 794; from *Zeitsch. phys.-chem. Unter.*, 1908, 21, 40).—Filter paper coloured with an alcoholic solution of diphenylamine, placed in the path of the spark, shows a yellow colour, which, after long action, develops a blue margin analogous to the reaction given by dilute nitric acid. J. V. E.

Red Phosphorus. GOTTLÖB E. LINCK and P. MÖLLER (*Ber.*, 1908, 41, 1404—1410).—Rydberg failed in an attempt to find a relation between the hardness and the m. p. of phosphorus, arsenic, antimony, and bismuth (*Abstr.*, 1900, ii, 322) because he compared modifications

of the elements which are not strictly comparable. Before commencing similar experiments, the authors have endeavoured in the present communication to ascertain whether red phosphorus is comparable with "mirror" or with metallic arsenic, and whether together with the crystalline modification an amorphous variety of red phosphorus exists, as several investigators claim.

Red phosphorus was prepared by Hittorf's method, and, after removal of the excess of lead by dilute nitric acid, the residue consisted of small, black, metallic, monoclinic crystals

$$[a:b:c=1.651:1:1.46; \beta=72^{\circ}40']$$

containing about 62% of lead. The substance therefore is not crystalline phosphorus as was supposed, but a compound of lead and phosphorus.

Washed and dried red phosphorus was heated in a vacuum tube at the temperature of melting lead; the sublimate was a dense, black, brittle mass, devoid of crystalline structure, containing 99.4% of phosphorus, and having $D^{18-20} 2.145-2.192$. The identity of this modification with commercial red phosphorus was indicated by prolonged heating at 450° , whereby both varieties are changed into a denser crystalline form, $D 2.280-2.304$.

The second object of the investigation was attacked by heating mixtures of red phosphorus and metallic arsenic; the density of the sublimate was determined by the floating method, and also calculated from the composition and the densities of red phosphorus, and of the several modifications of arsenic. The best agreement was obtained when the density of "mirror" arsenic was used. C. S.

Constitution of Phosphorous Acid. F. CARLO PALAZZO and F. MAGGIACOMO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 432-438).—The authors discuss the bearing of the work of previous investigators on the validity of the symmetrical, $P(OH)_3$, and unsymmetrical formulæ, $O:PH(OH)_2$, which have been proposed for phosphorous acid. Their own results indicate that the unsymmetrical formula is the correct one.

When phosphorous acid is treated in an atmosphere of dry carbon dioxide with diazoethane, it is converted completely into the diethyl salt, which, like the free acid, must hence have an unsymmetrical structure.

Under the same conditions, selenious acid gives an almost theoretical yield of *s*-diethyl selenite. This acid has therefore a symmetrical structure (compare Werner, *Abstr.*, 1895, ii, 225; *Zeitsch. anorg. Chem.*, 1895, 8, 194). T. H. P.

Decomposition of Arsenic Hydride. ALFRED STOCK, EUSEBIO ECHEANDIA, and PAUL R. VOIGT (*Ber.*, 1908, 41, 1319-1323).—The similarity between arsenic and antimony hydrides suggested the study of the decomposition of the arsenic compound from the same point of view as that already carried out for antimony hydride (compare this vol., ii, 503). The experiments were carried out, not in a flask, but in a Jena glass cylinder 10 cm. in length and 3.5 cm. in diameter, and heated by diphenylamine vapour (304°), a temperature which has

the disadvantage that the decomposition is somewhat slow, but a higher temperature is inadvisable, as otherwise arsenic sublimes into the capillary tube leading to the manometer. The velocity of decomposition of the arsenic hydride is greater at the beginning in a vessel free from an arsenic mirror, but as soon as the vessel is covered with arsenic the velocity decreases and then increases again. When a series of experiments is carried out in the same vessel, the velocity of the reaction diminishes from experiment to experiment. In a third experiment, the decomposition was complete after seven days, although 95% was decomposed during three days.

The mirror so formed is irregular in thickness, some portions of the vessel being free from arsenic, and others being covered with a non-transparent layer. A microphotograph is given, showing the ring formation round a large arsenic crystal.

Experiments carried out at 444° (b. p. of sulphur) show that the decomposition velocity is great, but no mirror is obtainable in the apparatus, as sublimation is immediate.

Air and hydrogen sulphide have no influence on the reaction.

The decomposition velocity increases with decreasing arsenic hydride concentration, and this agrees with the explanation that decomposition occurs in the adsorbed gas layer.

W. R.

The Hydrates of Arsenic Acid. VICTOR AUGER (*Compt. rend.*, 1908, 146, 585—588).—The hydrate of arsenic acid described by Joly and Auger (*Abstr.*, 1902, ii, 393), as $\text{As}_2\text{O}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, and subsequently prepared by Baud (*Abstr.*, 1907, ii, 761), is now shown to be $\text{As}_2\text{O}_5 \cdot 1\frac{2}{3}\text{H}_2\text{O}$.

The hydrate, $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, can give up water vapour even at -10° , and the dehydration of this substance, whether over phosphoric oxide, sulphuric acid, or potassium hydroxide, proceeds regularly at the ordinary temperature until the composition $\text{As}_2\text{O}_5 \cdot 1\frac{2}{3}\text{H}_2\text{O}$ is attained. There is no indication that pyroarsenic acid, $\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, is produced under these conditions as an intermediate product, as claimed by Baud. R. J. C.

Austenite. ED. MAURER (*Compt. rend.*, 1908, 146, 822—824).—Austenite, the solid solution of carbon in γ -iron discovered by Osmond, has hitherto only been obtained as an alloy with manganese steel containing 13% of manganese, and nickel steel containing 25% of nickel. The best specimen obtained by Osmond (from a cementation steel containing 1.6% of carbon) was two-thirds composed of austenite and one-third martensite. The author has heated specimens of three steels containing: (1) 3.73% of nickel, 1.21% of carbon, and 0.28 of silicon; (2) 1.83% of manganese, 1.18% of carbon, and 0.88% of silicon, and (3) 2.20% of manganese, 1.94% of carbon, and 0.94% of silicon, at 1050° for fifteen minutes and tempered them in ice-water. He finds that the two first specimens give martensite, but the third gives pure austenite. The austenite on metallographic examination is found to be constituted of cells exhibiting well-defined macles; it is not magnetic, and its hardness is relatively low. It can be transformed into martensite, and thus considerably hardened by mechanical deformation at the ordinary temperature, by annealing at about 400° , or

by immersion in liquid air. Photomicrographs are given: (1) of homogeneous austenite, (2) of austenite transformed by mechanical deformation, and (3) austenite transformed by annealing.

Similar treatment of a steel containing less manganese gives a metal consisting of both austenite and martensite. E. H.

Austenite. HENRI LE CHATELIER (*Compt. rend.*, 1908, 146, 824—826. Compare preceding abstract).—The author obtained homogeneous austenite on one occasion by heating a steel containing 1.5% of carbon and about 1% of manganese at 1200° for two hours and tempering in a reducing medium, but, failing to determine the essential conditions, has never succeeded in repeating the experiment. Maurer's discovery is important from a scientific point of view in that it facilitates the study of the properties of austenite normally stable only above 800°, and from a practical standpoint by furnishing a steel which is both cheaper and more readily worked than the manganese steel, used where great resistance to wear by friction is required, and the nickel steel employed on account of its extraordinary toughness. E. H.

Currents in Water due to the Dissolution of Carbon Dioxide. H. REBENSTORFF (*Chem. Zentr.*, 1908, i, 704; from *Zeitsch. phys.-chem. Unter.*, 1908, 21, 39).—Water, faintly-coloured by a trace of phenolphthalein and sodium hydroxide, in contact with carbon dioxide shows a colourless surface, and on standing, owing to convection currents, due to the density of the solution of carbon dioxide in water, and diffusion, the entire liquid becomes colourless. A similarly-coloured salt solution requires a much longer time for this to take place. J. V. E.

Preparation of Silicic Acids. GUSTAV TSCHERMAK (*Centr. Min.*, 1908, 225—230).—A reply to Mügge (this vol., ii, 277). L. J. S.

Experiments on the Condensation of Helium by Expansion. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 744—747).—The author describes the experiments which at first led him to announce the liquefaction of helium. He now considers that the phenomena observed were due to the presence of hydrogen as impurity in the sample of helium employed.

Nearly 7 litres of helium, purified by passing over heated copper oxide and over charcoal immersed in liquid hydrogen, were compressed at 100 atmospheres in a thick-walled tube immersed in liquid hydrogen, evaporating under such a pressure that solid hydrogen just appeared on the surface. When the compressed gas was allowed to expand, a dense, grey cloud appeared, from which solid masses separated, floating in the gaseous helium, and denser masses which passed slowly down the tube, but soon disappeared. There was no appearance of melting.

Subsequent investigation showed that this sample of helium contained about 0.4% by volume of hydrogen, and, when the latter was removed as far as possible, no cloud was noticed on repeating the above experiment, but on a subsequent occasion, with more rapid

expansion, a thin cloud was observed. This effect might, however, be due to the small traces of hydrogen still remaining.

The results first obtained are due in all probability to the solution phenomena of solid hydrogen in gaseous helium. It remains somewhat surprising, when the small amount of hydrogen (not much more than 1 mg.) is taken into account, that the tube, which held 7 c.c., was over its whole length about one-quarter full of a flaky substance.

G. S.

Electrolysis of Chlorides. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1908, [iv], 3, 532—543).—In a previous paper, it was shown that the presence of cobaltous oxide in a solution of potassium chloride undergoing electrolysis for the production of chlorate, inhibited the formation of chlorate, and this was regarded as evidence in favour of the view that hypochlorite is initially formed in this reaction, and is decomposed by the cobaltous oxide (Abstr., 1900, ii, 541; compare Foerster and Jorre, *ibid.*, 343; Guye, Abstr., 1903, ii, 586; Briner, Abstr., 1907, ii, 68, 734). The results recorded in the present paper support the view stated previously.

When alkali chlorides are electrolysed in a diaphragm apparatus, the percentages of the theoretical yields of the corresponding hydroxides actually obtained diminish as the experiment proceeds. The yields, expressed in percentages of the theoretical, obtained in the cases of the following chlorides, initially and after ten hours, are as follows: sodium chloride, 96 and 70·4; potassium chloride, 96 and 71·7, and barium chloride, 92 and 56.

The experiments on the influence of metallic hydroxides on the electrolytic formation of potassium chlorate have been extended and repeated in an apparatus permitting of agitation of the electrolyte, and it was found that hydroxides of cobalt or nickel strikingly reduce the yield of chlorate. Mercuric hydroxide also exerts this action, but to a less extent, and copper hydroxide to a still less extent, whilst hydroxides of lead, iron, zinc, aluminium, or chromium have little or no effect.

It was found that films of cobalt or nickel decompose solutions of hypochlorite rapidly, whilst metallic copper effects a slow decomposition of the salt. Iron and lead exert a considerable decomposing effect, whilst zinc has no action. In all these cases, oxygen is the chief gas evolved. When magnesium or aluminium is placed in a solution of sodium hypochlorite, energetic action ensues, but in these cases hydrogen is the chief gas evolved, so that these metals are probably attacked by the excess of alkali in the solution. It will be seen that it is precisely those metals the hydroxides of which inhibit the formation of potassium chlorate which decompose sodium hypochlorite.

Experiments show that cathodes of platinum, cobalt, copper, or tin, used in conjunction with platinum anodes, are all equally efficient in the electrolysis of potassium chloride to chlorate, but in using cobalt (or nickel) there is always a risk of the formation of the oxide of the metal, owing to stoppage of the current, and the same risk attends the use of cupric oxide cathodes. Carbon anodes behave rather differently

from platinum anodes, and the amount of oxygen evolved in this case is not a safe guide to the diminution in yield of chlorate, as part of the oxygen is used up in oxidising the carbon of the anode. Zinc electrodes would appear to answer the purpose best.

T. A. H.

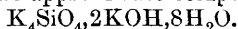
Study of the Solubility of Potassium Platinichloride. EBENEZER H. ARCHIBALD, W. G. WILCOX, and B. G. BUCKLEY (*J. Amer. Chem. Soc.*, 1908, 30, 747—760).—Since a knowledge of the solubility of potassium platinichloride is of considerable importance in analytical work, a study has been made of the solubility of the salt in water, methyl and ethyl alcohols, mixtures of these alcohols and isobutyl alcohol with water, and in solutions of potassium and sodium chlorides.

The weights of potassium platinichloride which dissolve in 100 grams of water are: at 2°, 0.4812; at 16°, 0.6718; at 25°, 0.8641; at 35°, 1.132; at 48°, 1.745; at 59°, 2.396; at 68°, 2.913; at 78°, 3.589; and at 92°, 4.484 grams. These results are compared with those of previous investigators. Potassium platinichloride is soluble at 20° to the extent of 0.0027 gram in 100 grams of methyl alcohol, and 0.0009 in 100 grams of ethyl alcohol. The platinichloride is less soluble in mixtures of ethyl alcohol and water than in aqueous solutions of either methyl or isobutyl alcohol. The solubility in potassium chloride solutions decreases as the concentration of the potassium chloride increases, until a concentration of 1 gram-mol. per litre is reached. Beyond this point, the concentration of the potassium chloride has no effect. The solubility in sodium chloride solutions increases rapidly up to a concentration of 0.05 gram-mol. per litre. In more concentrated solutions, the solubility increases very slightly, and almost proportionally to the increase in the concentration of the sodium chloride.

In the determinations of the solubility in alcohols, it was found that, on evaporating the solutions, reduction of the platinichloride took place. A colorimetric method of estimation was therefore adopted, involving the use of Nessler tubes, and was found to give accurate results.

E. G.

Silicates. VIII. Alkali Silicates. EDUARD JORDIS (*Zeitsch. anorg. Chem.*, 1908, 58, 98—101. Compare Abstr., 1905, ii, 161, 248, 317; this vol., ii, 103, 291).—From a strong solution of potassium silicate, after remaining for some months over sulphuric acid, thin plates separated which, after freeing as far as possible from the mother liquor, had the approximate composition



No crystalline silicate of potassium had been prepared previously.

When to fused sodium hydroxide, silica is added in the ratio 8NaOH:SiO₂, large, colourless leaflets are formed, which probably represent an orthosilicate of sodium, but the compound has not been obtained pure.

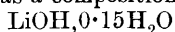
G. S.

Sodium Hypochlorite: Properties of the Electrolytic Bleaching Solution. H. PUSCH (*Centr. Bakt. Par.*, 1908, i, 46, 520—538).—A description is given in detail of the estimation and

technical preparation of a bleaching solution by the electrolysis of sodium chloride solution. The stability of the sodium hypochlorite solution when exposed to light, and its action on dyes and colouring matters of various types, including those of urine and blood, has been examined and the results, using bleaching solution of various strengths, tabulated. Its value as a disinfectant is strikingly shown by the results of a series of experiments with dilute solutions on town sewage effluent and certain pathogenic micro-organisms. J. V. E.

Action of Heat on the Lithium Hydroxides. ROBERT DE FORCRAND (*Compt. rend.*, 1908, **146**, 802—806).—The hydroxide, $\text{LiOH}\cdot\text{H}_2\text{O}$, prepared by Dittmar (*J. Soc. Chem. Ind.*, 1888, **7**, 731) in a not quite anhydrous condition, is obtained free from water by heating Dittmar's product in a current of hydrogen at 33° for one hour. Its heat of dissolution at $+15^\circ$ and $M/2$ dilution is $+0\cdot51$ Cal. When this hydroxide is kept in a vacuum desiccator for several weeks, or, better, heated for an hour in a current of hydrogen not above 140° , it is transformed into pure lithia, LiOH , a white, efflorescent substance, which is polymerised to the same extent as the hydrated compound. This is the only way that lithia can be prepared, and it cannot be obtained fused. Its heat of dissolution is $+4\cdot465$ Cal., from which the values $+3\cdot955$ Cal. and $+13\cdot615$ Cal. respectively for its heat of combination with liquid and gaseous water are deduced. From the latter figure, 181° is calculated as the dissociation temperature of the hydroxide, $\text{LiOH}\cdot\text{H}_2\text{O}$, and this is in accordance with the fact that it evolves water at 140° in a current of hydrogen.

Commercial pure lithia has a composition varying between



and $\text{LiOH}\cdot 0\cdot19\text{H}_2\text{O}$, after allowing for impurities. This does not evolve water when heated at 140° in a current of hydrogen, but at 445° it melts, loses a small quantity of water, and the product has the composition $\text{LiOH}\cdot 0\cdot125\text{H}_2\text{O}$, which is not altered by heating at 480° for several hours. The product, which forms a white, translucent, nacreous, fissured mass with a crystalline fracture, seems to be a condensed hydroxide at least as complex as would correspond with the formula $4\text{Li}_2\text{O}\cdot 5\text{H}_2\text{O}$. The heat of dissolution of $\text{LiOH}\cdot 0\cdot125\text{H}_2\text{O}$ is $+4\cdot091$ Cal. By heating this hydroxide in a current of hydrogen at 570° until water ceases to be evolved, it is transformed into an opaque, white, non-crystalline, enamel-like substance of the composition $\text{Li}_2\text{O}\cdot 0\cdot75\text{H}_2\text{O}$, probably a second condensed hydroxide polymerised to the same degree, $4\text{Li}_2\text{O}\cdot 3\text{H}_2\text{O}$, as the first. The heat of dissolution of $\text{Li}_2\text{O}\cdot 0\cdot75\text{H}_2\text{O}$ at 15° and $M/4$ dilution is $+16\cdot026$ Cal. During the transformation of the first condensed hydroxide into the second, no slackening in the evolution of water, which would indicate the formation of the compound $4\text{Li}_2\text{O}\cdot 4\text{H}_2\text{O}$, is observed. When heated in a current of hydrogen at 570° , the second condensed hydroxide very slowly loses water, but no other definite compound is formed. After heating in a current of hydrogen at 780° for two hours, it is transformed into anhydrous lithium oxide, Li_2O (or $n\text{Li}_2\text{O}$).

From the difference of the heats of dissolution of the two condensed hydroxides, $+31\cdot376$ Cal. and $+25\cdot348$ Cal. are deduced for the heats

of combination of $(4\text{Li}_2\text{O}, 3\text{H}_2\text{O}, 2\text{H}_2\text{O liq.})$ and $(4\text{Li}_2\text{O}, 3\text{H}_2\text{O}, 2\text{H}_2\text{O gas})$ respectively. The dissociation temperature, 572° , is calculated from the heat of combination with steam, and agrees with the observed value. This agreement supports the view that the two condensed hydroxides are equally polymerised. If it is assumed that lithium oxide also is equally polymerised, the value $+60.696$ Cal. is obtained for the heat of combination of $(4\text{Li}_2\text{O}, 3\text{H}_2\text{O liq.})$ and $+29.892$ Cal. for $(4\text{Li}_2\text{O}, 3\text{H}_2\text{O gas})$. The latter result gives 723.4° as the dissociation temperature of the trihydrate, also agreeing with experiment.

By melting together equal molecular quantities of the penta- and tri-hydrates, a product of the composition $4\text{Li}_2\text{O}, 4\text{H}_2\text{O}$, and having a heat of dissolution, $+12$ Cal., equal to the mean of those of its components, is obtained.

E. H.

Rubidium Dichromate. WILLEM STORTENBEKER (*Bull. Soc. chim.*, 1908, [iv], 3, 481—483. Compare Abstr., 1907, ii, 764).—A reply to Wyrouboff (this vol., ii, 181), in which the author maintains that (1) the two forms of this salt have different solubilities, and (2) that the monoclinic form in his experience is unstable, and suggests that the difficulty Wyrouboff finds in applying the phase rule to systems in which there is transformation of crystalline phases does not invalidate the rule, but merely requires its extension.

T. A. H.

Preparation of Pure Ammonium Chloride. F. WILLY HINRICHSSEN (*Zeitsch. anorg. Chem.*, 1908, 58, 59—64).—The preparation of pure ammonium chloride by electrolytic reduction of nitric acid is described. To avoid the formation of hydroxylamine, a mixture of nitric acid and copper sulphate was electrolysed at 10 volts and 4.5 amperes, a platinum dish being used as cathode and a rotating perforated platinum plate as anode. When reduction was nearly complete, more nitric acid was added, and the process continued. The reduction product was then placed in a desiccator, which also contained a platinum dish filled with hydrochloric acid. Excess of calcium oxide was added to the solution, and, on exhausting, the ammonia given off was absorbed by the acid. Finally, the ammonium chloride was purified by sublimation in quartz vessels. The results of atomic weight determinations with this salt will be communicated later.

G. S.

Existence of Different Modifications of Ordinary Grey Silver. LEO PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 367—376).—The heat effect observed on mixing solutions of silver and ferrous sulphates, dissolved in water, *N*-sulphuric acid, 10.5% mannitol solution, or 23.7% glycerol solution is found to vary with the conditions under which the reaction takes place. Similar variations are found to occur in the constant of the reaction: $\text{Ag}^+ + \text{Fe}^{2+} \rightleftharpoons (\text{Ag}) + \text{Fe}^{3+}$. Hence the conclusion is drawn that in these reactions a mixture of different modifications, probably two in number, of ordinary grey silver is precipitated.

T. H. P.

Certain Alloys of Silver. ERNESTO PANNAIN (*Gazzetta*, 1908, 38, i, 349—351. Compare Petrenko, *Abstr.*, 1907, ii, 346).—The author has examined various alloys of silver to ascertain whether they are suitable for coinage.

The binary alloys of silver with cobalt, nickel, iron, or manganese are not readily prepared, and are unsuitable for the purpose named; in presence of a third metal, the alloys are more readily formed. Silver, nickel and copper, or silver, cobalt and copper, or silver, manganese and copper, when fused together, give alloys containing the three metals in various proportions, and those which are rich in silver are white, compact, malleable, harder than alloys of silver and copper, and capable of being polished. Further, although an alloy consisting of equal parts of nickel and copper is not attracted by a magnet, alloys rich in silver and containing small proportions of copper and nickel are distinctly magnetic. This magnetic property persists if the nickel in these alloys is replaced wholly or partly by cobalt, or if the copper is replaced by another non-noble metal. A high temperature is necessary in the preparation of these alloys; otherwise, two alloys are formed, one rich in silver, and the other containing about 30% of this metal.

T. H. P.

The Colloidal and Gelatinous Salts of the Alkaline Earths. II. CARL NEUBERG and B. REWALD (*Biochem. Zeitsch.*, 1908, 9, 537—550. Compare *Abstr.*, 1906, ii, 753).—When carbon dioxide is passed through a methyl-alcoholic solution of barium oxide, the liquid remains clear; after a time it suddenly gets warm, and barium carbonate separates in a gelatinous form. On passing more carbon dioxide through the mass, a clear solution is formed of typical colloidal character of the consistency of thick collodium. The addition of sulphuric acid to this produces a thick clot of gelatinous barium sulphate. The barium carbonate colloid, as long as it contains methyl alcohol, is a reversible one, and readily redissolves on adding excess of solvent; if, however, completely freed from solvent, it only partly redissolves. It does not diffuse through the ordinary membranes when dialysed against water or methyl alcohol. Its electrical conductivity is $k = 31.5 \times 10^{-6}$, that is, it is practically a non-conductor. It is possible that this slight conductivity is due to incomplete removal of impurities. Various strontium compounds were also prepared by the action of acids on a solution of strontia in methyl alcohol (namely, a gelatinous sulphate, phosphate, and oxalate). The carbonate is formed in the same way as the corresponding barium compound; no separation of a gel, however, takes place.

By passing carbon dioxide into methyl alcohol containing calcium oxide in suspension, a colloidal solution of the carbonate can be obtained which, after some time, becomes converted into a gel. The solution is miscible with toluene, chloroform, benzene, and ether; the addition of acetone or carbon disulphide causes precipitation.

Similar colloidal compounds can be produced with magnesium. The biological importance of these facts, especially in reference to the formation of lipid soluble compounds of the alkaline earths, is discussed.

S. B. S.

Action of Ammonium Citrate on Calcium Phosphate. Diverse Reactions. A. BARILLÉ (*J. Pharm. Chim.*, 1908, [vi], 27, 437—441. Compare Grupe and Tollens, *Abstr.*, 1880, 825; 1881, 759, 845; Landrin, *Abstr.*, 1882, 604).—After twelve hours' digestion, 100 c.c. of the ammonium citrate solution, obtained by exactly neutralising 400 grams of citric acid with ammonia and diluting the solution to 1 litre, dissolves the mean quantity of 4.10 grams of dicalcium hydrogen phosphate, $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, and 1.40 grams of dry tricalcium phosphate. The solubility of both salts varies with their physical condition. Recently-prepared, gelatinous tricalcium phosphate is more soluble than the dry salt, and the latter becomes insoluble on calcination. Similarly, the dicalcium salt is less soluble when anhydrous, and becomes insoluble on calcination, being transformed into the pyrophosphate. Thus, contrary to the statements of several authors, precipitated tricalcium phosphate is appreciably soluble in ammonium citrate solution.

When a saturated solution of dicalcium hydrogen phosphate in neutral ammonium citrate solution is allowed to evaporate spontaneously, crystals are obtained containing ammonia, calcium, and citric and phosphoric acids. If the evaporation is accelerated, some ammonia is evolved, and a porcelain-like magma of crystalline needles produced. Both substances are probably true double salts. The first can also be obtained by precipitation with alcohol. The same results are obtained with tricalcium phosphate. The conclusion is drawn that ammonium citrate solution has not merely a solvent action on calcium phosphate, but forms true double salts with it.

E. H.

Preparation of Strontium Salts Free from Barium. H. CARON and D. RAQUET (*Bull. Soc. chim.*, 1908, [iv], 3, 493—495).—The method of preparation described is based on the data recorded in a preceding paper (this vol., ii, 535), which indicate that alkali chromates are the most satisfactory reagents for the elimination of barium from strontium. Where the product under examination contains more than 1% of barium, it is dissolved in ten times its weight of water, and the solution shaken continuously with strontium sulphate during about forty-eight hours. This treatment will reduce the amount of barium in solution to about 1%. To this, excess of a solution containing 3% of potassium chromate and 0.1% of potassium dichromate is added, and the mixture set aside for twenty-four hours, after which the precipitated barium chromate is filtered off and the strontium in solution is converted into carbonate (1) by adding a large excess of sodium carbonate, or (2) by pouring the strontium solution, little by little with continuous agitation, into excess of sodium carbonate. These precautions are necessary to prevent the formation of a slightly soluble double chromate, which would remain in the carbonate and stain it yellow. T. A. H.

Copper-Tin Alloys. OTTO SACKUR and H. PICK (*Zeitsch. anorg. Chem.*, 1908, 58, 46—58. Compare *Abstr.*, 1904, ii, 336, 818; 1905, ii, 524).—The potential of copper-tin alloys has been determined indirectly from the effect of shaking the finely-divided alloy with solutions of salts of certain other metals. Observations are made whether,

and to what extent, the metals are liberated, and, when the potential between the metal and its solution is known, the potential of the tin in the alloy and hence the nature of the alloy can be determined.

Copper-tin alloys containing 0—56% of copper precipitate lead from a solution of lead chloride up to the same equilibrium point as does tin itself, so that they contain free tin. Alloys containing 57—60% of copper do not precipitate lead from lead chloride solution, or copper from cuprous iodide solution, but cause the separation of copper from solutions of cuprous chloride and bromide. Alloys containing more than 60% of copper do not precipitate copper from the two solutions last mentioned, but do from solutions of the chloride and sulphate.

From the results, the conclusion is drawn that copper and tin form two compounds: one, containing 57% of copper, is probably Cu_3Sn , and has a potential about 0.2 volt higher than tin, and the other, containing 60% of copper, has a potential about 0.45 volt higher than tin, and is probably Cu_5Sn_2 or Cu_2Sn . The results are in fair agreement with the recent direct potential measurements of Pushin (Abstr., 1907, ii, 774, 837). G. S.

Reactions of Copper, Bismuth, and Silver with Nitric Acid.

JOHN H. STANSBIE (*J. Soc. Chem. Ind.*, 1908, 27, 365—367. Compare Abstr., 1907, ii, 25).—In continuation of his experiments on the action of nitric acids on metals, the author has studied the changes taking place when electrolytic copper, bismuth, and silver are dissolved in nitric acid, D 1.2, in an atmosphere of hydrogen at 65°. The apparatus employed is described and figured. The gases evolved are passed through sodium hydroxide solution and then into a measuring tube; when the metal is dissolved completely, the solution in the reaction vessel is run into a measured amount of a known sodium carbonate solution. The alkaline solutions are titrated with permanganate for nitrous acid, and with standard acid for excess of alkali. With copper and bismuth, the evolution of nitrogen peroxide is observed immediately the nitric acid comes in contact with the metal, and goes on steadily throughout the reaction; the red gas is absorbed completely by the sodium hydroxide solution. With bismuth, the evolution of the red gas is slightly less marked than with copper; both metals liberate considerable amounts of nitrogen. With silver, nitrogen peroxide is observed only towards the end of the reaction; the volume of gas liberated is smaller than with the other two metals, and nitrogen is not found in the measuring tube. On the other hand, the amount of nitrous acid found in the sodium carbonate is greatest with silver, which is considered to result from the greater stability of silver nitrite. The amount of nitrous acid found in the sodium hydroxide is almost equivalent to the alkali neutralised by the gases absorbed. If the absorption tube is filled with water instead of sodium hydroxide solution, less nitrous acid is found on titration, which is ascribed to its partial decomposition according to the equation: $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$. The nitric acid employed is almost completely accounted for. These results are considered to be in agreement with Divers' views on the action of nitric acid on metals (Trans., 1883, 43, 443; 1899, 75, 86). G. Y.

Oxides of Thallium. IV. OTTO RABE (*Zeitsch. anorg. Chem.*, 1908, 58, 23—38. Compare Abstr., 1906, ii, 285, 672; 1907, ii, 769).—The preparation and properties of a new oxide of thallium, $(\text{TlO})_x$ (probably $\text{Tl}_2\text{O}_3, \text{Tl}_2\text{O}$), are described.

To 15 grams of a 10% aqueous solution of thallous sulphate, 175—200 grams of 20% potassium hydroxide are added, the clear, filtered solution is cooled to -15° , and 3.5 grams of a 3% solution of hydrogen peroxide added with constant shaking. A red precipitate is momentarily formed, which rapidly gives place to the new bluish-black, lustrous oxide; the latter is separated by filtration, and washed with cooled anhydrous alcohol and ether.

Even cold water decomposes the oxide into a mixture of thallic oxide and thallous hydroxide, and dilute sulphuric and nitric acids act in an analogous way; neither free oxygen nor hydrogen peroxide is produced. On being kept in the air, the oxide absorbs carbon dioxide according to the equation: $\text{Tl}_2\text{O}_3, \text{Tl}_2\text{O} + \text{CO}_2 = \text{Tl}_2\text{O}_3 + \text{Tl}_2\text{CO}_3$; it becomes slowly oxidised at the ordinary temperature in air free from carbon dioxide. When a current of oxygen is passed over it at the ordinary temperature, it is oxidised completely to thallic oxide, which is remarkable, inasmuch as thallous salts are acted on only by powerful oxidising agents. G. S.

Scheme for the Separation of the Rare Earths. CHARLES JAMES (*Chem. News*, 1908, 97, 205—209. Compare Abstr., 1907, ii, 467; this vol., ii, 190).—A scheme for the qualitative separation of the rare earths is described in detail. Having obtained the earths in the form of oxalates, zirconium and thorium may be separated by boiling with a solution of ammonium oxalate, when the whole of the zirconium and nearly all the thorium pass into solution. On the addition of hydrochloric acid to the filtered solution, thorium oxalate alone is precipitated. Small quantities of the metals of the yttrium and cerium groups pass into the concentrated ammonium oxalate solution. From the former, thorium can be separated by means of the insolubility of potassium thorium sulphate in a solution of potassium sulphate, and from the latter by the solubility of thorium oxalate in ammonium oxalate or acetate solution, or by the addition of hydrogen peroxide to a solution containing thorium and the cerium earth metals.

The next step in the treatment of the mixed rare earth oxalates depends on the proportion of yttrium earths in the mixture, and on the presence or absence of thorium. When the material consists of more than 20% of the yttrium earths and practically no thorium, the oxalates are converted into sulphates, which are dissolved in ice-cold water and the solution stirred with solid sodium sulphate, which throws down the double sulphates of sodium and the cerium earths. If thorium is present, the mother liquor is then saturated with potassium sulphate, and the separation of the thorium is thus completed by reason of the insolubility of the double potassium sulphate.

Cerium may be separated by treating a neutral nitrate solution with excess of zinc oxide and addition of potassium permanganate; the precipitate obtained consists of cerium and manganese peroxides, together with thorium (if present) and a small amount of lanthanum,

praseodymium, and neodymium. The thorium can be removed by the peroxide method, and the cerium can then be separated from the other three rare earths by renewed treatment of the nitrate solution with zinc oxide and a quantity of potassium permanganate insufficient for complete precipitation.

Lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium are best separated by fractional crystallisation of the double magnesium nitrates. The separation of lanthanum from praseodymium is completed by fractional crystallisation of the double ammonium nitrates, and that of praseodymium from neodymium by fractional crystallisation of the double manganese nitrates.

For the separation of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, and scandium, the bromate method previously described (*loc. cit.*) is recommended. In the previous communication, the position of yttrium in the bromate fractionation was given as between terbium and dysprosium. It is now found that yttrium is obtained from the bromate fractions between holmium and erbium.

H. M. D.

Preparation of Aluminium Bromide and its Latent Heat of Fusion. IWAN A. KABLUKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 485—488).—For preparing aluminium bromide in large quantities, the author uses a glass retort, the tube of which connects with a sloping, hard glass tube heated in a combustion furnace and bent at the lower end so as to fit into a glass receiver. After the retort is charged with aluminium chips and the hard glass tube is heated sufficiently to prevent bromine or aluminium bromide from condensing in it, bromine is allowed to fall gradually on to the aluminium from a tap-funnel, bromine vapour from the receiver being conducted to a draught by means of a tube. After redistillation, the aluminium bromide is obtained as a colourless liquid solidifying to a white mass. Any iron in the aluminium is precipitated according to the reaction : $\text{Fe}_2\text{Br}_6 + 2\text{Al} = \text{Al}_2\text{Br}_6 + 2\text{Fe}$.

The mean specific heat of aluminium bromide between 22° and 76° is 0.08912. Determinations of the latent heat of fusion of the bromide gave the values: 10.35, 10.58, and 9.98 Cals. per 1 gram. Taking the value 10.47 for the latent heat, van't Hoff's formula gives the molecular depression of the freezing point of aluminium bromide as 262; experiments with solutions of stannic bromide in aluminium bromide give the mean value 279 for molecular concentrations of stannic bromide not exceeding 12%.

T. H. P.

Ferronitrosulphides. VI. ITALO BELLUCCI and PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 424—431. Compare this vol., ii, 111).—When the salt $\text{KFe}_4\text{S}_3(\text{NO})_7 \cdot \text{H}_2\text{O}$ is heated with dilute sulphuric acid and silver sulphate solution, four of the nitrogen atoms are evolved as nitric oxide and the other three as nitrous oxide. Under similar conditions, the salt $\text{K}_2\text{Fe}_2\text{S}_2(\text{NO})_4$ yields $2\text{NO} + 2\text{N}_2\text{O}$. Pavel (Abstr., 1883, 297) has shown that, when heated with alkali hydroxide solution, the hepta-salt is decomposed according to the equation : $2\text{KFe}_4\text{S}_3(\text{NO})_7 + 4\text{KHO} = 3\text{K}_2\text{Fe}_2\text{S}_2(\text{NO})_4 +$

$\text{Fe}_2\text{O}_3 + \text{N}_2\text{O} + 2\text{H}_2\text{O}$. When, however, cadmium hydroxide is present in addition to potassium hydroxide, both the hepta- and tetra-salts yield all their nitrogen in the form of nitrous oxide. The absence of nitric oxide and of ferrous iron from the products of this decomposition shows that the ferrous iron has reduced the nitric oxide to nitrous oxide, thus: $2\text{FeO} + 2\text{NO} = \text{Fe}_2\text{O}_3 + \text{N}_2\text{O}$. All the authors' observations are in accord with the view that the iron present in these nitrosulphides exists in the ferrous condition. Cambi's results (see this vol., ii, 288) are discussed.

T. H. P.

The Utilisation of Native Iron-Aluminium Phosphates. HEINRICH SCHRÖDER (D.R.-P. 192591).—A mixture of iron-aluminium phosphate and calcium and magnesium chlorides is ignited, when aluminium chloride sublimes, and is collected in a cold concentrated solution of sodium chloride, where it forms the double sodium-aluminium chloride. The ferric chloride which subsequently sublimes is collected in a special receiver; the residue is worked up for phosphate soluble in citric acid.

G. T. M.

Reducing Power of Ferropyrphosphates. P. PASCAL (*Compt. rend.*, 1908, 146, 862—864. Compare this vol., ii, 193).—Solutions containing the alkali ferropyrphosphates reduce gold and silver salts in the cold; platinum salt solutions are not reduced even on boiling. In the case of dilute solutions, the reduced gold and silver are in the colloidal condition, and are so strongly coloured that the reaction may be made the basis of a colorimetric method for the estimation of the metals.

Mercuric salts are reduced to mercurous, and then to mercury; in dilute solutions, the mercury is obtained as a colloidal solution, which has a maroon colour by transmitted, and a grey colour by reflected, light.

From cupric salt solutions, a colloidal cuprous hydroxide solution is obtained, which is yellow by transmitted, and green by reflected, light. The production of this yellow colour furnishes a very sensitive test for copper.

After some days, the yellow colour becomes darker, and the cuprous hydroxide is reduced to metallic copper. At 100° , the copper is deposited on the glass as a thin film.

H. M. D.

Freezing-point Diagram of the Cobalt Sulphides. K. FRIEDRICH (*Metallurgie*, 1908, 5, 212—215).—Mixtures containing from 0% to 33.6% sulphur have been investigated.

Practically pure cobalt separates from alloys rich in cobalt, the freezing-point curve falling to a eutectic point at 26.6% S and 879° . It then rises to a maximum at 935° and 29.3% S, corresponding with the compound Co_4S_3 , the existence of which appears to be established. This compound forms solid solutions containing up to 72.3% of cobalt. The form of the equilibrium diagram also points to the existence of a compound CoS , but alloys of this composition lose sulphur under the ordinary pressure. At lower temperatures, a compound, Co_6S_5 , also appears to exist.

The mixtures become porous as the sulphur is increased. The colour changes progressively through the series from cobalt-white to a bronze-like yellow. Only alloys containing more than 68·7% of cobalt are attracted by the magnet.

C. H. D.

Behaviour of the Potassium Chromates at High Temperatures. ERICH GROSCHUFF (*Zeitsch. anorg. Chem.*, 1908, 58, 102—112).—Potassium chromate, m. p. 971°, exists in two crystalline modifications, the transition temperature being at 666°. The α -form, stable above that temperature, is completely miscible with α -potassium sulphate (hexagonal), the β -form with β -potassium sulphate, and neither the freezing point nor transition curve shows maxima or minima. The change of colour shown by the β -chromate on heating does not appear to be connected with the transition, as it is gradual, and is evident even at 260°.

Chromic acid melts with slight decomposition at about 196°, and it is probable that the true melting point is still higher. Attempts to obtain freezing-point curves of mixtures of chromic acid and potassium chromate containing more than 50 mol. % of CrO_3 were unsuccessful, owing to the decomposition of the former on heating. Potassium dichromate suffers considerable decomposition on heating at the melting point of the monochromate.

The freezing-point curve of mixtures of potassium chromate and dichromate was determined in the usual way, the mixtures being heated in a nickel resistance furnace. The curve falls regularly from the melting point of the chromate to a eutectic point at 393°, the mixture containing 99% of the dichromate, and then rises to the melting point of the latter, 396°. At the transition temperature, $\alpha\text{-K}_2\text{CrO}_4 \rightleftharpoons \beta\text{-K}_2\text{CrO}_4$, 666°, the mixture contains about 75·5% of the dichromate.

G. S.

Anhydrous Molybdates. I. ERICH GROSCHUFF (*Zeitsch. anorg. Chem.*, 1908, 58, 113—119).—Molybdic anhydride, MoO_3 , melts without decomposition at 791°. The observation of Boeke (Abstr., 1906, ii, 750) that anhydrous sodium molybdate, Na_2MoO_4 , exists in four modifications is confirmed.

The freezing-point curve of mixtures of sodium molybdate and molybdic anhydride shows a well-defined maximum, corresponding with the composition of sodium dimolybdate, $\text{Na}_2\text{Mo}_2\text{O}_7$ (prismatic crystals), m. p. 612°, and two eutectic points at 551° and 73 mol. % and 495° and 24·5 mol. % of sodium molybdate respectively.

G. S.

Determination of the Molecular Weight of Uranous Oxide. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1908, 163—164).—The determinations were made by decomposing uranyl chloride, UO_2Cl_2 , by means of a current of hydrogen. The results obtained ranged in one set of experiments between 270·1 and 270·4. In others, numbers lying between 271 and 272 were obtained.

T. A. H.

Colloidal Zirconium. EDGAR WEDEKIND [with S. JUDD LEWIS] (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 289—293. Compare Abstr., 1905, ii, 596).—Colloidal zirconium (Berzelius) was prepared by

heating potassium zirconium fluoride with potassium in a special apparatus in absence of air, the product was washed successively with warm alcohol and warm water, then treated with dilute hydrochloric acid, and successive quantities of water added to it on a filter. At first an acid solution passed through, but later a neutral colloidal solution of the metal was obtained. When the precipitate no longer yielded a colloid on washing, this property could be re-imparted to it by renewed treatment with acid.

The colloidal solution thus obtained is greyish-white by transmitted, and black and opalescent by reflected, light; it is relatively stable towards acids, but is reprecipitated by alkalis and by salts which become alkaline by hydrolysis. The effect of a large number of electrolytes on the stability of the solution is described. The particles are positively charged. The appearance of the solution when examined with the ultramicroscope is very much like that of colloidal platinum.

The product is by no means pure, containing more or less oxide. When prepared by the original method of Berzelius, it only contains about 36% of the metal and much oxide, but by a modified method a product containing up to 70% of the metal was obtained. G. S.

Sulphur Compounds of Thorium. ANDRÉ DUBOIN (*Compt. rend.*, 1908, 146, 815—817).—Thorium chloride containing a trace of the oxychloride is obtained by passing chlorine mixed with carbon tetrachloride vapour over heated thoria. When a mixture of this chloride with excess of sodium or potassium chloride, contained in a porcelain boat, is heated in a current of dry hydrogen sulphide, the product, after washing out the alkali chloride, consists chiefly of brown, micaceous lamellæ, together with small quantities of yellow crystals and of an amorphous substance. The brown lamellæ, which can be isolated by means of a sieve, are composed of *thorium sulphide*, ThS_2 ; they act very slightly on polarised light, and have D_D^{20} 6.7. By treating the siftings with nitric acid at 40° , the brown lamellæ are violently attacked and dissolved, leaving the yellow crystals, which are only acted on very slowly. The latter consist of *thorium oxysulphide*, ThOS ; they are uniaxial and optically negative, and have D_D^{20} 8.42. E. H.

Vanadium-Iron Alloys. RUDOLF VOGEL and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1908, 58, 73—82).—The alloys used in the investigation were prepared by an alumino-thermal method. As it was found impossible to obtain alloys rich in vanadium by fusing the latter with alloys rich in iron, the former alloys were prepared by alumino-thermal reduction of mixtures of ferric oxide and vanadium pentoxide in a crucible, the interior of which was lined with so-called "fusible" magnesia. When the lining was not used, the mixture dissolved about 7% of silicon from the walls of the vessel, and these impure alloys were also investigated. The higher temperatures were determined with a Wanner pyrometer.

The freezing-point curve of the almost pure alloys of iron and vanadium falls from the melting point of iron to a minimum at 32%

of vanadium, and then rises to the melting point of the latter element ($1750 \pm 30^\circ$). Except at the minimum, the crystallisation intervals are considerable, and, as the alloys are homogeneous throughout, the metals form a complete series of mixed crystals. The behaviour of the alloys containing silicon is considerably more complicated; the minimum on the freezing-point curve is lower, and at 1380° there is a break in miscibility from 55 to 90% of vanadium. In the alloys containing 20 to 52% of vanadium, there is a transition between 1100° and 1250° , the nature of which has not been elucidated.

The vanadium steels, except those very rich in iron, are hard and fairly brittle, but can be filed and hammered. The presence of silicon greatly increases the hardness and brittleness. Pure vanadium-iron alloys are acted on by nitric acid, but those containing silicon only by hot aqua regia. G. S.

Decomposition of Antimony Hydride. ALFRED STOCK, EUSEBIO ECHEANDIA, and PAUL R. VOIGT (*Ber.*, 1908, 41, 1309—1318. Compare Abstr., 1907, ii, 180, 181).—The earlier investigation was carried out at 25° , and the present paper deals with the decomposition at 0° , 50° , and 75° in order to test whether the adsorption equation $M = aC^p$ also held good for these temperatures and also to ascertain if the constant, p , increased with the temperature to approximately unity, or if the quantity absorbed, M , becomes proportional to the concentration of the hydride, C . The alteration in the velocity of decomposition may be represented by the equation $\Lambda = 1/C_t^{1-p}$, t being the time.

The experiments were carried out in the same manner as before, the only alteration being the substitution of a mirror scale for the cathetometer, as at the higher temperatures employed rapid decomposition and therefore rapid alterations in pressure occurred. The correction for the departure from Boyle's Law due to molecular attraction at 760 mm. was found to be 13.2 mm. at 0° , 10.8 mm. at 25° , 8.2 mm. at 50° , and 6.2 mm. at 75° .

From the values obtained, the following conclusions are drawn: (1) that the alteration in the velocity of the reaction found at all four temperatures is in agreement with the equation $\Lambda = 1/C_t^{1-p}$; (2) that the constant p increases with rise in temperature, and (3) that the observed phenomena are in agreement with the view that the decomposition occurs in the adsorption layer.

The temperature-coefficients for $0-10^\circ$, $30-40^\circ$, and $60-70^\circ$ have been calculated to be 2.05, 1.80, and 1.66. W. R.

Compounds of Antimony Sulphate with Metallic Sulphates. AUGUST GUTMANN (*Arch. Pharm.*, 1908, 246, 187—190. Compare Abstr., 1899, ii, 33; Metzl, Abstr., 1906, ii, 174; Weinland and Kuhl, Abstr., 1907, ii, 626—627).—Double sulphates of antimony and the commoner alkali metals have already been described (*loc. cit.*), and in the present paper compounds of the same type containing the rarer alkali metals lithium, rubidium, caesium or silver, and thallium are described. They are obtained by adding antimony oxide to a solution of the sulphate of the other metal in dilute sulphuric acid, have the general

formula $\text{SbM}'(\text{SO}_4)_2$, crystallise for the most part in colourless needles, and are slowly decomposed by water, yielding basic salts. T. A. H.

Action of Sugars on Gold Chloride Solutions. LUDWIG VANINO (*Chem. Zentr.*, 1908, i, 446—447; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 51—53. Compare Abstr., 1906, ii, 618).—In diffused daylight the addition of $\text{AuCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ to a dilute sugar solution causes a blue coloration, owing to inversion of the sugar and formation of colloidal gold. This change takes place more slowly in the dark, and when illuminated by a mercury lamp a violet colour is rapidly produced, metallic gold separating on the surface. When warmed, the violet colour first produced changes to red, whilst in presence of larger quantities of gold a permanent violet-blue colour is obtained. Sodium hydroxide gives a red coloration, whilst acids cause the gold to separate in the ordinary form. $\text{AuCl}_3 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}$ produces slightly different colorations. Twice distilled, sterilised water was used, ordinary distilled water being found to reduce gold solutions. J. V. E.

Platinum-Thallium Alloys. L. HACKSPILL (*Compt. rend.*, 1908, 146, 820—822).—Spongy platinum thrown on to the surface of fused thallium dissolves as easily as in fused lead. The melting point of the resulting alloy does not exceed that of thallium until the proportion of platinum reaches 10%, but as the amount increases to 48·8% it rises to 685°. As the proportion of platinum is further increased, the m. p. at first falls slightly, but then rises continuously, reaching 855° for 65% and afterwards exceeding 1000°. Micrographic examination of the alloys rich in thallium shows that they consist of very brilliant white crystals, easily polished, surrounded by a darker, very soft eutectic. As the composition approximates to the formula TiPt (48·8% Pt), the number and size of the crystals increase until they constitute the entire alloy. Alloys still richer in platinum are susceptible of a higher polish; their surface appears homogeneous, but their composite character is shown on oxidation in a Bunsen flame.

The alloy PtTi is obtained in the form of steel-grey, prismatic needles by the gradual action of nitric acid (10%) on alloys containing less than 10% of platinum. It has D_{20}^{25} 15·65; hardness 3 (Mohs' scale); m. p. 685°, and specific heat, 0·0450. It loses a little thallium on continued heating above the melting point, but does not give pure platinum even on prolonged fusion in the oxyhydrogen flame. The alloy is attacked by the halogens, and dissolved by warm aqua regia; the latter on boiling, however, gives the insoluble thallium platinum-chloride. It is not attacked by hydrochloric acid, and only superficially acted on by sulphuric and nitric acids and by potassium hydrogen sulphate. It resists the action of the fused alkali carbonates, and is only very slowly attacked by sodium peroxide. It dissolves easily in fused zinc, lead, or silver, and forms an amalgam with mercury. Its quantitative analysis, rendered very difficult by its properties, was effected by cupellation with four times its weight of silver and three times its weight of lead.

The compound PtTl is very similar, especially in its physical properties, with the alloy PtPb (Doerinckel, Abstr., 1907, ii, 785).
E. H.

Mineralogical Chemistry.

Origin of Jet. PERCY E. SPIELMANN (*Chem. News*, 1908, 97, 181—183. Compare *ibid.*, 94, 281).—Determinations of the heating values and chemical composition lead the author to the conclusion that jet must be classed with cannel coal rather than with lignite. When jet is extracted with carbon disulphide, about 7% of a thick, dark brown oil, smelling like petroleum, is obtained. Having this in mind, the suggestion is made that the particles of jet may be surrounded by a film of the petroleum-like substance, causing the difference between the electrifying power of jet and that of cannel coal. The attempt of McIntosh (*Chem. News*, 1906, 94, 314) to connect closely jet and amber is criticised.

J. V. E.

Stephanite Crystals from Arizpe, Sonora, Mexico. WILLIAM E. FORD (*Amer. J. Sci.*, 1908, [iv], 25, 244—248).—A description is given of some large crystals, 2—3 cm. across, and of some smaller twinned crystals with a rich development of faces. Analysis agrees with the usual formula $5\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$.

Ag.	Sb.	S.	Total.
68·36	15·30	16·33	99·99

L. J. S.

Helium in Minerals Containing Uranium. FRÉD. BORDAS (*Compt. rend.*, 1908, 146, 896—898. Compare this vol., ii, 430).—By employing the method already described, the author finds that uraniferous minerals do not lose helium until heated above 250°. It is thus possible to remove moisture from the finely-divided mineral without incurring appreciable loss of helium. This gas was found to be absent in some highly radioactive pitchblende which had been kept in closed bottles for several years; chemical analysis, moreover, failed to detect uranium in these specimens. Helium was found in abundance, associated with uranium, in samarskite, euxenite, naëgite, yttrantalite, and annerödite. In less abundance it was present in wöhlerite, pyrochlore, polycrase, trögerite, xenotime, gummite, thorite-orangite, and niobite-columbite. Minerals containing well-defined or crystalline salts of uranium do not liberate helium. Examples of this class are torbernite, autunite, and carnotite. Helium has been characterised by the line $d=5878$ in native bismuth from Saxony.

W. O. W.

Physicochemical and Mineralogical Investigations of the Occurrence of Bromine and Iodine in the Potassium Salt Deposits. H. E. BOEKE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 439—441).—The part played by bromides and iodides in the

crystallisation of the halogen salts of sodium, potassium, and magnesium has been examined.

Magnesium chloride and magnesium bromide hexahydrates form a complete series of mixed crystals; potassium chloride and bromide exhibit the same phenomenon. Carnallite and bromo-carnallite both belong to the rhombic system, but show considerable crystallographic differences. They represent an isodimorphous pair, for which the interval between the two series of crystals is very small. At 25°, a solution in which the molecular ratio of the bromine compound to the sum of the bromine and chlorine compounds is 0.302 is in equilibrium with the two kinds of mixed crystals.

Sodium chloride shows little tendency to form mixed crystals with sodium bromide, but from a solution in which the molecular ratio of bromide to the sum of bromide and chloride is greater than 0.82, mixed crystals of the dihydrated salts are obtained which are isomorphous with sodium bromide dihydrate.

The formation of mixed crystals containing potassium chloride and bromide and crystals containing carnallite and bromocarnallite is not influenced by the presence of large quantities of sodium chloride. The presence of considerable quantities of magnesium chloride increases the tendency of sodium chloride and potassium chloride to take up the corresponding bromides from solution.

These results agree with the observation that the percentage of bromide in the different Stassfurt layers is approximately proportional to the quantity of carnallite present. The chlorides above mentioned do not yield mixed crystals with the corresponding iodides. The iodide present in the Stassfurt mother liquors must therefore have accumulated in these and have been decomposed by oxidation in contact with the air.

H. M. D.

Decomposition of Dolomite. NICHOLAS KNIGHT (*Chem. News*, 1908, 97, 217).—The dolomite of Iowa and other sections of the country belonging to the Niagara period of the Upper Silurian undergoes disintegration where exposed to air. The following figures were obtained on analysis of the massive (I) and the disintegrated (II) rocks:

	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaCO ₃ .	MgCO ₃ .	Total.
I.	0.83	0.34	0.25	53.62	44.96	100.00
II.	0.56	0.74		48.43	50.56	100.09

The disintegrated rock is overlaid by a clay, which has probably been formed by further slow decomposition of the dolomite. Analysis gave:

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Total.
16.68	60.37	6.18	0.22	0.03	17.14	101.12

G. Y.

Manganese Ore Deposits of the Queluz District, Brazil. ORVILLE A. DERBY (*Amer. J. Sci.*, 1908, [iv], 25, 213—216).—The extensive deposits of manganese ore (psilomelane?) in the Queluz district of Minas Geraes were formerly considered by the author

(Abstr., 1901, ii, 558) to have been derived by the weathering of rocks rich in manganese garnet (spessartite). A recent visit to the quarries, after the surface material has been removed, proves, however, that the rock from which the black manganese oxide has been derived consists largely of manganese carbonate. This is a dark-coloured rock (anal. I and II by E. Hussak) resembling a limestone, and consisting of rhodochrosite (?), tephroite, and spessartite, with a little rhodonite :

	CO ₂ .	SiO ₂ .	MnO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.
I.	22·62	11·80	47·52	7·50		3·76	6·27
II.	4·59	27·67	57·48	1·41	2·48	1·82	4·60

L. J. S.

Two New Boron Minerals of Contact-Metamorphic Origin.

A. KNOPF and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1908, [iv], 25, 323—331).—The Alaskan deposits of tin ore, situated in the extreme western part of the Seward Peninsula, are genetically associated with granitic masses intrusive into limestones; the latter have been intensely metamorphosed by contact and pneumatolytic action, with the production of tourmaline and various other minerals, including the two new species now described.

Hulsite occurs abundantly with idocrase, magnetite, garnet, and fluorite in a matrix of coarse, white calcite; it has a black colour and streak with a strong sub-metallic lustre, and is opaque; the tabular crystals are probably orthorhombic, and possess a good prismatic cleavage, the cleavage angle being $57^{\circ} 38'$; D 4·28, H 3. The mineral is readily soluble in hydrochloric acid and in hydrofluoric acid, and it is readily fusible before the blowpipe.

Anal. I of pure non-magnetic material corresponds with the formula $7(\text{Fe}, \text{Mg})\text{O}, \text{Fe}_2\text{O}_3, \text{H}_2\text{O}, 4\text{B}_2\text{O}_3$, and II is the mean of several analyses of material intimately intergrown with about 20% of magnetite. In these analyses, the iron was determined volumetrically, since when precipitated for gravimetric determination it carries down some of the boric acid; it was also found that, when the mineral is ground to a fine powder, some of the ferrous iron is oxidised, and the material absorbs water from the air :

	FeO.	MgO.	Fe ₂ O ₃ .	H ₂ O.	B ₂ O ₃ .	Insol.	Total.
I.	33·27	10·17	17·83	[1·81]	[27·42]	10·00	100·00
II.	34·44	8·48	27·64	1·66	25·27	2·24	99·73
III.	44·48	1·44	16·72	2·03	20·89	14·35	99·91

Paigite occurs with tourmaline, fluorite, idocrase, mispickel, &c., in the metamorphosed limestone. It is coal-black, lustrous, and opaque, and presents the form of matted fibres and long needles with a foliated appearance; D 4·71, H 3. The mineral is readily soluble in hydrochloric acid and in hydrofluoric acid. Anal. III corresponds with the formula $6(\text{Fe}, \text{Mg})\text{O}, \text{Fe}_2\text{O}_3, \text{H}_2\text{O}, 3\text{B}_2\text{O}_3$.

The two minerals, although very similar in composition, are strikingly different in physical characters. Related minerals are ludwigite ($4[\text{Fe}, \text{Mg}]\text{O}, \text{Fe}_2\text{O}_3, \text{B}_2\text{O}_3$), pinakiolite, and warwickite. L. J. S.

Tungstite and Meymacite. THOMAS LEONARD WALKER (*Amer. J. Sci.*, 1908, [iv], 25, 305—308).—A heavy, golden-yellow mineral

with a resinous lustre, and apparently an alteration product of wolframite, occurs in veins of gold quartz near Salmo, in British Columbia. It is traversed by darker-coloured veins, and encloses specks of gold and other impurities. Minute crystals from cavities possess a perfect cleavage in one direction, perpendicular to which is a bisectrix of the optic axes. The portion of the material dissolved by ammonia or sodium hydroxide contains 80.08% WO_3 , and a bulk analysis gave:

WO_3 .	CaO .	FeO .	Fe_2O_3 .	H_2O .	Total.
86.20	0.54	[1.21]	4.14	7.72	99.81

This corresponds with 86.29% $\text{WO}_3 \cdot \text{H}_2\text{O}$, together with some scheelite, wolframite, and limonite. The sp. gr. calculated for the pure material is 5.517.

These results indicate that the mineral is related to the meymacite of A. Carnot (1874), for which the formula is given as $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ (although the water shown in the three analyses varies from 6.85 to 12.93%, and 6% Fe_2O_3 is present). It is pointed out, however, that the tungstite of B. Silliman (1822) has never been analysed, and that the crystallographic constants quoted for this refer to the artificial anhydrous oxide. It is therefore suggested that tungstite and meymacite are identical, being hydrated tungstic oxide, and that the former name be the one adopted.

L. J. S.

Barytes from the Binnenthal, Switzerland. HEINRICH BAUMHAUER and CHARLES OTTO TRECHMANN (*Zeitsch. Kryst. Min.*, 1908, 44, 609—617).—Crystallographic descriptions are given of four types of crystals of barytes from the white, crystalline dolomite of the Binnenthal. Crystals of one of these types resemble those described by Neminar, in 1876, as "barytocelestite." These contain 98.15% BaSO_4 , and on ignition there was a loss of 1.324%, due to the presence of liquid enclosures; no trace of strontium is present. The existence of barytocelestite at this locality is very doubtful.

L. J. S.

A New Mineral from the French Congo. ALFRED LACROIX (*Compt. rend.*, 1908, 146, 722—725).—Associated with the crystals of diopside from Mindouli, in the French Congo, is a blue, fibrous copper silicate, which forms botryoidal masses or fibrous veins in limestone. The fibres are optically biaxial and apparently positive, and extinguish parallel to their length. Analysis by F. Pisani gave:

SiO_2 .	CuO .	FeO .	H_2O .	Total.	Sp. gr.
37.16	59.20	trace	4.50	100.86	3.36

This gives the formula $5\text{H}_2\text{O} \cdot 15\text{CuO} \cdot 12\text{SiO}_2$, which may be written as a basic metasilicate, $\text{H}_2(\text{CuOH})_8\text{Cu}_7(\text{SiO}_3)_{12}$. The water is expelled only at a red heat. The new mineral, for which the name *plancheite* is proposed, also differs from diopside in being more difficultly decomposed by acids and without the separation of gelatinous silica.

The copper deposits at Mindouli consist of masses and veins of argentiferous copper-glance in limestone; near the surface, various

secondary minerals, malachite, diopside, native silver, chrysocolla, cuprite, cerussite, wulfenite, pseudomalachite, pyromorphite, &c., are present.

L. J. S.

Physiological Chemistry.

Cutaneous Respiration. GIUSEPPI FRANCHINI and LUIGI PRETI (*Biochem. Zeitsch.*, 1908, 9, 442—452).—Experiments were carried out on the arms and hands of the investigators. The parts of the body under investigation were enclosed in a cylinder containing oxygen. The apparatus was so arranged that the amount of gas at the beginning and the end of the experiments, which lasted one hour, could be accurately estimated. The gas was analysed both at the beginning and the end, and the absorbed oxygen and excreted carbon dioxide determined. It was estimated that the whole body absorbs at 36° 5.5 litres of oxygen in twenty-four hours, that is, about 1% of the quantity absorbed in pulmonary respiration. The amount of carbon dioxide excreted was calculated to be 4.8 litres, also about 1% of that due to pulmonary respiration. S. B. S.

Respiratory Metabolism of the Isolated Spinal Cord of the Frog. HANS WINTERSTEIN (*Zentr. Physiol.*, 1908, 21, 869—873).—The fresh spinal cord of the frog was stimulated in Thunberg's micro-respirometer, and found to have a high respiratory exchange; per unit of weight, it is two to three times greater than that of the body as a whole. Strychnine poisoning causes no increase. W. D. H.

Nature of the Combination of Gases in Blood and its Constituents. Preliminary Notice. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 294—301).—On the basis of the experimental data of Loewy and others, it is shown that for the taking up of carbon dioxide by solutions of hæmoglobin and by blood, and of oxygen by blood, the laws of absorption are closely followed, and the conclusion is therefore drawn that the fixation of gases by blood and its constituents is mainly a physical process, connected with the large surface of the colloidal particles. G. S.

Blood-formation in Spleen and Liver in Experimental Anæmia. A. VON DOMARUS (*Arch. exp. Path. Pharm.*, 1908, 58, 319—342).—By protracted poisoning with phenylhydrazine, pyrogallol, &c., organic changes are produced in rabbits which resemble those seen in pernicious anæmia in man. These changes (in bone marrow, spleen, blood corpuscles, &c.) do not occur in acute poisoning; they are most marked in embryonic animals, and are an expression of the inability of the blood-forming organs to cope with the increased destruction of blood corpuscles. W. D. H.

Are the Antigen and the Amboceptor-fixing Substance of the Blood Corpuscles Identical? J. FORSSMAN (*Biochem. Zeitsch.*, 1908, 9, 330—352).—According to Ehrlich's theory, the amboceptor-fixing substance, and the substance which on injection produces hæmolysis (antigen), should be identical. This is not in accord with the results obtained previously by Bang and Forssmann. Experiments were therefore carried out to separate the antigen from the amboceptor-fixing substance. The former appears to be simpler than the latter, as it resists heating. It was thought therefore that separation might be accomplished by dialysis. To test this hypothesis, blood-stromata of ox were suspended in saline, and the mixture enclosed in a collodium capsule, which was implanted in the peritoneal cavity of a rabbit. Several such experiments were carried out, but only in a certain number of cases was a hæmolytic serum produced. In all these cases it was found that the contents of the capsule had become contaminated with bacteria, which apparently caused the separation of the antigen from the stromata; the former dialysed through the capsule and produced the lysis. A similar result could be produced from sterile capsules by the addition of steapsin. In some cases, where the capsule had remained for a sufficient length of time in the peritoneum, the contents lost their hæmolytic-producing powers (as tested by injection into another rabbit), and the antigen had entirely dialysed out. The residue, however, when treated with a mixture of inactivated (by heat) hæmolytic serum (amboceptor) and normal serum (complement) deprived this of its hæmolytic power; the centrifuged solid stromata became strongly hæmolytic, and these had combined with the amboceptor. The antigen and amboceptor-fixing substances are therefore not identical. S. B. S.

Decomposition of Blood Platelets, Blood Coagulation, and Muscle Coagulation. K. BÜRKE (*Chem. Zentr.*, 1908, i, 537; from *Zentr. Physiol.*, 1907, 21, 651).—The statement of Pflüger (*Pflüger's Archiv*, 1904, 102, 36) that the breaking down of blood platelets is determinative of blood coagulation, and the fate of the other constituents of the blood have been investigated. By investigating the influence of the same substance on muscle coagulation, it is shown that parallel with the effect on the decomposition of blood platelets and the blood coagulation there is an increased stimulation of the muscle.

J. V. E.

The Behaviour of Certain Polypeptides towards the Red Corpuscles and Platelets of Ox-Blood. EMIL ABDERHALDEN and WILFRED H. MANWARING (*Zeitsch. physiol. Chem.*, 1908, 55, 377—383).—The red corpuscles were obtained free from plasma by washing with salt solution in the centrifuge. The platelets were obtained by fractional centrifugalisation. The results agree with those previously obtained with horses' blood (*Abstr.*, 1907, ii, 889). Irregular results given by the platelets are attributed to the difficulty experienced in obtaining them pure. W. D. H.

Researches in Phagocytosis. HARTOG J. HAMBURGER and EBEL HEKMA (*Biochem. Zeitsch.*, 1908, 9, 275—306. Compare *Abstr.*, this vol., ii, 205).—Loeb found that pure sodium chloride had a

poisonous action on the eggs of certain marine animals, but this is not so for phagocytes in a 0.9% solution of the salt; phagocytosis is about equally active in this solution and in serum. Diminution of the hydroxyl ions in serum by adding acid depresses phagocytosis; increase beyond a certain point has the same effect. In solutions of sodium chloride, these effects are more marked. Fluorine, citric acid ions, and sulphurous acid ions are harmful. Potassium chloride also lessens phagocytosis, the leucocytes being permeable to potassium ions. Calcium ions favour phagocytosis; an addition of 0.005% calcium chloride increases it by 22%.
W. D. H.

The Biology of Phagocytes. Influence of Hæmoglobin, &c., on Phagocytosis. HARTOG J. HAMBURGER and EBEL HEKMA (*Biochem. Zeitsch.*, 1908, 9, 512—521).—The phagocytic power was determined by estimating the percentage of the leucocytes in serum or aqueous suspension which had taken up added charcoal particles. It was found that free hæmoglobin in concentrations greater than actually occur in life (in pathological cases) exerts no action on the phagocytic power. Créde colloidal silver, in concentrations of 0.02% and more, exerts an inhibitory influence. Quinine also exerts a marked inhibitory influence, even in concentrations of 0.005%. This observation is of practical importance, as the administration of 1 gram of quinine hydrochloride can occasion a blood-content of 0.01% of the salt. The serum of a different species from that from which the leucocytes have been obtained can also diminish the phagocytic action. Urea, even in 2% concentration, is without influence.
S. B. S.

The Behaviour of Certain Polypeptides towards the Plasma of Ox-Blood. EMIL ABDERHALDEN and JAMES S. MCLESTER (*Zeitsch. physiol. Chem.*, 1908, 55, 371—376).—Oxalate plasma was prepared from ox-blood and freed from formed elements by the centrifuge. It does not split glycyl-L-tyrosine, although the corpuscles do so. If, however, the plasma contains hæmoglobin, splitting of the dipeptide occurs. The plasma splits *dl*-alanylglycine, diglycylglycine, and glycyl-*dl*-alanine; the last-named dipeptide is only split in small measure; the plasma of the horse does not split it at all.
W. D. H.

The Influence of Resorbed Salicylic Acid on the Opsonic Functions of the Serum. MARTIN JACOBY and ALBERT SCHÜTZE (*Biochem. Zeitsch.*, 1908, 9, 527—532).—The experiments were carried out with leucocytes of guinea pig, a bouillon suspension of typhus culture, and serum of rabbit. A comparison was always made with the serum of the same animal before and after administration of salicylic acid. The phagocytic action in each case was determined by making film preparation of the centrifuged leucocytes, after they had remained with the serum and the suspension of typhus culture. It was found in most cases that the administration of salicylic acid caused an increase of phagocytic power, that is, it increased the opsonic power of the serum.
S. B. S.

The Action of Resorbed Salicylic Acid in Blood Serum. MARTIN JACOBY (*Biochem. Zeitsch.*, 1908, 9, 522—532).—Salicylic acid after ingestion *per os* appears in large quantities in the blood. It seems to have entered into some form of combination with the serum proteins. If the serum from an animal to which salicylic acid has been administered is half saturated with ammonium sulphate, the precipitate which is formed carries down with it only a small trace of the acid; on complete saturation with the salt, a second precipitate is obtained which contains nearly all the salicylic acid. If, however, salicylic acid is added to a normal serum, it does not appear in the precipitate produced by complete saturation with ammonium sulphate, but in the filtrate. These facts indicate that the ingested salicylic acid is removed from the digestive tract by entering into combination with serum proteins. It can be set free from this combination by the action of acids. Diluted serum from an animal to which salicylic acid has been administered gives on boiling a precipitate which contains very little salicylic acid; the filtrate from this precipitate on acidification with acetic acid gives a precipitate, however, which is rich in salicylic acid. S. B. S.

The Amount of Albumose in Blood. ERNST FREUND (*Biochem. Zeitsch.*, 1908, 9, 463—488).—A continuation of the controversy with Abderhalden (see this vol., ii, 117, 305). S. B. S.

The Lysinogen of the Blood-disks. KENJI TAKAKI (*Beitr. chem. Physiol. Path.*, 1908, 11, 274—287).—Bang and Forssman found that by extracting blood corpuscles or their stromata with ether, a substance is extracted which produces hæmolysis when injected into animals, and the immune substance there developed is identical with that obtained by injection of blood corpuscles. The lysin-yielding material (lysinogen) is most easily dissolved by boiling acetone, in which it remains dissolved after cooling. Bang and Forssman stated that the material is not a protein, and they were unable to identify it with any known phosphatide or cerebroside. The present paper is a further attempt to identify it, and describes its solubilities in various reagents; the raw material contains 35% of ash. It gives a positive Molisch reaction, and dissolves most easily in decinormal alkali, but is not precipitated by neutralisation. If, however, alkali is used for extracting it directly from the corpuscles, neutralisation produces a precipitate of protein which apparently carries down the lysinogen with it, for the filtrate is inactive. The material in question is certainly not a protein; it contains phosphorus and a carbohydrate group; it is probably a lipid, but cannot be identified with any known phosphatide. W. D. H.

The Chemical Hæmolysins. IV. Acids. ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1908, 22, 147—154. Compare Abstr., 1907, ii, 792; this vol., ii, 49).—The hæmolytic powers of the twenty-four acids examined are by no means in the same order as their strengths; some weak organic acids produce hæmolysis at a lower normality than the strongest mineral acids. In the fatty series,

the hæmolytic power decreases from formic to propionic acid, and then increases again; formic acid is an especially powerful hæmolysin.

G. B.

Influence of Certain Proteins and other Colloids on Hæmolysis. KURT MEYER (*Arch. Hygiene*, 1908, 65, 292—304).—The inhibition, by serum, of the hæmolytic action of soaps (von Liebermann, Abstr., 1907, ii, 973; Noguchi, Abstr., 1907, ii, 974) and of bile-salts is due to the proteins in the serum. Hæmolysis by saponin is not inhibited by these proteins, but is, on the other hand, prevented by cholesterol, which does not inhibit hæmolysis by soaps and by bile-salts. In their inhibitory action, the serum-albumin and -globulin cannot be replaced by other colloids, or even by other proteins, such as edestin, caseinogen, or egg-albumin; the inhibition does not depend on any reduction of the power of soap or bile-salts for dissolving lipid. At high concentrations, dextrin, gum, and gelatin agglutinate red blood-corpuscles, and thus render them more susceptible to hæmolysis.

G. B.

The Influence of Temperature on Motor and Sensory Nerves of the Frog. MAX HAFEMANN (*Pflüger's Archiv*, 1908, 122, 484—500).—The death temperature of nerves in cold-blooded animals is placed by Alcock at 42°; this is lower than in warm-blooded animals, and is the temperature at which the electrical "sign of life" disappears. Brodie and Halliburton, in their study of heat contraction in nerve, found similar differences in the two groups of animals; in the frog, 40—42° is the temperature at which the first step in contraction occurs, and coincides with the coagulation temperature of the first protein in nervous tissues. Miram placed frogs' nerves in Ringer's solution, and estimated the death temperature by the disappearance of excitability as judged by the absence of contraction in the attached muscles when the nerve was stimulated. He found 47° to be the temperature at which this disappeared, and associates death with the coagulation of the second protein in nerve structures.

In the present research, the frog's sciatic nerve immersed in Ringer's solution was also employed; the temperature of this was raised, and the nerve stimulated at intervals; the attached gastrocnemius finally ceased to contract, and the fatal temperature for motor fibres was thus determined. Similar determinations in the case of the sensory fibres were made by keeping the nerve attached to the spinal cord, and recording the contraction of the gastrocnemius of the opposite side. The conclusions drawn are that a temperature of 42° leaves the conductivity of both kinds of nerve fibre intact; a temperature of 50° is fatal to both; temperatures of 44—48° are fatal to sensory, but not to motor, nerves.

W. D. H.

Influence of Certain Food-adjuncts on the Action of the Digestive Enzymes. K. TOGAMI (*Biochem. Zeitsch.*, 1908, 9, 453—462).—The influence of infusions of tea, coffee, and chicory on the digestive power of ptyalin, pepsin, and trypsin were investigated, the methods of Wohlgemuth for ptyalin and of Fuld for pepsin and

trypsin (edestine hydrochloride digestion) being chiefly employed. The rate of digestion of the enzyme dissolved in the infusion was compared with the rate when dissolved in distilled water. It was found that the infusions in the strength in which they are ordinarily ingested exert no deleterious action on the enzymes. In higher concentrations they (and especially tea) exert an inhibitory influence.

S. B. S.

"Specific Dynamic Action" of Protein. GRAHAM LUSK (*Zentr. Physiol.*, 1908, 21, 861—862).—Rubner showed that by the administration of proteins, the heat-production of the body is increased by 30 calories for each 100 protein-calories. This is explained as follows: under ordinary conditions, proteins are split into amino-acids in the intestine without any production of heat. If, however, the amino-acids are deamidised, heat is lost; for instance, in the conversion of alanine (4372 cal.) with lactic acid (3661 cal.) there is a loss of 16%. The heat thus formed may not be of importance for the ordinary processes of life. If, however, protein feeding is followed by nitrogenous output, that part of the protein so utilised has no specific dynamic action, as its amino-acids are not deamidised, but built into the food protein.

W. D. H.

Influence of Amides on Protein Metabolism. KONRAD FRIEDLAENDER (*Pflüger's Archiv*, 1908, 122, 511—516).—Polemical. A reply to Völtz on this question, and a further contribution to a much prolonged controversy.

W. D. H.

Digestion of Proteins in the Alimentary Canal of the Dog. IV. EMIL ABDERHALDEN, E. S. LONDON, and BERTHOLD OPPLER (*Zeitsch. physiol. Chem.*, 1908, 55, 447—454).—In observations on dogs with fistulæ, it appears certain that in ordinary digestion, little or no liberation of amino-acids occurs in the stomach, but this does take place in the small intestine. The small yield of these in any particular segment of the intestine is probably explained by rapidity of absorption of the cleavage products; some, however, of the cleavage products which are not completely broken down into the final amino-acids, appear to be absorbed in the duodenum, and the remainder pass down the intestine to undergo more complete cleavage there. Just as in experiments *in vitro*, certain amino-acids (such as tyrosine) are more readily split off from the protein molecule than others (such as glutamic acid). The paper is of a preliminary nature.

W. D. H.

Origin and Destiny of Cholesterol in Animals. I. Hippocoprosterol. II. Excretion of Cholesterol by the Dog. CHARLES DORÉE and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1908, 80, B, 212—226, 227—238).—Many divergent views are held in reference to the physiological significance of cholesterol. Flint was, however, correct in his statement that it is found in human fæces in the form of a material he named stercorin. This was re-discovered by Bondzynski, who termed it coprosterol; it crystallises in long needles (m. p. 95—96°), is dextrorotatory, and gives colour reactions similar to

those of cholesterol. It has the formula $C_{27}H_{48}O$; it behaves as a saturated alcohol, and is regarded as a dihydrocholesterol formed by bacterial reduction in the intestine. The hippocoprosterol of horses' faeces has been regarded as a substance of similar origin. The present experiments show, however, that it is not a product of animal metabolism, but a constituent of the grass taken as food; it is passed unchanged by all herbivorous animals fed on grass. Its name is misleading, and the new term *chortosterol* is proposed. It is an alcohol, with the formula $C_{27}H_{56}O$, or more probably $C_{27}H_{54}O$. It gives none of the usual colour reactions. The faeces contain no cholesterol; that in the bile must either be reabsorbed or destroyed. It is therefore difficult to believe that cholesterol is an excrementitious product got rid of in the faeces through the agency of bile.

In the dog fed on either cooked vegetable or meat diet, cholesterol is normally excreted as such. If fed on raw brain, coprosterol only was obtained. Further experiments on the possible absorption of cholesterol in the intestine are in progress.

W. D. H.

Relation of Creatine to Autolysis. R. STANGASSINGER. **Formation and Destruction of Creatine in Perfused Organs.** RUDOLF GOTTLIEB and R. STANGASSINGER (*Zeitsch. physiol. chem.*, 1908, 55, 295—321, 322—327. Compare Abstr., 1907, ii, 637).—The ferments named creatase and creatinase act best in a weakly acid medium. Toluene used as an antiseptic inhibits them but little. They are inhibited by protoplasmic poisons, and by urea and sodium chloride in high concentration. By the autolysis of liver and blood (dog), creatine is formed at first, especially in well-fed animals. Liver extracts destroy creatinine, and the quantity of creatine is thus markedly increased. The liver and kidneys appear to be the situations where creatine is normally destroyed. By perfusion experiments, it is shown that both creatine formation and creatine destruction occur in the liver.

W. D. H.

Acetone Formation in the Liver. III. GUSTAV EMBDEN and ALFRED MARX. **Formation of Acetoacetic Acid in the Liver.** G. EMBDEN and HANS ENGEL. **Formation of Acetoacetic Acid in the Liver of Diabetic Dogs.** G. EMBDEN and LEONE LATTES. **The Destruction of Acetoacetic Acid in the Animal Body.** I. G. EMBDEN and LOUIS MICHAUD. **The Behaviour of Isomeric Leucines in the Liver.** G. EMBDEN (*Beitr. chem. Physiol. Path.*, 1908, 11, 318—322, 323—326, 327—331, 332—347, 348—355. Compare Abstr., 1906, ii, 375).—Experiments were performed as in previous work by perfusing the liver with fatty acids, and noting the amount of acetone formed. Comparative figures were as follows: *n*-butyric acid, 128; *n*-valeric acid, 20; *n*-hexoic acid, 100; *n*-heptoic acid, 12; *n*-octoic acid, 60; *n*-nonoic acid, 19; *n*-decoic acid, 58. That is to say, only the acids with an even number of carbon atoms cause any increase in the amount of acetone formed, and the increase diminishes as the number of carbon atoms rises. The acids with an odd number of carbon atoms produce no more increase of acetone than blood by itself does.

Amino-*n*-butyric acid forms no acetone, whereas, as just noted, *n*-butyric acid does. On the other hand, *n*-valeric acid forms no acetone, but its amino-derivative does; amino-*n*-hexoic acid also forms no acetone.

The various substances which lead in this way to acetone formation, also lead to an intermediary production of acetoacetic acid, and presumably of β -hydroxybutyric acid as well.

In dogs rendered diabetic either by extirpation of the pancreas or administration of phloridzin, the liver forms far more acetone than in normal animals. The figures given relate to total acetone, that is, acetone already present *plus* that derived from acetoacetic acid. The latter is, however, the larger fraction of the two, contributing from 76 to 85% of the total. The exact mechanism of the change (increase of ferment action, &c.) is undecided. The animals in question were in a state of inanition, but that by itself is ineffective in producing an increase of acetone formation.

The fresh organs of the body (liver, kidney, spleen, muscle, &c.) in a finely-minced condition, mixed with acetoacetic acid, produce its disappearance if kept in the incubator; acetone also similarly disappears, but only in a small degree. It is possible that this may result in the formation of acetic acid, but methods have yet to be devised to render this a certainty.

d-Leucine acts as an acetone former; the racemic leucine acts in the same way in virtue of its dextrorotatory constituent; the natural *l*-leucine has no such action unless it is given in very large quantities. The view is advanced that the "non-natural" component is not broken down, for, as is well known, the unusual amino-acids are broken down with difficulty in the organism; it is believed to be used synthetically for the formation of acetoacetic acid or acetone.

W. D. H.

Can the Liver Form Glycogen from Optically Active Amino-acids? KARL GRUBE (*Pflüger's Archiv*, 1908, 122, 451—454).—As in a previous research (Abstr., 1907, ii, 565), the tortoise liver was perfused with Ringer's solution, various amino-acids were added to the fluid, and no increase found in the hepatic glycogen; these acids, however, were optically inactive; in the present research, *d*-alanine, *l*-leucine, and glycine were employed with the same negative result.

W. D. H.

Creatine and Creatinine in Frog's Muscle. T. GRAHAM BROWN and E. PROVAN CATHCART (*Proc. physiol. Soc.*, 1908, xiv—xv; *J. Physiol.*, 37).—A small increase in the total creatinine was found in isolated frog's muscles after stimulation. If, however, the muscles are stimulated through the skin, and the circulation is intact, there is a decrease.

W. D. H.

Chemistry of Bone-marrow. JOSEPH NERKING (*Biochem. Zeitsch.*, 1908, 10, 167—191).—The following substances were isolated: hypoxanthine, lactic acid, inosite, serum-albumin, serum-globulin, denteroalbumose, a nucleo-proteid containing iron, and a pentose group.

Estimations of the water-content, ash, and fat were made. The fat constants both for red and yellow bone-marrow were also determined.
S. B. S.

Skeletal Substances in Anthozoa. III. Cornicrystallin. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1908, 55, 223—235. Compare Abstr., 1905, ii, 310).—Various conjectures as to the nature of Krukenberg's cornicrystallin, which he obtained by hydrolysis of the skeletal material of *Gorgonia* and other anthozoa, are all incorrect. The material in question consists of elementary iodine. W. D. H.

Monoamino-acids of Byssus. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1908, 55, 236—240).—Byssus is the secretion of a gland of certain mussels, which in the air sets into silk-like threads. It is stated that in the past it has been woven into textures. Thirty grams were obtained from *Pinna nobilis*, a quantity which did not allow of quantitative analysis. It is similar to silk fibroin in many points. It yields a good deal of glycine and *l*-tyrosine, also *d*-alanine, *l*-aspartic acid, and proline, probably also valine, leucine, and phenyl-alanine; tryptophan appears to be absent; the presence of glutamic acid is uncertain.
W. D. H.

Chemical Investigations on the Octopus. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1908, 55, 433—444).—Many organs of the octopus yield pentose, which is believed to originate from a reserve supply of pentosans. The eggs also yield glucosamine. The pentose obtained from the muscles is probably *l*-xylose. The nucleo-protein of the hepato-pancreas contains N, 14.23; P, 0.92; Cu, 0.96, and pentose (*l*-xylose), 5—6%; the same organ contains fats and cholesterol.
W. D. H.

Chemical Composition of the Skeletal Substance of Velella spirans. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1908, 55, 445—446).—The organic substance in the skeleton of this *siphonophore* is chitin.
W. D. H.

Composition of Chrysalis Oil (from Silk-Worms). MITSUMARU TSUJIMOTO (*J. Coll. Eng. Tokyo*, 1908, 4, 63—74. Compare Lewkowitsch, Abstr., 1907, i, 521).—The unsaponifiable portion (1.63%) is not cholesterol (compare Lewkowitsch, *loc. cit.*), but phytosterol. For the rest, the oil consists of glycerides of fatty acids, of which 25% are saturated (palmitic acid is present, but probably not stearic acid). The 75% of unsaturated acids consist of oleic, linolenic, and *isolinolenic* acids, together with isomerides of linoleic acid.
G. B.

Erepsin. ELSE RAUBITSCHKE (*Chem. Zentr.*, 1908, i, 870; from *Zeitsch. exp. Path. Ther.*, 1907, 4, 675—680).—The action of dry powdered intestinal mucus membrane on peptones and various albumins leads to the conclusion that there exists a specific intestinal ferment which gives amino-acids from albumoses, and has no action on natural albumin. This ferment is active in small quantities, requiring

about six hours to produce its maximum effect. The addition of substances which pass through the intestine, such as blood, bile, calcium chloride, and sodium sulphate, neither inhibits nor aids the activity of the ferment.

J. V. E.

Urinary Secretion in the Frog. WINIFRED C. CULLIS (*Proc. physiol. Soc.*, 1908, xvi—xvii; *J. Physiol.*, 37).—If a diuretic, such as sodium sulphate, is added to the oxygenated Ringer's solution employed to perfuse frog's kidneys, there is a great increase in the secretion. If the gases are removed from the perfusing fluid, the restriction in oxygen supply leads to a much slower excretion. This favours the view that secretory activity and not mere filtration is the factor concerned.

W. D. H.

Lævulose in Diabetic Urine. L. BORCHARDT (*Zeitsch. physiol. Chem.*, 1908, 55, 241—259).—The most important outcome of the research is that there is no ground for the statement that diabetic urine contains lævulose. The best method of testing for this substance is to boil equal quantities of urine and 25% hydrochloric acid and a fragment of resorcinol in a test-tube for a short time; if a red coloration appears, the mixture is cooled under the tap, poured into a beaker, made alkaline with sodium carbonate, returned to the test-tube, and shaken with ethyl acetate. If lævulose is present, the ethyl acetate becomes yellow. Many mis-statements about lævulose in urine are due to want of care in testing for it.

W. D. H.

Glycine of Normal Urine. GUSTAV EMBDEN and ALFRED MARX (*Beitr. chem. Physiol. Path.*, 1908, 11, 308—317).—Normal human urine undoubtedly yields glycine; in order to obtain it all in combination with β -naphthalenesulphonyl chloride, care must be paid to the degree of alkalinity produced. The question is discussed whether this glycine is free in the urine or in combination, and the answer is strongly in favour of the former alternative.

W. D. H.

The Limits of Hippuric Acid Formation in Man. JOHANN LEWINSKI (*Arch. exp. Path. Pharm.*, 1908, 58, 397—412).—Previous observers state the limit of hippuric acid formation in man at about 3% to 4% of the total nitrogen; in herbivora it is higher. In the present experiments, benzoic acid was given, and the number was increased to 20—30% if there is much protein in the diet, but less if the diet is protein-poor (10—16%). Even in cases of nephritis, it reached 12%.

W. D. H.

The Scission of Hippuric Acid by Bacteria; the Detection of Benzoic Acid and Glycine in Urine. Y. SEO (*Arch. exp. Path. Pharm.*, 1908, 58, 440—449).—Very contradictory results have been obtained by different observers, who have administered benzoic acid to the human subject. Some have obtained large quantities of hippuric acid in the urine, and others only small quantities. The discrepancies are due to the fact that hippuric acid readily undergoes scission in the

presence of bacteria. If the urine of a normal individual is sterilised or is kept with antiseptics, but little free benzoic acid will be found. If, however, no precautions for asepsis be taken, the hippuric acid will readily undergo scission into benzoic acid and glycine; the latter substance can be isolated by means of naphthalenesulphonyl chloride.

The free benzoic acid can be estimated by direct extraction with light petroleum, and the conjugated benzoic acid by hydrolysing the urine (after separation of the free benzoic acid) with sulphuric acid, steam distilling, and extraction of the distillate with light petroleum. The bacteria which bring about the hydrolysis of hippuric acid are *Staphylococcus albus* and *S. aureus*. Various streptococci have a similar action. *B. coli*, *typhus* and paratyphus bacilli, and *B. pyocyaneus* are without action.

The presence of free benzoic acid in freshly-collected urine is possibly of some diagnostic value. S. B. S.

A Thermo-soluble Protein, said to be that of Bence Jones. ALBERT GASCARD and DEVALMONT (*J. Pharm. Chim.*, 1908, [vi], 27, 371—374. Compare this vol., ii, 212).—When heated by itself, the urine described was coagulated at 50°, and became almost clear between 80° and 100°. The precipitates formed by various protein reagents redissolved at 100°. The urine gave the biuret reaction, and yielded a precipitate when saturated with ammonium sulphate, but not with magnesium sulphate. On addition of an equal volume of 90% alcohol, no precipitate was formed on heating to 70°.

After acidification with acetic acid, the urine yielded hardly any precipitate on heating, and after dialysis the solubility of the albumose in acetic acid was further increased. G. B.

Pancreatic Diabetes in Selachian Fishes. V. DIAMARE (*Zentr. Physiol.*, 1908, 21, 863—869. Compare Abstr., 1907, ii, 285).—Complete extirpation of the pancreas in these fishes causes an intense glycaemia. Partial extirpation, even if three-quarters of the organ are removed, does not produce the effect, even though the injury to vessels and nerves is as great as in the complete operation. Necrosis of the stomach, duodenum, or spleen does not take place.

W. D. H.

Antagonistic Action of Calcium and Magnesium. SAMUEL J. MELTZER and JOHN AUER (*Proc. Roy. Soc.*, 1908, 80, B, 260—261; *Amer. J. Physiol.*, 1908, 21, 400—419).—A detailed account of work recorded previously (this vol., ii, 312).

W. D. H.

The [Physiological] Action of Strontium compared with that of Calcium and Magnesium. SAMUEL J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1908, 21, 449—453).—Strontium salts do not cause anaesthesia, nor do they affect sensibility and reflex action. They cause paralysis slowly, and only after very large subcutaneous doses. Strontium does not neutralise the inhibitory effect of magnesium; it causes a slight improvement of respiration, but otherwise it aggravates the inhibitory symptoms due to magnesium,

especially the paralysis. Calcium is not antagonistic to the effects of strontium; if anything, it increases them. Physiologically, strontium differs radically from both calcium and magnesium.

W. D. H.

Antagonistic Action of Barium Chloride and Sodium Sulphate on the Heart Action. V. SCAFFIDI (*Biochem. Zeitsch.*, 1908, 9, 489—497).—The experiments were carried out on the heart of frogs and tortoises by the method of Engelmann. Barium chloride gives rise to a lengthened systolic period and pause, with a diminution of the number of heart-beats per minute. If sodium sulphate is injected half an hour after the barium chloride, it exerts no influence; on the other hand, if the barium salt is injected half an hour after the sodium salt, the latter inhibits the action of the former. If equivalent quantities of the two salts are injected simultaneously, the antagonistic action is complete. The chemical action of the two salts on the heart muscle is discussed.

S. B. S.

Therapeutic Value of Methyl Benzoylsalicylate (Benzosalin). MARIO VARANINI (*Chem. Zentr.*, 1908, i, 666; from *Arch. Farm. speriment.*, 1907, 6, 623—630).—The action of saliva on benzosalin is shown to be very slight, only a small quantity of salicylic acid being formed; the addition of pepsin hydrochloride increases the amount somewhat, whilst pancreatin readily breaks down the benzosalin, especially in presence of sodium hydroxide at 37°. Normal and excessively acid gastric juice even after long contact at 37° have no action on benzosalin, whereas it is rapidly decomposed in an alkaline gastric juice. The conclusion is drawn therefore that benzosalin is decomposed in the intestine by the pancreatic juice in alkaline solution, and not in the stomach.

J. V. E.

Physiological Effects of Colchicine. WALTER E. DIXON and WALTER MALDEN (*J. Physiol.*, 1908, 37, 50—76).—Colchicine, like muscarine, excites the nerve-endings in plain muscle, but has no action on those in the heart or in glands. Pilocarpine, physostigmine, and colchicine act on different constituents of the nerve-ending. Colchicine, even in enormous doses, is a slow poison, especially in herbivora; the delay is due to slow absorption into the central nervous tissues, and death is caused by vaso-motor paralysis. It causes marked leucocytosis, the varieties of white corpuscles, which are increased, being different in carnivora and herbivora. There is increased activity of the bone marrow, all the elements of which may be found in the circulation after large doses. Increase of leucocytes, body temperature, and coagulation time of the blood run approximately parallel.

W. D. H.

Action of Digitalin. KURT HULDSCHINSKY (*Arch. exp. Path. Pharm.*, 1908, 58, 413—433).—Digitalin produces inhibition of the frog's heart; this is mainly due to excitation of the inhibitory nervous mechanism, and partly to action on the heart muscle.

W. D. H.

Action of Digitalis on the Vagus. CAMILL LHOTÁK VON LHOITA (*Arch. exp. Path. Pharm.*, 1908, 58, 350—365).—In severe poisoning by substances of the digitalis group, the vagus nerves lose their excitability; they are finally paralysed, and a "vagus pulse" is the result. This condition is increased by physostigmine, and lessened by apomorphine. It lasts thirty to fifty minutes. W. D. H.

The Degradation of 2:5-Diketopiperazines in the Organism of the Rabbit. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1908, 55, 384—389).—After administration of glycine anhydride to a rabbit, both glycine and glycyglycine could be isolated from the urine in the form of the naphthalenesulphonyl derivative. After administration of *dl*-alanine anhydride, *l*-alanine could be detected in the urine; there was also some evidence in this case that an alanylalanine was also excreted. After administration of *dl*-serine anhydride, *d*-serine could be isolated in the form of the *p*-nitrobenzoyl derivative. It appears therefore that the piperazines are first hydrolysed to the dipeptides, which, on further hydrolysis, yield amino-acids. It is not, however, quite certain that the peptides and amino-acids are not formed as secondary products by the action of the alkaline urines on the piperazines. This seems improbable, however, as optically active amino-acids were formed. S. B. S.

The Physiological Behaviour of Inosite. II. PAUL MAYER (*Biochem. Zeitsch.*, 1908, 9, 533—536).—Inactive lactic acid is found in the urine of rabbits after injection of inosite. This fact is of interest, as those organs (for example, muscles) which contain inosite also contain lactic acid. S. B. S.

Behaviour of Sajodin [Calcium Iodobehenate] in the Organism. GEORG BASCH (*Zeitsch. physiol. Chem.*, 1908, 55, 397—406).—A small portion of this substance is excreted unchanged in the faeces; the greater part is absorbed, and retained in the body, especially in bone marrow, fatty tissue, and thyroid gland, passing later into the blood and reaching the urine as alkali iodide. W. D. H.

The Material in the Brain which Unites with Tetanus Toxin. KENJI TAKAKI (*Beit. chem. Physiol. Path.*, 1908, 11, 288—303).—Hot alcohol extracts from dried brain material a substance which combines with the tetanus toxin. The material present which acts in this way is cerebrin; the cerebrin acids have a weaker action. Of the cleavage products of cerebrin, cerebrinic acid and its methyl ester are active in the same direction. The white matter of the brain is, however, capable of combining with more poison than the amount of cerebrin in it accounts for; the grey matter is more powerful than the white, and contains less cerebrin. There must be therefore other substances which are capable of combining with the tetanus toxin. W. D. H.

Influence of Certain Poisons in the Fibrillary Contraction of the Heart. HEINRICH WINTERBERG (*Pflüger's Archiv*, 1908, 122, 361—379).—Poisons which paralyse the inhibitory mechanism of the

heart also prevent the occurrence of fibrillary contractions which follow faradic stimulation. These contractions, however, occur if, as under the influence of nicotine, the conduction of the nerve fibres concerned is alone interfered with. The phenomenon is increased if the cardiac vagus is in a condition of increased excitability, as it is under the influence of physostigmine. On the same grounds, muscarine is believed to stimulate the cardiac vagus. Toxic stimulants, such as physostigmine and calcium, which produce extra systoles, can by simultaneous faradic stimulation of the vagus bring the auricles into fibrillary delirium. W. D. H.

Munchi Arrow Poison and Strophanthin. GEORGE RALPH MINES (*J. Physiol.*, 1908, 37, 37—49).—Strophanthin is the chief toxic ingredient of the Munchi arrow poison. It is antagonistic to veratrine in its action on skeletal muscle. W. D. H.

Poisonous Substances in Blood. G. LEFMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 255—273).—The intravenous injection of lipoids prepared from red corpuscles of a different species of animal produces in cats, dogs, and rabbits poisonous symptoms (fall of blood pressure, paralysis, narcosis, &c.). If, however, the lipoids are prepared from the same kind of animal, they are non-toxic, or only slightly toxic. The toxic material is soluble in anhydrous ether, but not in alcohol or chloroform. By shaking an emulsion of it in salt solution with olive oil, the lipoids are in great measure removed. They are in such an emulsion thermostable. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Nitrogen-fixing Bacteria. III. F. LÖHNIS and N. K. PILLAI (*Centr. Bakt. Par.*, 1908, ii, 20, 781—799).—The authors are repeating some of the work which other investigators have published on this subject, and in the present communication deal with (1) the carbon compound to be used in the culture solution; (2) the effect of manuring on the nitrogen-fixing power of soil, and (3) the variation in nitrogen-fixing power from month to month.

(1) *The Best Carbon Compound for the Culture Solution.*—Mannitol and xylose were found to be the most effective, and humus (for example, Merck's humic acid neutralised by potash) least. The substances tried and the amount of nitrogen fixed in ten days per gram of substance were as follows:

Mg. of nitrogen
fixed.

7·5 to 10	Mannitol, xylose, lactose, lævulose, inulin, galactose, maltose, arabinose, dextrin, sucrose + CaCO_3 .
5 to 7·5	Dextrose, sucrose, sodium tartrate + CaCO_3 , glycerol + CaCO_3 .
2·5 to 5	Starch, sodium tartrate, sodium succinate, calcium lactate.
1 to 2·5	Sodium propionate, sodium citrate, glycerol.
Nil	Calcium butyrate, potassium oxalate, humus.

(2) *Effect of Manuring.*—Culture solutions made up with mannitol were inoculated with soil off the experimental plots which are each year manured in the same way. The amount of nitrogen fixed, No. 1 unmanured being taken as 100, and the average crop for the past three years were :

	Unmanured.			Dung.	Sodium nitrate, potassium salts, lime.	Sodium nitrate, potassium salts, lime, super- phosphate.	Sodium nitrate, lime, super- phosphate.
	I.	VI.	XI.	III.	VII.	VIII.	X.
Nitrogen fixed	100	104	153	114	122	206	224
Crop	100	94	85	119	139	152	147

It will be observed that on this particular soil, dung has not greatly increased the nitrogen-fixing power, but superphosphate exerts a considerable effect. The crop returns run in somewhat the same sense. The experimental error appears to be considerable.

Effect of the Time of the Year.—Samples taken from the plots in different months show varying powers of fixing nitrogen when inoculated into culture solutions; in some cases, the power increases steadily from early spring until late autumn, and in others there is a falling off during the summer, so that two maxima are observed, one in spring and the other in autumn; the authors regard the latter as the typical case. The following results may be quoted :

	March.	April.	May.	July.	October.
Samples taken in milligrams <i>N</i> fixed by unmanured soil (Plot VI)	1.52	2.11	2.74	4.00	7.94
Samples taken in milligrams <i>N</i> fixed by soil fully manured (Plot VIII)	3.19	10.8	10.93	13.08	13.8

In making these experiments, 10 grams of soil were inoculated into 100 c.c. of the culture solution.

E. J. R.

Fixation of Free Atmospheric Nitrogen by *Lolium Temulentum*, infested with a Fungus. E. HANNIG (*Ber. deut. bot. Ges.*, 1908, 26a, 238—248).—As found by Hiltner in 1896, the above grass is peculiar in assimilating small quantities of free nitrogen, although it has no symbiotic root organisms. It is generally, however, infested by a parasitic fungus, which lives in the seeds; other species of *Lolium*, without a fungus, do not assimilate free nitrogen.

This observation is now confirmed, and the comparison was effected, not, as before, with other species of the same genus, but with fungus-free individuals of the same species. If no combined nitrogen was given in the food, the amount of nitrogen in the plants without the fungus was the same as in the seeds, but in the plants with the fungus it was approximately double. (With a nitrogenous soil, the amount of nitrogen in the plant may be one hundred times that of the seed.) The investigation was mainly directed towards excluding the bacterial action in the roots; the seeds were sterilised (except as regards the fungus parasite, which is inside the seed-coat) by ten minutes' immersion in 1% mercuric chloride, and the plants were grown in a special apparatus in such a way that their roots remained inaccessible to bacteria.

G. B.

Nitrification in Acid Soils. ALFRED D. HALL, NORMAN H. J. MILLER, and CONRAD T. GIMMINGHAM (*Proc. Roy. Soc.*, 1908, 80, B, 196—212).—The Rothamsted grass plots which receive large quantities of ammonium salts as manure are found to be acid to litmus paper, and to contain practically no calcium carbonate, instead of 2% to 5% as in the other plots. The character of the vegetation is fundamentally affected; there is a rank herbage consisting almost entirely of three species of grass growing in coarse tufts with bare, peaty patches between. Previous investigation has shown that soils from these plots are almost free from nitrifying organisms, and this observation is now fully confirmed. In general, there was no nitrification when the soil was inoculated into culture solutions, and very little when 1 or 2 kilos. of moist soil were exposed to air under favourable conditions. Whilst it cannot be said that no nitrification takes place, there is so little that the plants cannot obtain in the form of nitrates all the nitrogen they take up from the soil, but must draw the larger portion directly from the ammonium salts supplied as manure.

An aqueous extract of the soil was found to be acid, and to contain humates, chlorides, and sulphates. Since free humic acid is not a normal product of decay in the soil, it seems probable that the acid originates from the ammonium salts; this view is supported by the fact that the amount of freely soluble acid of the soil is of the same order of magnitude as the quantity of sulphuric and hydrochloric acids contained in one year's application of ammonium salts. The authors therefore suppose that the acid splits off from the ammonium salt, and slowly acts on the calcium humate present in the soil, forming calcium chloride and sulphate, which wash away in the drainage water, and free humic acid, which remains in the soil.

Experiments were made to find if any agency existed in the soil capable of splitting up ammonium salts so as to set free the acids therein. No purely chemical or physical hypothesis was satisfactory; free acid does not arise from the interactions of ammonium salts with either the double silicates or the calcium humate in the soil, neither is there any dissociation of the salts followed by adsorption or evaporation of ammonia leaving an acid residue. The soil was, however, found to contain certain moulds, *Penicillium glaucum* and another allied to *Mucor*, capable of taking the ammonia from ammonium sulphate and leaving behind the free acid until the acidity is about $N/80$, when action ceases. The authors conclude therefore that the acidity of the soil is due to the action of these moulds.

Although the soil is acid, nitrification is not entirely checked; probably this results from the lack of uniformity of the soil. Particles of calcium carbonate still remain, each of which is a centre of nitrification. When the soils becomes uniformly acid, all nitrification must cease.

E. J. R.

Bacteria as Agents in the Oxidation of Amorphous Carbon. M. C. POTTER (*Proc. Roy. Soc.*, 1908, 80, B, 239—259).—Lamp black, charcoal, coal, and peat can all be oxidised by a *Diplococcus* obtained from garden soil, and no doubt by other organisms as well. The action is only small, but it was quite clearly established (1) by

passing a stream of air, freed from all traces of carbon dioxide, over the material and determining the presence of carbon dioxide in the issuing gas by absorption with baryta and titration with oxalic and hydrochloric acids; (2) by determining the rise of temperature due to oxidation by means of a thermopile and galvanometer, and (3) by detecting, in the case of charcoal, the presence of calcium carbonate in the flasks inoculated with the bacteria. Oxidation only takes place under conditions favourable to bacterial activity; thus the rate increases with the temperature to 40°, but at 100° there is no oxidation at all. Similarly, oxidation ceases when the amount of moisture present is insufficient for bacteria. It follows that micro-organisms are entirely responsible, and the author refers to various consequences of such an action, suggesting, among other things, that the heat generated by the bacterial activity may be an important factor in determining the spontaneous combustion of coal, or firing a mixture of explosive gases in contact with it.

E. J. R.

Ten Years' Experiments on Denitrification in Arable Soil. GASPARE AMPOLA (*Ann. R. Staz. chim. agrar. sper. Rome*, 1907, [ii], 1, 29—73).—Application of fresh farmyard manure in conjunction with sodium nitrate and minerals gives lower yields than nitrates and minerals alone; the reduction in yield increases with the amount of straw in the manure. Humification of the manure diminishes the reducing action of the denitrifying organisms.

Calcium nitrate is less subject to denitrification than the sodium salt.

In practice, nitrates, when used in conjunction with farmyard manure, should be applied after the straw has had time to decompose sufficiently; no loss by denitrification is then to be feared.

N. H. J. M.

Butyric Acid Fermentation. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1908, 41, 1410—1419).—In this preliminary note on the production of compounds containing 4 atoms of carbon by the fermentation of substances containing three or six, the results of two experiments on dextrose and glycerol, and a detailed account of the analysis of the products of fermentation, are quoted.

The solution of dextrose or of glycerol in the presence of nutritive inorganic salts and calcium carbonate was fermented for many weeks by *Bacillus butylicus*. The same products were obtained in each experiment: ethyl and butyl alcohols, formic, acetic, butyric, and lactic acids, carbon dioxide, and hydrogen, but, whilst glycerol yielded large amounts of the alcohols and only small quantities of acetic and butyric acids, the converse was found to be the case with dextrose.

The authors suggest the following course of the fermentation. In both cases, lactic acid is an intermediate product (Abstr., 1906, ii, 790) which yields formic acid and acetaldehyde (compare Schade, Abstr., 1907, ii, 857; this vol., i, 136); the latter polymerises to aldol, which either undergoes intramolecular change to butyric acid, just as glyceraldehyde yields lactic acid, or else loses water, giving crotonaldehyde, which by reduction yields butyl alcohol or the corresponding aldehyde.

C. S.

Sarcinæ causing Disease in Beer. OLDŘICH MIŠKOVSKÝ (*Chem. Zentr.*, 1908, i, 665; from *Zeitsch. ges. Brauwesen*, 1908, 31, 3—6, 16—19, 27—29).—In the presence of Witte's peptone, the *Pediococci* *A*, *B*, *F* will grow in solutions of dextrose and maltose from which the usual inorganic salts are removed. Somatose and yeast-nucleic acid are not developed when only amino-acids are the source of nitrogen. The addition of dipotassium phosphate causes an increase of *Sarcinæ* in beer wort; monopotassium phosphate has a retarding effect. *Sarcinæ* development is detected by the smell, increase of acidity, and by a cloudy appearance, the last being dependent, not only on the organism employed, but also on the chemical composition of the culture solution. *Pediococcus F* in malt extract forms inactive lactic acid, also traces of formic acid and alcohol, but no acetone. J. V. E.

Chemical Monograph of the Cladoniaceæ. WILHELM ZOPF (*Ber. deut. bot. Ges.*, 1908, 23, 51—113. Compare Abstr., 1907, i, 218).—The author has examined more than fifty species and varieties of lichens, chiefly as regards acids soluble in acetone. In some respects, the chemical relationship corresponds with that deduced from morphological characters, but in others there is marked disagreement. The colouring matter, to which the red colour of the apothecia of many species is due, was obtained crystalline and named *rhodocladonic acid*. It has the composition $C_{14}H_{10}O_7$ or $C_{12}H_8O_6$, dissolves slightly in hot acetic acid and chloroform with a yellow colour, and decomposes between 200° and 300°. It is soluble in sodium and potassium hydroxides and in sodium hydrogen carbonate with a reddish-brown colour, and reduces cold alkaline permanganate solution. A relationship to alizarin is suggested. G. B.

Composition of the Milk and Ferments of the Fruit of *Cocos nucifera*. E. DE KRUYFF (*Chem. Zentr.*, 1908, i, 746; from *Bull. Dépt. Agric. Indes. néerland*, 4).—The liquid from cocoanut contains gases composed of 98% CO_2 , 0.2% oxygen, and 0.3% nitrogen, besides sucrose, diastase, oxydase, and catalase. Lipase, a proteolytic diastase, amylase, catalase, and peroxydase are also found in the substance of the fruit. J. V. E.

Examination of *Grindelia*. II. FREDERICK B. POWER and FRANK TUTIN (*Proc. Amer. Pharm. Assoc.*, 1907, 55, 337—344. Compare Abstr., 1906, ii, 885).—The portion of *Grindelia* resin soluble in light petroleum consists of a complex mixture of liquid acids and their glycerides. The acids are optically active and unsaturated, and some appear to contain benzene nuclei, and some are hydroxy-acids. Cerotic and palmitic acids are present in small amounts.

The ethereal extract of the resin contains very small amounts of a crystalline alcohol, $C_{17}H_{36}O_3$ or $C_{23}H_{38}O_4$, m. p. 256—257°, yielding an acetyl derivative, m. p. 161°, and a yellow, crystalline phenolic substance, $C_{14}H_{12}O_5$, m. p. 227—228°, and yielding an acetyl derivative, m. p. 154°. G. B.

Constituents of the Root-bark of *Morinda citrifolia*. OTTO A. OESTERLE and ED. TISZA (*Arch. Pharm.*, 1908, 246, 150—164).—Perkin and Hummel have shown that this material contains morindin (*Trans.*, 1894, 65, 851), and the present paper confirms this observation and records the occurrence in the plant of two new constituents and several substances previously found by Perkin and Hummel (*loc. cit.*) in the related plant *M. umbellata*.

The portion of the root-bark soluble in alcohol, after the removal of morindin, was separated into (a) matter insoluble in water, and (b) matter soluble in water. The part (a) was subdivided into constituents (c) soluble in and (d) insoluble in chloroform.

The constituents included in (b) were: (1) a dihydroxymethylanthraquinone, which was named *soranjidiol*, $C_{15}H_{10}O_4$, m. p. 276° , and crystallises in dark reddish-brown needles, dissolves readily in alcohol or ether, slightly in water, and yields a *diacetyl* derivative, m. p. 230° , which crystallises in lemon-yellow needles. (2) An amorphous resin, dissolving in alkalis with a red coloration. (3) A substance, $C_{16}H_{10}O_5$, identical with one found by Perkin and Hummel in *M. umbellata*, and (4) an indefinite product, *morindanigrin*, resembling those obtained by Tschirch and his collaborators from senna, &c. (*Abstr.*, 1900, i, 681).

The constituents present in (c) were: (1) a wax, $C_{18}H_{28}O$, and (2) a monomethyl ether of a trihydroxyanthraquinone, both identical with substances found by Perkin and Hummel in *M. umbellata*.

The portion (d) contained, in addition to indefinite resinous matters, a second dihydroxymethylanthraquinone, which was named *morindadiol*, $C_{15}H_{10}O_4$, m. p. 244° . This crystallises in yellow needles, sublimes in slender, red needles, is readily soluble in alcohol or acetic acid, less so in ethyl acetate or toluene, and insoluble in ether or light petroleum; the *diacetyl* derivative, m. p. 229° , crystallises in lemon-yellow needles.

On extraction of the bark with dilute sulphuric acid, morindin and its decomposition product, morindone, were obtained together with much chlororubin, possibly produced by the action of the acid on the morindanigrin referred to above. No morindone was obtained by extraction of the bark with ether, so that this substance does not occur preformed.

T. A. H.

The Constituents of Simaruba Bark. CHARLES GILLING (*Pharm. J.*, 1908, [iv], 26, 510—513).—The bark of *Simaruba amara* contains 0.05—0.1% of a bitter substance $C_{22}H_{30}O_9$, forming rosettes of small, white needles from dilute methyl alcohol, m. p. $229—230^\circ$ (decomp.); $[\alpha]_D$ in chloroform solution 67.6° , in alcohol solution 58° . The bark further contains a fixed oil, a resin, and a crystalline non-bitter substance; the presence of a fluorescent substance was indicated.

G. B.

Natural Factors in the Dissolution of Tricalcium Phosphate in Soil. RENATO PEROTTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 448—451).—When nitrogen is administered in the form of various compounds to cultures of soil bacteria in a nutrient medium containing tricalcium phosphate, a considerable amount of phosphoric

oxide goes into solution when the nitrogen compound added is physiologically acid, but only a small amount is dissolved when the compound is physiologically alkaline. The compounds employed were ammonium tartrate, potassium nitrate, ammonium sulphate, urea, and asparagine; the effect of the ammonium sulphate is by far the greatest, both in intensity and in duration (compare Prianischnikoff, *Abstr.*, 1906, ii, 796).
T. H. P.

Influence of Manures on the Composition of Wheat. HARRY SNYDER (*J. Amer. Chem. Soc.*, 1908, 30, 604—608).—Analyses were made of sixty samples of wheat grown at twelve different places under various manurial conditions. Application of manures resulted in larger, better filled and better coloured grain, especially in cases in which the yield was increased. In eight experiments, phosphates increased the weight per bushel, and in five experiments potash produced a similar result. Nitrogen sometimes increased and sometimes diminished the weight per bushel, but when applied alone had less beneficial effect than minerals alone. Unfavourable seasons affect crops grown on soils of low fertility more than on soils of high fertility.

As regards the composition of the grain, it was found that nitrogenous and mineral manures sometimes improved the quality of the wheat, although the increase in protein was only slight. Nitrogen alone may increase the amount of protein, and at the same time injure the quality of the wheat.

No constant relationship seems to exist between the percentage of protein in the grain and flour and the bread-making value; in many cases, the increase in nitrogen was coincident with a negative value. On the whole, however, the experiments show that both the yield of wheat and the bread-making value can be increased by manuring. In thirty out of forty-one experiments, the manures which gave the greatest yields also produced wheats of the highest value for bread making.

N. H. J. M.

Phosphoric Acid in Barley. WILHELM WINDISCH (*Chem. Zentr.*, 1908, i, 865; from *Jahrb. Vers. Lehr. Brauerei*, 1907, 10, 56—58).—This acid is present in barley as phytin, the calcium magnesium salt of anhydro-oxy-methylenediphosphoric acid, which gives phosphoric acid and inositol when acted on by strong acids or enzymes.
J. V. E.

Manganese Compounds as Fertilisers for Maize. WALTER F. SUTHERST (*Transvaal Agric. J.*, 1908, 6, 437).—The experiments were made in pots 3 feet high with an area of about 1 square yard. Manganese was added to the soil in the form of chloride (2 grams), sulphate (2 grams), and pyrolusite (5 grams per pot). Photographs of the plants show that pyrolusite gave much the best results. With manganous chloride, a considerable improvement both in size and quality was obtained as compared with the unmanured plants, whilst manganous sulphate had less effect.
N. H. J. M.

Action of Manganese on Potatoes and Sugar Beet. ACH. GRÉGOIRE, J. HENDRICK, and EM. CARPIAUX (*Bul. Inst. Chim. Bact. Gembloux*, 1908, No. 75, 66—72. Compare Birner and Lucanus, *Landw. Versuchs-stat.*, 8, 128; Wagner, *ibid.*, 13, 69, 278; Bertrand, *Abstr.*, 1897, ii, 493; 1898, i, 53 and ii, 128; 1906, ii, 121; Giglioli, *ibid.*, 1901, ii, 527; Loew, Honda, and Fukutome, *ibid.*, 1904, ii, 766; Passerini, *ibid.*, 1906, ii, 117; Voelcker, *ibid.*, 1906, ii, 388; van Dam, *ibid.*, 1907, ii, 649).—Results of field experiments with potatoes showed that an application of manganous sulphate (50 kilos. per hectare) resulted in an average increase of 7%. A smaller amount (10 kilos.) was without effect. Similar experiments with sugar beet showed that manganese sulphate diminished the yield of roots, whilst the percentage of sugar in the roots was increased; the yield of sugar was the same in both cases. N. H. J. M.

Analytical Chemistry.

Differential Method of Blood-Gas Analysis. JOSEPH BARCROFT (*J. Physiol.*, 1908, 37, 12—24).—A full account with mathematical data of the method previously published (see this vol., ii, 319).

W. D. H.

New Capillary and Capillary-Analytical Investigations. FRIEDRICH GOPPELSROEDER (*Chem. Zentr.*, 1908, 1, 760—761; from *Verh. Naturf.-Ges. Basel*, 1907, 19, 1—81).—A large number of experiments with pure filter paper as capillary agent. The velocity of the capillary action per minute and its final extent were measured; this depends largely on atmospheric pressure. The process is recommended for the detection of minute traces of such substances as strychnine hydrochloride, morphine hydrochloride, and stovaine hydrochloride; a reaction may then be obtained on the paper. The capillary action seems to depend on the molecular weight, but there are exceptions to this rule. The test may be useful in milk analysis; the components are separated from each other, and may be identified. The mineral constituents are found at the bottom of the paper. Watered milk rises highest.

L. DE K.

Electrolytic Analysis. FRITZ FOERSTER (*Zeitsch. Elektrochem.*, 1908, 14, 208—211).—ALEXANDER CLASSEN (*ibid.*, 239).—A continuation of the polemic on this subject (this vol., ii, 226, 322, 432).

T. E.

Use of the Filtering Crucible in Electrolytic Analysis. FRANK A. GOOCH and F. B. BEYER (*Amer. J. Sci.*, 1908, [iv], 25, 249—255; *Zeitsch. anorg. Chem.*, 1908, 58, 65—72).—A device for

handling loosely-adhering metallic deposits, consisting of a modified Gooch perforated platinum or porcelain crucible serving as electrode. For details, the illustrations in the original article should be consulted. Four different methods are given. L. DE K.

Estimation of Halogen Elements in Organic Chloro-bromo-compounds. HENRI BAUBIGNY (*Compt. rend.*, 1908, 146, 931—933.* Compare Abstr., 1903, ii, 510; 1904, ii, 203).—In order to estimate the chlorine and bromine in organic compounds, the compound is oxidised with a chromic acid mixture in the presence of silver sulphate (Abstr., 1899, ii, 328), and the liberated chlorine and bromine absorbed in an alkaline solution of alkali sulphite; this solution is made up to 500 c.c. and then divided into two equal parts, and the total halogens estimated in one part by the usual method. The other part is neutralised and concentrated to 20 to 25 c.c., the excess of sulphite destroyed by potassium permanganate, the bromine eliminated by the method described previously (Baubigny and Rivals, Abstr., 1897, ii, 385), and the chlorine in the residue determined in the usual way. M. A. W.

Thiocyanoselenious Acid and the Estimation of Selenium. W. N. IWANOFF (*Chem. Zeit.*, 1908, 32, 468).—A solution containing 0.1—0.4 gram of selenium in 600 c.c. is mixed with 25 c.c. of ammonium thiocyanate (1:5), and then with 150 c.c. of 25% hydrochloric acid. The liquid is heated in a water-bath for twelve hours, and then left overnight. The thiocyanoselenious acid formed at first is decomposed with separation of selenium, which is then collected on a weighed filter, dried at 105°, and weighed. It contains, however, some admixed sulphur, which must be estimated by treatment with nitrohydrochloric acid, precipitation with barium chloride, &c., and then allowed for.

Thiocyanoselenious acid, $(\text{HCNS})_2\text{H}_2\text{SO}_3$, forms a bulky, crystalline mass of lustrous, transparent, white, quadrangular leaflets, gradually turning yellow, and rapidly decomposed by hot water. L. DE K.

Estimation of Nitrogen. H. DROOP RICHMOND (*Analyst*, 1908, 33, 179—183).—*The Nitrogen Factor for Casein.*—The experiments recorded give an average value of 15.65% of nitrogen in casein, as estimated by Kjeldahl's method; this corresponds with a factor of 6.39. Nitrogen is not evolved as gas in the Kjeldahl method, and high results obtained by Dumas' method were found to be due to unburnt carbon monoxide.

Triazo-nitrogen.—A process is given for the estimation of nitrogen in the series of compounds containing the triazo-group described by Forster and Fierz (*Trans.*, 1905, 87, 826; 1907, 91, 855, 1350, 1942; 1908, 93, 72). The substance was washed into a nitrometer with successive small quantities of alcohol, 2 drops of 40% formaldehyde solution were added, and then the concentrated sulphuric acid. After reading off the volume of gas, the sulphuric acid was transferred to a flask, 2 grams of zinc dust were added, and an estimation of the

* and *Bull. Soc. chim.*, 1908, [iv], 3, 630—633.

nitrogen was made by Kjeldahl's method. The ratio of the nitrogen found as ammonia to the total nitrogen varied from 1:1.83 to 1:2.02.
W. P. S.

Method for the Estimation of Ammonia in Urine. HANS MALFATTI (*Zeitsch. anal. Chem.*, 1908, 47, 273—278).—Ten c.c. of the urine under examination are diluted with 50 c.c. of water, and the acidity is neutralised by the addition of *N*/10 sodium hydroxide solution, using phenolphthalein as indicator (a considerable quantity of the latter must be added). Three c.c. of neutral 40% formaldehyde solution are now added, and the solution is again titrated. The quantity of alkali required for the second titration corresponds with the ammonia present, as it is the amount used to neutralise the acid liberated from the ammonium salts by the combination of the ammonia with the formaldehyde. A further quantity of formaldehyde may be added to the neutralised solution; if the first quantity of formaldehyde was insufficient to combine with all the ammonia, the solution becomes acid, and the titration must be continued. If amino-acids are also present in the urine, they are estimated along with the ammonia; an estimation of the ammonia by Schloesing's method will show whether they are present or not.
W. P. S.

Estimation of Phosphorus in Ash Analysis. SHERMAN LEAVITT and J. ARTHUR LECLERC (*J. Amer. Chem. Soc.*, 1908, 30, 617—618).—The authors now state that the loss in phosphorus (this vol., ii, 428) is not due to volatilisation, but to its conversion into a form in which it is no longer precipitated by molybdate solution.

This may be remedied by heating the ash with sulphuric and nitric acids.
L. DE K.

A New Method of Estimating Phosphorus in Organic Compounds. ISIDORE BAY (*Compt. rend.*, 1908, 146, 814—815).—The method described is analogous to that proposed for sulphur (this vol., ii, 319). The substance is burnt with magnesia and sodium carbonate in a "bayonet" tube, the product dissolved in dilute acetic acid, and the phosphate titrated against a solution containing 40 grams of uranium nitrate per litre, potassium ferrocyanide being used as an indicator. The results agree well with those obtained by Carius' method.
E. H.

Titration of Phosphoric Acid in Superphosphates. S. KOHN (*Chem. Zeit.*, 1908, 32, 475—476).—Twenty grams of the superphosphate are extracted with a litre of water, and 50 c.c. of the filtrate are diluted to 300 c.c. and titrated with *N*/10 alkali hydroxide (free from carbonate), with methyl-orange as indicator; the result is calculated to free phosphoric acid. A considerable excess of neutral calcium chloride is added, also a few drops of phenolphthalein, and the titration is continued. If the total number of c.c. used = *m*, whilst *n* c.c. were necessary to convert the free phosphoric acid into the primary salt, then the total amount of phosphoric acid is found from

the difference $m - n$; 1 mol. of phosphoric oxide = 4 mols. of sodium hydroxide. L. DE K.

Hæmatoxylin as an Indicator in the Titration of Phosphoric Acid. ALBERT B. LYONS (*Pharm. Rev.*, 1908, 26, 97—101).—Phosphoric acid may be titrated with great accuracy with standard alkali, using hæmatoxylin as indicator, although this does not appear to be a good general indicator. The conditions for a successful titration are that the first change of colour (from yellow to pink) should be taken as the end reaction, and that the alkali should be checked with phosphoric acid of approximately the same strength as the sample taken for analysis. Chlorides interfere somewhat with the test. L. DE K.

The Leo Process for the Estimation of the Acidity of the Monometallic Phosphates in Gastric Juice. MICHELE BARBERIO (*Chem. Zentr.*, 1908, i, 986; from *Deutsch. med. Woch.*, 1908, 34, 104—105).—Leo's process, consisting in neutralising any free hydrochloric acid in the gastric juice by means of calcium carbonate previous to titration of the acid phosphate, has been found to give uncertain results. L. DE K.

Detection of Arsenic by means of Mercuric Chloride Solution. R. LOCHMANN (*Chem. Zentr.*, 1908, i, 485; from *Zeitsch. Österr. Apoth. Ver.*, 1907, 45, 744—745).—The apparatus consists of a small flask fitted with a perforated cork through which passes a delivery tube bent twice at right angles; the end which dips into the reagent is drawn out to a point. A few pieces of granulated zinc and 50 c.c. of water are introduced into the flask, also a sufficiency of hydrochloric acid. The gas evolved is passed through a test-tube containing a 5% solution of mercuric chloride, but in case of sulphides a small wash-bottle containing lead acetate is interposed. When satisfied that the zinc and acid are arsenic-free, the solution supposed to contain the arsenic is introduced, and, if present, a flocculent, pale yellow mercurial precipitate will form and, after some time, crystals of arsenious acid become visible. Antimony gives a white turbidity; in this case, some hydrochloric acid should be added to the mercuric chloride solution, but no separation of arsenic crystals then takes place. L. DE K.

Detection of Arsenic in Sulphur. J. BRAND (*Chem. Zentr.*, 1908, 1, 762—763; from *Zeitsch. ges. Brauwesen.*, 1908, 31, 33—34).—Five grams of the finely-powdered sample are digested for fifteen minutes in 25 c.c. of dilute ammonia (1:1), the filtrate is evaporated to dryness, and the residue oxidised with a few drops of nitric acid. After evaporation of the acid, the residue is dissolved in 8—10 c.c. of dilute sulphuric acid, a little pure zinc is introduced, and, after closing the top of the tube with a piece of cottonwool, the hydrogen evolved is tested for arsenic hydride as usual by means of a disk of filter paper moistened with a drop of strong silver nitrate. L. DE K.

Detection of Arsenic [in Fabrics]. ALFRED BEHRE (*Pharm. Zentr.-h.*, 1908, 49, 355—357).—If any substance is found to be free from arsenic by the Gutzeit test (yellow spot on filter paper impregnated with silver nitrate), it may be passed as satisfactory, but should the test be positive it is still necessary to apply the Marsh test as well.

In any case, it is advisable to get rid of any sulphides in the colouring matters by oxidation with nitric acid and evaporation with sulphuric acid, or by means of hydrochloric acid and potassium chlorate; the Gutzeit test is then more trustworthy. L. DE K.

Parr's Method of Estimating the Heat of Combustion of Coal. SAMUEL W. PARR (*Zeitsch. angew. Chem.*, 1908, 21, 970—976. Compare *ibid.*, 1906, 19, 1796; Abstr., 1900, ii, 710; 1902, ii, 432).—Attention is drawn to the fact that unless anhydrous sodium peroxide is used, it is necessary to estimate the amount of moisture absorbed by this substance before it is used for combustion purposes; experimental data are given which show the importance of this point. Complete combustion is best aided by the addition of potassium chlorate to the sodium peroxide, but it is found that two parts of potassium persulphate and one part of ammonium persulphate form an excellent mixture for this purpose. The heat of combustion of carbon and also of hydrogen (to liquid water) is shown to be in each case 73% of the total heat of the reaction with sodium peroxide. The following table of correction factors is given, together with examples of their use with various varieties of coal:

Sulphur	0.006° for 1% in 0.5 gram substance.
Ash	0.001 „ 1% „ 0.5 „ „
Water of combination.....	0.0033 „ 1% „ 0.5 „ „
Potassium chlorate	0.040 „ 0.5 gram.
Fuse	0.008 „ 10 mg. burnt.

J. V. E.

Estimation of Carbon Monoxide, Especially in Tobacco Smoke. H. MARCELET (*Bull. Soc. chim.*, 1908, [iv], 3, 556—558).—Estimations of the amount of carbon monoxide in tobacco smoke, using cuprous chloride in hydrochloric acid as an absorbent, showed that one gram of tobacco, smoked in cigarette form, yields from 20 to 80 c.c. of this gas, whilst the same amount, smoked in a pipe, yields from 53 to 100 c.c. Some difficulty was experienced in confirming these results when the carbon monoxide was estimated by means of iodic acid, but eventually by diluting the smoke with air, so that the mixture contained 0.8 to 1.0 per cent. of carbon monoxide and using a modified form of Levy and Pecoul's apparatus, similar results were obtained. T. A. H.

Separation of Silica and Alumina in Iron Ores. T. GEORGE TIMBY (*J. Amer. Chem. Soc.*, 1908, 30, 614—615).—A criticism of the process devised by Dean (Abstr., 1907, ii, 818). The ignition method with or without addition of sulphur is not universally applicable to the accurate estimation of silica and alumina in iron ores. L. DE K.

Determination of Alkalinity by Electrochemical Means.

A. E. LANGE (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 453—468).—An exhaustive investigation, illustrated with a curve and tables; the following conclusions have been arrived at. The point of neutrality obtained by determining the conductivities or by employment of "concentration chains" does not coincide with that obtained by the usual indicators; it agrees best with that given by phenolphthalein. The point of neutrality of pure sucrose to which acid or alkali has been purposely added may be sharply determined by either of the two electric methods, but with raw sugars or molasses the two methods utterly fail. For the determination of alkalinity in raw sugars, phenolphthalein is to be recommended as a suitable indicator.

L. DE K.

Volumetric Estimation of Alkali Hydroxides Containing Carbonates by Winkler's Method.

SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeitsch. anal. Chem.*, 1908, 47, 279—294).—It is shown that trustworthy results can only be obtained by this method if the precipitation with barium chloride is carried out whilst the solution is hot and when the solution contains only normal carbonate, or, at most, a minute quantity of free alkali. If the solution contains the latter or a hydrogen carbonate, a sufficient quantity of either hydrochloric acid or sodium hydroxide, as the case may be, must be added before the solution is warmed, in order to remove the free alkali or alkali hydrogen carbonate. The requisite amount to be added is ascertained by a previous titration. If solutions of pure normal alkali carbonates are precipitated whilst hot with barium chloride, only normal barium carbonate is thrown down; if the precipitation takes place in the cold, more or less barium hydrogen carbonate is formed, and the supernatant solution becomes alkaline. The statement by Le Blanc (*Abstr.*, 1907, ii, 505), that the solution becomes acid in these circumstances, is probably due to his having worked with alkali carbonate containing hydrogen carbonate. If the solution contains alkali hydroxide, the precipitate of barium carbonate will contain more or less basic carbonate, according to the quantity of alkali hydroxide present.

W. P. S.

Estimation of Potassium by the Platinichloride Method.

HENRI J. F. DE VRIES (*Chem. Weekblad*, 1908, 5, 261—269. Compare this vol., ii, 430).—Experiments showing the extent to which potassium may be retained in the barium sulphate formed on converting potassium sulphate into chloride by means of barium chloride. Addition of hydrochloric acid does not diminish the extent of the occlusion.

Hence, in using Stohmann's process, the loss will be such that, instead of, say, 27% of K_2O , at most 26.6% will be found. It must be remarked that the loss would be even greater were it not that in practice the volume of the precipitate formed is neglected. This volume may be approximately determined by noticing the amount of barium chloride used for precipitation, and dividing the calculated weight of the sulphate by 4.2.

L. DE K.

Estimation of Potassium in Soils. LÉON RONNET (*Ann. Chim. Anal.*, 1908, 13, 141—143).—Twenty-five grams of the soil are heated

in a flat porcelain dish with 25 c.c. of nitric acid (more if carbonates are present) for three hours. Some water and a few drops of barium nitrate solution are added, the solution is evaporated to dryness, and the residue heated to incipient redness. Ferric and aluminium nitrates are quite decomposed, and those of calcium and magnesium but partly.

The residue is treated with water and 10—20 grams of oxalic acid, and the whole is again evaporated to dryness. The residue is heated to redness until all the oxalic acid has disappeared; by this treatment, the calcium, magnesium, and barium are also rendered insoluble. The mass is powdered and introduced into a flask, and treated with hot water (250 c.c.); when cold, water is added up to the mark, and also an extra 10 c.c. to compensate for the volume occupied by the insoluble matter. Two hundred c.c. of the filtrate are then evaporated to dryness, and the residue ignited once more with a few grams of oxalic acid. The mass is then dissolved in a little hot water, and, after acidifying the filtrate with hydrochloric or nitric acid, the potassium is estimated either by the platinum or the perchlorate process.

L. DE K.

Practical Modification of the Method for Determining the Hardness of Water. Value of the Process. FERNAND TELLE (*J. Pharm. Chim.*, 1908, [vi], 27, 380—389).—Clark's process, as modified by Boutron and Boudet, is placed on a decimal basis by adopting as standard a solution containing 0.344 gram of crystallised calcium sulphate per litre; 50 c.c. of this solution, corresponding therefore with 0.01 gram of calcium carbonate, are titrated with soap solution, slightly alkaline to phenolphthalein, and contained in an ordinary 50 c.c. burette. One degree of hardness, on this basis, is exactly equivalent to 0.01 gram of calcium carbonate per litre, and corresponds therefore pretty closely with a degree in Boutron and Boudet's modification (0.0103 gram).

The amounts of calcium carbonate and sulphate found by the soap method, in general agree closely with the results of direct analysis.

G. B.

Detection of Barium in Strontium Salts. H. CARON and D. RAQUET (*Bull. Soc. chim.*, 1908, [iv], 3, 483—493).—A detailed study of the sensibility of the various tests for barium alone, and in presence of strontium or calcium salts, has been made. The following are the limits of sensibility of the reagents investigated. In each case, the first fraction expresses the minimum ratio of barium to water in a solution which will give a precipitate with the reagent; the second, the minimum ratio of barium to strontium, and the third (where given) the minimum ratio of barium to calcium which can be detected by means of the reagent. Hydrofluosilicic acid, $1/2500$ and $1/15$; hydrofluosilicic acid, in presence of alcohol, $1/20,000$, $1/75$, and $1/60$; strontium sulphate, $1/30,000$ and $1/50$; potassium dichromate, $1/100,000$, $1/150$, and $1/150$ (approx.); strontium chromate, $1/250,000$ and $1/1000$; potassium chromate (3%), $1/2,500,000$, $1/15,000$, and $1/1,000,000$. Smaller

quantities of barium can be detected by most of these reagents by allowing the mixture to remain for a time; the second figures given above are for 10% solutions of strontium salt in contact with the reagent during a few minutes.

Hydrofluosilicic acid is apt under certain conditions to deposit gelatinous silica, which may be mistaken for barium silicofluoride. Many strontium salts contain strontium sulphate, which may be precipitated when the solutions are boiled, particularly in presence of acids. The impression that the addition of acetic acid to chromates, and of sodium diacetate to dichromates, make these reagents more delicate as tests for barium is, in the author's experience, erroneous. Ammonium vanadate and potassium iodate have also been suggested as reagents for detecting barium in presence of strontium, but they are of little value for this purpose in presence of a large excess of strontium. Full details are given in the original as to the best methods of applying these various reagents as tests for barium.

T. A. H.

Electrolytic Depositions on Inclined Electrodes. R. GOLDSCHMIDT (*Bull. Soc. chim. Belg.*, 1908, 22, 138—145).—It is shown that trustworthy results may be obtained in the electrolytic deposition of zinc if, instead of a rotating electrode, a fixed electrode be used and, at the same time, a movement is given to the solution. The author employs a strip of zinc 40 cm. long and 5 cm. wide as the anode; this is placed in a narrow metal trough, which serves as the cathode, the two being fixed at a distance of about 5 mm. apart by means of glass rods placed at the edges of the anode. The whole is inclined, and the solution is allowed to flow down the trough and over the anode, and then into a collecting vessel. From this, the solution is pumped up to a vessel placed above the electrodes, and is again allowed to flow over the latter, and so on. The pump consists of a rubber tube laid in a wooden trough, and the solution is caused to pass up the tube by means of two rollers, which pass upwards over the tube, compressing it so that the solution is forced upwards. The rollers are driven by an electric motor. The electrolyte employed consisted of hydrofluosilicic acid which had been neutralised with zinc oxide or carbonate, and the best results as regards hardness and adherence of the deposit were obtained when the electrolyte contained fine sand in suspension.

W. P. S.

Estimation of Lead in Ores. ALBERT H. LOW (*J. Amer. Chem. Soc.*, 1908, 30, 587—589).—The impure lead sulphate obtained in due course is dissolved in a boiling solution of acid sodium acetate (made by adding 40 c.c. of glacial acetic acid to 500 c.c. of a cold saturated solution of sodium acetate diluted with 500 c.c. of water). The lead is now precipitated by potassium dichromate, and the lead chromate is next treated with a boiling solution of oxalic acid (1 part of cold saturated solution to 3 parts of water). A little alcohol is also added to assist in reducing the chromate. The lead oxalate so obtained is washed and then treated with hot dilute sulphuric acid, when the

oxalic acid liberated, which represents the lead, is titrated as usual with standard permanganate, checked by lead as described.

L. DE K.

Comparison of Two Tests of Red Lead. EUGENE E. DUNLAP (*J. Amer. Chem. Soc.*, 1908, 30, 611—613).—Two tests are in common use for the evaluation of red lead. One consists in treating the sample with dilute nitric acid and weighing the residual peroxide, or this may be determined volumetrically. The author cannot recommend this method, but has obtained good results with the lead acetate process. The excess of lead oxide in a sample of red lead may be determined accurately by boiling with solution of lead acetate and re-weighing the undissolved matter.

L. DE K.

Rapid Analysis of Copper-plating Baths. ERNESTO PANNAIN (*Gazzetta*, 1908, 38, i, 352—355).—The following method for estimating the copper sulphate and the free sulphuric acid contained in copper-plating baths is rapid and gives good results. The liquid is first diluted to ten times its volume, and 25 c.c. then treated with an excess of powdered potassium iodide, the iodine set free being estimated by titration with *N*/10 sodium thiosulphate; the amount of copper sulphate is calculated by means of the equation: $2\text{CuSO}_4 + 4\text{KI} = \text{Cu}_2\text{I}_2 + 2\text{I} + 2\text{K}_2\text{SO}_4$. The free acid is estimated in the same solution by adding potassium iodate and titrating the liberated iodine with sodium thiosulphate.

T. H. P.

Analysis of White Metal and Similar Alloys. E. SCHÜRMANN and WILHELM SCHARFENBERG (*Chem. Zentr.*, 1908, i, 986; from *Mitt. K. Materialprüfungs-Amt.*, 25, 270—274).—A method based on Clarke's oxalic acid process. One gram of the alloy is dissolved in 10 c.c. of hydrochloric acid containing bromine, and, after removing the latter by a current of carbon dioxide, 3—4 grams of tartaric acid are added and then a slight excess of ammonia. After removing any copper and lead by Finkener's method, the liquid is acidified with sulphuric acid and heated to 60°, and the tin, antimony, and arsenic are precipitated with hydrogen sulphide. The precipitate is redissolved in bromohydrochloric acid and then neutralised with ammonia, and at once mixed with 5 grams of oxalic acid. The solution is now diluted to 400 c.c., heated to boiling, and a current of hydrogen sulphide is passed for one hour. The precipitate containing arsenic and antimony is at once collected, the filtrate is neutralised with ammonia, again acidified slightly with acetic acid, and once more treated with hydrogen sulphide for three hours at the boiling temperature. The tin sulphide is collected, washed with water containing ammonium sulphate, and finally converted into oxide by means of nitric acid. It is as well to redissolve the antimony precipitate in hydrochloric acid and bromine, and to precipitate once more with hydrogen sulphide. The precipitate is then dissolved in sodium sulphide, and the antimony precipitated electrolytically; any arsenic remains in solution.

Pig lead is dissolved in nitric and tartaric acids, and most of the lead precipitated with sulphuric acid.

L. DE K.

A System of Qualitative Analysis for the Common Elements. III. Analysis of the Aluminium and Iron Groups, including Glucinum, Uranium, Vanadium, Titanium, Zirconium, and Thallium. ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR (*J. Amer. Chem. Soc.*, 1908, 30, 481—565).—After removing the metals of the hydrogen sulphide group, the solution is mixed with ammonia and ammonium sulphide, which precipitates the metals of the aluminium and iron group, including also glucinum, uranium, vanadium, titanium, zirconium, and thallium. The usual separation of nickel and cobalt by means of dilute hydrochloric acid has been abandoned, but the precipitate is dissolved in hydrochloric acid with the aid of nitric acid. The solution is then boiled with excess of sodium hydroxide and sodium peroxide, which causes the following metals to pass into solution as sodium salts: aluminium, glucinum, zinc, chromium, uranium, and vanadium. For further particulars, the tables in the original article should be consulted. L. DE K.

Estimation of Iron in Reduced Iron. GUSTAV FRERICHES (*Arch. Pharm.*, 1908, 246, 190—205).—The process answers both for reduced and powdered iron. One gram of the sample is dissolved in 25 c.c. of dilute hydrochloric acid, and diluted to 100 c.c. Twenty c.c. of the filtrate are then mixed with 100 c.c. of water and 10 c.c. of nitric acid, and heated for some time, but not to boiling. The iron is then precipitated with ammonia, and finally weighed as oxide. Powdered iron should contain at least 98% of real iron, whilst reduced iron may be pronounced pure if it yields 96.6%. L. DE K.

Estimation of Iron by Permanganate after Reduction with Titanous Sulphate. H. D. NEWTON (*Amer. J. Sci.*, 1908, [iv], 25, 343—345 *).—The ferric sulphate solution is reduced by means of titanous sulphate, the excess of which is rendered harmless by oxidation with bismuth oxide. The ferrous iron is then titrated with permanganate.

The titanous sulphate for this purpose may be readily prepared by fusing commercial titanous acid with potassium sodium carbonate, decomposing the mass with sulphuric acid, and reducing the solution with zinc. L. DE K.

Estimation of Ferrous Oxide in Rock Analyses. ROBERT MAUZELIUS (*Chem. Zentr.*, 1908, i, 765; from *Sveriges geol. Undersökning, Afhandl. och uppsatser.*, Ser. C, 206).—In presence of titanium, the volumetric estimation of ferrous oxide still presents difficulties. On finely powdering a mineral, the ferrous oxide may have become partly oxidised; in analyses, a coarse powder should therefore be used. Rocks are best attacked with a mixture of sulphuric and hydrofluoric acids. L. DE K.

Assay of Ferrochrome with High Carbon Content. A. CAFFIN and F. DHUIQUE-MAYER (*Chem. Zentr.*, 1908, i, 986—987; from *Mon. Sci.*, 1908, [iv], 22, 88—91).—The estimation of the

* and *Zeitsch. anorg. Chem.* 1908, 58, 378—380.

chromium by fusion with sodium peroxide gives satisfactory results. The carbon is estimated by heating 0.25 gram of the powdered sample, mixed with 1.5 grams of lead peroxide and placed in a porcelain boat, for four to five hours in a porcelain combustion tube in a current of oxygen. The gases are passed through three pear-shaped absorbing flasks containing ammoniacal barium chloride solution (1 vol. of 10% barium chloride; 1 vol. of ammonia). The solution is heated for two hours on the water-bath to precipitate fully the barium carbonate, which is then converted into sulphate and weighed. Iron is estimated by fusing 0.5 gram of the powder with 5 grams of sodium peroxide, the iron is dissolved in dilute sulphuric acid, precipitated with ammonia, again redissolved in acid and reprecipitated with ammonia, and heated to redness for three hours. It is then fused with potassium sodium carbonate, dissolved in hydrochloric acid, reduced with zinc, and titrated with standard permanganate. L. DE K.

Electrolytic Estimation of Nickel in Nitrate Solutions and its Separation from Copper. ALFRED THIEL (*Zeitsch. Elektrochem.*, 1908, 14, 201—208).—Nickel may be deposited quantitatively from an ammoniacal nitrate solution provided it is free from nitrite and contains a sufficient excess of ammonia. The nitrite is most readily destroyed by simple boiling; about 80 c.c. of ammonia (D 0.91) in 120 c.c. of solution are necessary to prevent the deposition of nickel oxide on the anode. Platinum anodes are dissolved unless protected by a skin of nickel oxide; this skin dissolves at the end of the operation, and the dissolved platinum is deposited at the cathode. The error due to this is avoided by using straight iron wires as anodes; the wires are brought into the passive state before use by dipping them in concentrated nitric acid, washing with alcohol, and drying. In the separation of copper and nickel, the copper is not completely precipitated at 70° if nitrous acid is present; by depositing the greater part of it at the ordinary temperature and finishing the electrolysis at 55°, this difficulty is avoided. Ammonia is then added, and the electrolysis completed with a higher current density at 70°. In presence of excess of ammonia, small quantities of nickel cannot be recognised by the addition of ammonium sulphide, since the brown colour does not appear. It is therefore advisable to continue the electrolysis for a few minutes after the first weighing of the nickel deposit in order to make sure that no further deposit occurs. T. E.

Method for the Rapid Estimation of Nickel in the Presence of Cobalt. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim. Belg.*, 1908, 22, 155—156 *).—The volume of the precipitate obtained on precipitating the nickel as molybdate (this vol., ii, 229) may be measured and compared with that of a known quantity of nickel molybdate in order to ascertain the amount of nickel present. The solution containing the nickel and cobalt is neutralised, concentrated, and treated with an excess of saturated ammonium molybdate solution. The mixture is placed in a tube provided with a narrow graduated neck. A mixture is also prepared with a known quantity of nickel, and is placed in a second tube. The contents of both tubes are heated, so as to cause

* and *Ann. Chim. anal.* 1908, 13, 217—218.

the insoluble nickel molybdate to separate, and are then submitted to centrifugal action for three minutes, the precipitate being collected in the graduated part of the tube. The volume of the precipitate in the solution under examination is then compared with that of the known quantity of nickel molybdate.

W. P. S.

Separation and Estimation of Nickel in the Presence of Cobalt and all other Elements which are not Precipitated by Hydrogen Sulphide in Acid Solution. M. EMMANUEL POZZI-ESCOT (*Ann. chim. anal.*, 1908, 13, 185—186; *Bull. Soc. chim. Belg.*, 1908, 22, 158—162).—The method of estimating nickel described previously (this vol., ii, 229) may be applied to solutions of nickel also containing cobalt, iron, zinc, manganese, chromium, uranium, aluminium, magnesium, barium, strontium, &c. The precipitate of nickel molybdate obtained is boiled with an excess of ammonia; all the nickel goes into solution, whilst the iron, aluminium, chromium, manganese, and zinc, which are also precipitated, either remain insoluble or are removed in the subsequent treatment of the nickel solution. This treatment consists in boiling the solution with potassium hydroxide in order to expel the ammonia and then adding bromine. The nickel oxide is collected on a filter, washed, dissolved in an acid, and estimated electrolytically.

W. P. S.

Estimation of Vanadic and Molybdic Acids in the Presence of one Another. GRAHAM EDGAR (*Amer. J. Sci.*, 1908, [iv], 25, 332—334 *).—The process is based on the fact that under certain conditions molybdic acid is not reduced by sulphur dioxide.

The solution, which should contain at most 0.2 gram of molybdic acid in 50 c.c. and 1 c.c. of free sulphuric acid, is heated to boiling, and a current of sulphur dioxide is passed until the vanadium is reduced to the state of tetroxide. The excess of sulphur dioxide is boiled off, and the last traces expelled by a current of carbon dioxide. The liquid is then titrated for vanadic acid with standard permanganate.

By increasing the sulphuric acid to 5 c.c., reduction of molybdic acid does not take place even with 0.4 gram of the same in 25 c.c. of liquid.

L. DE K.

Reduction of Vanadic Acid by Zinc and Magnesium. FRANK A. GOOCH and GRAHAM EDGAR (*Amer. J. Sci.*, 1908, [iv], 25, 233—238).—Glassmann's process (*Abstr.*, 1905, ii, 208) for the titration of vanadium in presence of molybdenum is based on the assumption that a solution of vanadium when reduced by magnesium and hydrochloric acid contains V_2O_3 , and that, when zinc has been employed and the solution exposed to the air, V_2O_2 is present. The authors, after having made many experiments, state that this view is quite erroneous.

L. DE K.

Assay of Sulphur Antimonii Auratum. FELIX JACOBSON (*Chem. Zentr.*, 1908, i, 763—764; from *Gummi Zeit.*, 1908, 22, 368—387).—Admixed sulphur may be estimated by extraction with carbon

* and *Zeitsch. anorg. Chem.* 1908, 58, 375—377.

disulphide. The total sulphur is found by repeated evaporation with fuming nitric acid; the residue is then extracted with water, and treated with barium chloride as usual. The antimony is found by evaporation with nitric acid and ignition of the residue. This, however, is not pure antimony peroxide, but may contain calcium sulphate and other inert matters. The author has devised a simple and fairly satisfactory plan for an indirect estimation of the antimony, consisting in heating the residue with ammonium chloride, which causes the antimony to volatilise and does not react with calcium sulphate. The sulphur in actual combination with the antimony may be found by heating the extracted sample with hydrochloric acid and estimating the hydrogen sulphide evolved by passing it through an ammoniacal silver nitrate solution. The acid solution may then be used for further investigation. L. DE K.

Electrolytic Estimation of Bismuth. FLOYD J. METZGER and H. T. BEANS (*J. Amer. Chem. Soc.*, 1908, 30, 589—593).—The solution containing at most 0.4 gram of bismuth is neutralised with sodium hydroxide, using phenolphthalein as indicator; 20 c.c. of 50% acetic acid and preferably also 2 grams of boric acid are added, and the whole is diluted to 250 c.c. and submitted to electrolysis, the conditions being about as follow: ND_{40}^2 0.2—0.15; voltage, 2.1—2.80; temperature, 74—79°; time, three-quarters of an hour to three and a half hours.

The metal is obtained quantitatively as a firmly-adhering deposit, no peroxide being deposited on the anode. L. DE K.

Influence of Microbes on the Composition of Waters. CH. ROUCHY (*J. Pharm. Chim.*, 1908, [vi], 27, 374—380).—The chemical analysis of water, like the bacteriological examination, should be undertaken as soon as possible after the collection of the sample, on account of the chemical changes which are brought about by the bacteria contained in it. These changes consist principally in the oxidation of ammonia and of nitrites to nitrates, and stress is laid on the rapidity of this process. G. B.

Chloroform Balance. AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1908, vi—viii; *J. Physiol.*, 37).—The principle of the balance is to weigh a closed glass bulb in an atmosphere of chloroform vapour in air. If the mixture to be administered to the animal or patient is passed through the balance case, the rise and fall of the beam, which can be registered by a pointer on a slowly moving drum, indicates changes in the percentage of the chloroform from that which it is desirable to administer. W. D. H.

Volumetric Estimation of Reducing Sugars. II. The Limits of Accuracy of the Method under Standard Conditions. ARTHUR R. LING and G. CECIL JONES (*Analyst*, 1908, 32, 160—167. Compare Abstr., 1905, ii, 487).—The authors have subjected the method to a critical investigation, and find that it is quite as trustworthy as the gravimetric process. The average error appears to be 1 in 400 in the case of dextrose, 1 in 300 in the case of maltose,

and 1 in 100 in the case of lævulose. Assuming the concentration of the sugar solution to be constant, the number of c.c. required for any titration is directly proportional to the volume of Fehling's solution employed, at all events, when this lies between the limits of 5 and 20 c.c. A table is also given showing the quantities of dextrose, lævulose, invert sugar, and maltose in 100 c.c. of solution when from 20 to 43 c.c. of the latter are required to reduce 10 c.c. of Fehling's solution. The composition of the indicator given previously (*ibid.*) requires correction; the quantity of hydrochloric acid should be 2.5 c.c. (not 50 c.c.), and the amount of ammonium thiocyanate should be increased to 1.5 grams. W. P. S.

Volumetric Estimation of Reducing Sugar. III. Estimation of Sucrose and Invert Sugar in Mixtures. ARTHUR R. LING and THEODORE RENDLE (*Analyst*, 1908, 33, 167—170).—The influence of sucrose on the estimation of invert sugar in mixtures containing these two sugars is practically negligible until the proportion on the total sugar amounts to 30%, at which point the invert sugar is overestimated to the extent of 0.2%. In the case of a mixture of equal parts of sucrose and invert sugar, the latter would be returned as 50.4%, instead of 50%, that is to say, it would be overestimated by 0.8%, whilst a mixture containing 99% of sucrose would yield 1.14% of invert sugar on titration, or 14% too much. W. P. S.

Detection of Lævulose in Presence of other Natural Sugars. J. PIERAERTS (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 830—848).—The author has examined a number of reagents in order to ascertain whether it is possible, by their means, to detect lævulose rapidly and certainly in products containing other sugars which occur naturally, these being *l*-arabinose, *l*-xylose, dextrose, *d*-mannose, *d*-galactose, maltose, lactose, sucrose, and raffinose.

The results show that, for this purpose, Fehling's solution is useless, but that certain results are given by (1) various modifications of Ost's solution containing copper sulphate, potassium carbonate, and potassium hydrogen carbonate; (2) solutions containing per litre 6 grams $\text{Cu}(\text{OH})_2$, 50 grams (or 75 grams) KHCO_3 , and 100 grams K_2CO_3 ; the second of these solutions is very stable, remaining unchanged after six months; (3) a solution containing 12 grams glycine, 6 grams cupric hydroxide, and 50 grams potassium carbonate per litre, which is also stable. Details are given for the preparation of the various solutions.

Solution (3), which yields the most satisfactory results, is not reduced in the cold in twenty-four hours by any of the reducing sugars named above with the exception of lævulose, and with this sugar the time required for reduction varies from four to nine hours, as its concentration varies from 4—5% to 1—2%. Also a 3% solution of lævulose reduces this solution in one hour at 30°, under which conditions none of the other sugars mentioned causes reduction.

These solutions may also be utilised for detecting lævulose in commercial products, such as honey, marmalade, invert sugars, &c., the preliminary procedure being as follows: 20 or 25 grams of the

material are dissolved in 150—200 c.c. of cold water, the solution then being defecated by adding basic lead acetate solution drop by drop so as to avoid excess. The liquid is well shaken and filtered, the lead in the filtrate being precipitated by means of cold saturated sodium sulphate solution. After half an hour, the liquid is filtered, and the proportion of reducing sugar present estimated approximately by means of Fehling's solution. This proportion is reduced by dilution to about 5% calculated as dextrose. The presence of lævulose can then be detected as described above.

T. H. P.

Evaluation of Commercial Starch. EDMUND PAROW and FRANZ NEUMANN (*Chem. Zentr.*, 1908, i, 557; from *Zeitsch. Spirit. ind.*, 1907, 30, 561—562).—Ten grams of the sample are converted into dextrose by heating for one hour in the boiling water-bath with 20 c.c. of a solution composed of 200 grams of sodium chloride dissolved in 800 c.c. of water and mixed with 220 c.c. of 25% hydrochloric acid. Ten c.c. of basic lead acetate are added, and when cold the liquid is made up to 100 c.c. After decolorising with a little animal charcoal, the liquid is examined in a 200 mm. tube. By multiplying by a certain factor, the reading at once gives the percentage of starch. The following factors are used: For potato starch 8.288, for maize starch 8.478, for rice starch 8.497, and for wheat starch 8.420.

L. DE K.

Polarimetric Estimation of Starch in Cereals, &c. ERICH EWERS (*Zeitsch. öffentl. Chem.*, 1908, 14, 150—157).—Five grams of the finely-powdered sample are well mixed in a 100 c.c. flask with 25 c.c. of 1.124% hydrochloric acid, and the starch is then washed down from the neck of the flask by the addition of a further 25 c.c. of the same acid. The flask is immersed in a boiling water-bath for exactly fifteen minutes, the contents being shaken during the first three minutes. When the heating is finished, the contents are diluted with cold water to a volume of 90 c.c., cooled to a temperature of 20°, about 2 c.c. of a 22% sodium molybdate solution are added, the whole is diluted to 100 c.c., and filtered. The filtrate is then examined in the polarimeter, in a 200 mm. tube. Under these conditions, the reading (in degrees of the Ventzke-Soleil polarimeter) multiplied by the factor 1.892 gives the percentage of starch in the cereal. It is found that on macerating wheat flour with water for twenty-four hours, a loss of starch, varying from 2.5 to 8.5% and due to enzyme action, takes place. Maize starch also undergoes a similar loss, whilst rice starch is scarcely affected.

W. P. S.

Lactic Acid in Wine. GIULIO PARIS (*Chem. Zentr.*, 1908, i, 773; from *Staz. sperim. agrar. ital.*, 1907, 40, 689—718).—The only trustworthy method seems to be the one proposed by Partheil (*Abstr.*, 1903, ii, 189). The author heats the lactate with concentrated sulphuric acid in a current of carbon dioxide, and collects the carbon monoxide evolved in a nitrometer over aqueous sodium hydroxide. From the volume of gas, the lactic acid is calculated. The lactic acid owes its origin mainly to fermentation of malic acid.

L. DE K.

Citric Acid in Wines. A. HUBERT (*Ann. Chim. anal.*, 1908, 13, 139—141).—Experiments showing that, as citric acid occurs naturally in wines, the addition of small quantities of this acid cannot be detected. Both Dénigès' mercury test and Moeslinger's microscopic (calcium citrate) test were employed. L. DE K.

Volumetric Estimation of Thiosulphonates. AUGUST GUTMANN (*Zeitsch. anal. Chem.*, 1908, 47, 294—303).—The method described previously (Abstr., 1907, ii, 812) for the estimation of thiosulphates may be applied to the estimation of thiosulphonates. The filtrate from the silver cyanide and thiocyanate must be treated with an excess of zinc nitrate solution and placed aside for some time in order to precipitate sulphur compounds still remaining in solution. After adding ferric sulphate solution, the excess of silver is then titrated in the usual way. The zinc-sulphur compound is not removed before the titration, as it is insoluble and without effect on the operation. The reaction proceeds according to the equation: $R'SO_2SM' + KCN = R'SO_2M' + KCNS$, where R' is an organic radicle and M' a univalent metal. One litre of *N*/10 silver nitrate solution corresponds with 0.1 molecule of thiosulphonate. W. P. S.

Estimation of Fat, &c. in Animal Tissues. JOHAN C. BERNTROP (*Biochem. Zeitsch.*, 1908, 10, 192).—A reply to Kumaga and Sutō (this vol., ii, 331). A claim for priority with regard to an extraction apparatus (Abstr., 1902, ii, 366). S. B. S.

Colour Reactions of the Toxic Glucosides of Digitalis. LÉON GARNIER (*J. Pharm. Chim.*, 1908, [vi], 27, 369—371).—Comparison of the reactions of Kiliani, modified by Keller, of Brissemoret and Derrien, and of Lafon. All three give a coloration with crystalline digitoxin, but only the first two with amorphous digitalin. G. B.

Gall-Iron Inks. F. WILLY HINRICHSSEN and ERICH KEDESKY (*Chem. Zentr.*, 1908, 1, 990—991; from *Mitt. K. Materialprüfungs-Amt.*, 25, 244—261).—In technical ink analysis, where the gallic acid is only about 1/5 of the total gallo-tannins, it may be assumed that the iodometric estimation gives the same value for gallic as for tannic acid. The joint acids are best obtained by extraction with ethyl acetate. The titration should be carried out in presence of sodium hydrogen carbonate, 2 grams for every 0.1 gram of tannins supposed to be present. After eighteen hours, the excess of iodine is titrated with thiosulphate. A blank experiment should be made, as the sodium hydrogen carbonate itself absorbs iodine to a slight extent.

L. DE K.

General and Physical Chemistry.

Refractive Indices of Gaseous Nitric Oxide, Sulphur Dioxide, and Sulphur Trioxide. CLIVE CUTHBERTSON and E. PARR METCALFE (*Proc. Roy. Soc.*, 1908, *A*, 80, 406—410).—The refractive index of nitric oxide for sodium light is 1·0002939. This is greater than the value calculated from the indices of nitrogen and oxygen. For sulphur dioxide and trioxide, the values of the index are respectively 1·0006609 and 1·000737. These numbers are much smaller than those calculated from the indices of sulphur and oxygen.

H. M. D.

Refractive Index and Dispersion of Light in Argon and Helium. W. BURTON (*Proc. Roy. Soc.*, 1908, *A*, 80, 390—405. Compare Scheel and Schmidt, this vol., ii, 333).—The measurements were made by Jamin's interferometer method. The refractive index for the D₁ line at 0° and 760 mm. is for argon 1·0002837; for helium, 1·00003500. The constants A and B in the dispersion equation $n = A + B/\lambda^2$ are for argon 1·0002792 and $1·6 \times 10^{-14}$; for helium, 1·00003478 and $7·5 \times 10^{-16}$.

H. M. D.

Dispersion of Gaseous Mercury, Sulphur, Phosphorus, and Helium. CLIVE CUTHBERTSON and E. PARR METCALFE (*Proc. Roy. Soc.*, 1908, *A*, 80, 411—419. The results obtained for the refractive index and dispersion can be expressed by the formulæ: mercury, $\mu - 1 = 0·001755 (1 + 2·265/\lambda^2 \cdot 10^{10})$; sulphur, $\mu - 1 = 0·001046 (1 + 2·125/\lambda^2 \cdot 10^{10})$; phosphorus, $\mu - 1 = 0·001162 (1 + 1·53/\lambda^2 \cdot 10^{10})$; helium, $\mu - 1 = 0·0000347 (1 + 2·4/\lambda^2 \cdot 10^{11})$. The refractive index of sulphur for infinitely long waves is, within 2%, four times that of oxygen; the dispersions also are approximately as 4:1. The index of phosphorus for infinitely long waves is exactly four times that of nitrogen; the dispersions are almost exactly as 2:1. The index of helium is, within 1·6%, one-eighth of that of argon.

H. M. D.

Energetics and Chemistry of Banded Spectra. JOHANNES STARK (*Physikal. Zeitsch.*, 1908, 9, 356—358. Compare this vol., ii, 138).—Polemical against Kauffmann (*Physikal. Zeitsch.*, 1908, 9, 311). The nitro-compounds mentioned by Kauffmann as forming exceptions to the author's view of the dependence of fluorescence on the position of the absorption bands are not suitable substances for the examination of the validity of the theory; absorption bands due to groups other than the nitro-group condition the fluorescence of these substances.

H. M. D.

The Spectra of Oxygen (Doppler Effect with Canal Rays). JOHANNES STARK (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 554—577).—The canal rays in oxygen have been examined, and it is found that three of the series lines show the Doppler effect, although only under

specially favourable conditions. The spark lines show the effect the more strongly the greater their intensity. Bands are also conspicuous in the canal ray spectrum of oxygen.

The observations on canal rays in different elements lead to the conclusion that the carriers of the line spectra are the positive ions. It appears also that by the loss of one or more electrons, an atom may give rise to positive ions of different valency. C. H. D.

The Distribution of Intensity in the Spectra of the Canal Rays in Hydrogen. JOHANNES STARK and W. STEUBING (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 578—585).—The relation between the distribution of intensity of spectral lines in canal rays and the velocity of the rays has been investigated. With increasing velocity the ratio of the intensity of a line to that of a less refrangible line of the same series increases the more rapidly the smaller the ratio of the wave-lengths of the two lines. C. H. D.

The Resonance Spectra of Sodium Vapour. ROBERT W. WOOD (*Phil. Mag.*, 1908, [vi], 15, 581—601*).—Sodium vapour in an exhausted steel tube, heated to about 400°, shows an extremely complex absorption spectrum consisting of a multitude of very fine absorption lines; the very large scale photographs taken show, for example, about 6000 lines in the bluish-green. If the vapour is illuminated with white light, it becomes fluorescent and gives an emission spectrum which is the exact counterpart of the absorption spectrum. By exciting the vapour with monochromatic light, only a few lines appear in the emission spectrum. These spectra are called "resonance spectra," because they appear to be due to resonance of an electron of the system when monochromatic radiation plays upon it. The principal peculiarities of the resonance spectra are: (1) they always contain a line of the wave-length of the exciting line; (2) they contain one or more series of other lines spaced almost equally; the lines are usually 38 to 39 Ångström units apart. The bluish-green lithium line ($\lambda = 4972$) excites the same series of lines as the barium line 4934. Only light of certain wave-lengths can excite the resonance spectra, for example, the line 5209 is the only one in the spectrum of the silver arc which is active. The electron theory indicates that a non-radiating system of electrons, when disturbed by absorption of radiation of the same frequency as that of one of the electrons, should emit radiations giving a system of equally spaced lines.

Another remarkable spectrum is obtained by exciting the vapour with cathode rays; this is being studied in detail. T. E.

The Long Wave-length Portion of the Barium Spectrum. VICTOR HOELLER (*Zeitsch. wiss. Photographie Photophysik Photochem.*, 1908, 6, 217—234).—The arc spectrum of barium has been photographed between λ 5160 and λ 7090, the first order being employed and compared with the ultra-violet iron spectrum in the second order. A number of new lines are recorded. The bands between λ 5800 and λ 6600 have also been studied, Fabry's formula being found best to express the relations of the oscillation-frequencies. The weak lines in

* And *Physikal. Zeitsch.* 1908, 9, 450—461.

the bands are very numerous, and it was found necessary to compute the position of the heads of the bands.

A comparison with the spectra of the alkaline earths leads to the conclusion that the bands in the barium spectrum are due to the metal, and not to the oxide. C. H. D.

The Spectrum of Iron Observed in the Oxyhydrogen Blow-pipe Flame. GUSTAVE A. HEMSALECH and CHARLES DE WATEVILLE (*Compt. rend.*, 1908, 146, 962—965).—The method previously described for studying the spectrum of iron in a hydrogen flame (this vol., ii, 336) has been adapted to the study of spectra in the oxyhydrogen flame. Oxygen was passed through a bulb containing iron electrodes between which extremely powerful electric sparks were discharged. The issuing gas was mixed with hydrogen in the burner previously described, and produced a very white and brilliant flame.

Both the visible and the ultra-violet parts of the spectrum were examined, about 200 lines being identified and their relative brightness determined. Some of the ultra-violet lines were obscured by the bands of the water-vapour spectrum.

In the spectrum of iron at the oxyhydrogen flame temperature, there appears to be a concentration of energy between the wave-lengths 3500 and 3900. When air is substituted for oxygen, not only is the general brightness of the spectrum diminished, but the relative intensity of the lines is altered. The lines of the oxyhydrogen flame are those which appear brightest in the arc spectrum of iron, but the relative intensities are different in this case also. The brightest line from the blowpipe flame is 3860.03, whilst the brightest from the arc is 4383.70.

Practically all the lines attributed to iron in the spectrum of the star Sirius have been found in the blowpipe spectrum except the lines of "proto-iron" ("enhanced lines") described by Lockyer.

R. J. C.

Influence of Temperature and Magnetisation on Selective Absorption. HENRI E. J. G. DU BOIS and G. J. ELIAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 839—850).—In continuation of previous work (this vol., ii, 336), the absorption spectra in the visible region of certain solid compounds of chromium, uranium, praseodymium, neodymium, samarium, and erbium have been further examined, mostly at 193°. The effect of magnetisation in resolving and shifting the position of the lines at 193° has been examined, the results for the green, yellowish-green, and red regions of the spectrum of erbium nitrate being given in considerable detail. G. S.

Application of Optical Properties of Liquids to the Study of Polymerisation and Analogous Phenomena. N. N. ANDRÉEFF (*J. Russ. Phys. Chem. Soc. (Phys.)*, 1908, 40, 191—201).—Substances which, like tartaric acid, exhibit anomalous rotatory dispersion without absorption are regarded as consisting of at least two kinds of molecules having opposite rotatory powers. The author describes a

method by which the number of different kinds of molecules may be determined in this and similar cases.

If q represents any additive property, for example, the rotation of a substance containing molecules of two different kinds, then $Pq = a_1q_1 + a_2q_2$ and $P = a_1 + a_2$, where q_1 and q_2 are the respective values of this property for the two kinds of molecules and P , a_1 , and a_2 denote the total weight and the weights of the different molecules respectively. The values of q_1 and q_2 depend only on the wave-length of the light employed, whilst a_1 and a_2 vary only with external conditions, such as the temperature. Hence at three different temperatures, with which correspond the values a_1' and a_2' , a_1'' and a_2'' , and a_1''' and a_2''' , the three following pairs of equations hold:

- (1) $q' = a_1'q_1/P + a_2'q_2/P$; $a_1' + a_2' = P$;
- (2) $q'' = a_1''q_1/P + a_2''q_2/P$; $a_1'' + a_2'' = P$;
- (3) $q''' = a_1'''q_1/P + a_2'''q_2/P$; $a_1''' + a_2''' = P$.

From these, it can be readily calculated that $(q'' - q')/(q''' - q') = (a_1'' - a_1')/(a_1''' - a_1')$, so that $(q'' - q')/(q''' - q')$ is independent of the wave-length. The constancy of this expression for different wave-lengths is hence a criterion for the presence of two kinds of molecules in the substance investigated.

By applying this method to the rotations of tartaric acid, and of dimethyl, diethyl, and dipropyl tartrates for light of various wave-lengths, the author finds that each of the substances contains molecules of two different types.

On the above lines, the author has developed a general theory which leads to a number of determinants, $\delta_1, \delta_2, \delta_3, \dots, \delta_n$; and it is shown that if δ_n is the first of these which has the value zero, the substance contains molecules of n different kinds possessing other than zero values for the optical property considered.

T. H. P.

Relation Between the Rotatory Power of Optically Active Compounds and their Chemical Structure. II. D. A. CHARDIN

(*J. Russ. Phys. Chem. Soc.*, 1908, 40, 592—598. Compare Abstr., 1907, ii, 830).—In the present paper is described the investigation of the hexyl alcohol, $\text{CHMeEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, the corresponding bromide, $\text{CHMeEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$, and the hexylbenzene,



on the lines indicated in the previous communication.

From the values of the specific rotation of the hexyl alcohol, the atomic product for oxygen is calculated to be 129.28, the number obtained from a study of active amyl alcohol being 132.32 and the theoretical value 139.4.

Taking the number 211.9 for the atomic product of bromine (*loc. cit.*), the value of $[\alpha]_D^{112.5}$ for the hexyl bromide is calculated to be $+15.23^\circ$, which deviates from the actual experimental number, $+14.48^\circ$, by about 5%; if, however, the reverse calculation is made from the rotation $+14.48^\circ$, the atomic product for bromine becomes 130.4, which differs from the theoretical value, 211.9, by about 38.5%.

Consideration of the numbers obtained for the hexyl benzene indicates that the linkings of the hydrogen to the carbon atoms in

benzene do not lie in the plane of the ring, but perpendicular to that plane, as suggested by Erlenmeyer, jun. T. H. P.

Anomalous Magnetic Rotation (of the Plane) of Polarisation of the Rare Earths. G. J. ELIAS (*Physikal. Zeitsch.*, 1908, 9, 355).—In reference to Wood's investigation of the anomalous magnetic rotation of neodymium (*Phil. Mag.*, 1908, [vi], 15, 270), the author recalls a similar phenomenon already observed by him in the case of a solution of erbium chloride. H. M. D.

Triboluminescence of Mineral Substances. ADRIEN KARL (*Compt. rend.*, 1908, 146, 1104—1106).—The triboluminescence of many mineral substances is only observed when the eye has become sensitised by a prolonged sojourn in the dark. In other cases, excessive resistance to fracture, or great fragility, has prevented the detection of this property. Triboluminescence is similar to phosphorescence in that it requires the presence of large quantities of a diluent with small quantities of a triboluminogen. Pure substances are not triboluminescent. A triboluminescent system almost always retains the property when subjected to chemical change; thus a triboluminescent manganiferous zinc oxide retains the property when transformed into nitrate or sulphate; the fluoride, however, is inactive.

The study of series of mixtures indicates the existence of an optimum proportion of triboluminogen. These optima are quite different from those of cathodic phosphorescence for the same mixtures. The persistence of triboluminescence in spite of repeated fractionation is very great for some diluents, but purification leads finally to a disappearance of the property.

In the mixtures studied, the diluent was zinc sulphide or oxide, and the triboluminogens, oxides and sulphides of silver, lead, tungsten, tin, bismuth, copper, cadmium, nickel, manganese, uranium, tantalum, niobium, thorium, iron, chromium, zirconium, barium, calcium, vanadium, praseodymium, samarium, dysprosium, magnesium, and silicon. Intimate admixture was effected by simultaneous precipitation or evaporation of the mixed solutions.

The colour of the emitted light varies with the triboluminogen, and is also influenced by the diluent; thus lead gives blue and manganese orange; the system (TiO_2, ZnO) has a pale violet triboluminescence, whilst that of (TiO_2, ZnS) is dark green. The colour is different from that of the phosphorescence of the same mixtures. E. H.

Electrochemistry of Light. II. WILDER D. BANCROFT (*J. Physical Chem.*, 1908, 12, 318—376. Compare this vol., ii, 448).—In the present paper, the mode of action of sensitisers is discussed, the available data being adduced in the form of extracts from the writings of Eder, Vogel, Abney, Timiriazeff, Bothamley, and others. A distinction is drawn between optical sensitisers, which make silver bromide sensitive for certain rays of the spectrum on account of their optical absorption bands, and chemical sensitisers, which are mainly effective by reacting chemically with iodine and bromine.

As to the mode of action of dyes as sensitisers, Abney's view that the dye is oxidised by light is not in accord with the experimental facts, and Eder's suggestion that the dye acts as a catalytic agent is in many respects unsatisfactory. The only theory which accounts satisfactorily for the facts is that of Grothuss, according to which sensitisers act directly or indirectly as depolarisers. All sensitisers are sensitive to light, and are either reducing agents in the wide sense of the term or are converted into reducing agents by light. The mode of action of cyanin and the eosin dyes as sensitisers is discussed.

There is no connexion between sensitising power and fluorescence.

G. S.

Radioactivity. WILLY MARCKWALD (*Ber.*, 1908, 41, 1524—1561).—A lecture delivered to the German Chemical Society.

G. Y.

Radioactivity. ANDRÉ DEBIERNE (*Bull. Soc. chim.*, 1908, [iv], 3, i—xxxix).—A lecture delivered to the French Chemical Society.

J. C. C.

Law of Transformation in Stages and Radioactivity. GERHARD C. SCHMIDT (*Jahrb. Radioaktiv. Elektronik.*, 1908, 5, 115—119).—The successive formation of disintegration products of the various radioactive substances is supposed to be due to the operation of the general law, according to which the spontaneous transformation of any substance is determined by the least possible diminution of free energy. In consequence of this law, it is improbable that more than one α -particle is emitted in each stage of the disintegration process.

H. M. D.

Radioactivity of Water from Martos and Onteniente. FAUSTINO DIAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 290—291).—The following table shows the character of the water from the localities named:

Locality.	Spring.	Temperature.	Initial activity, volts per hour-litre.
Martos	—	20—22°	30.4
Onteniente	El Principal	—	45.8
„	El Pocito	—	74.8

W. A. D.

Radioactivity of Water from Castromonte and Puertollano. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 291—292).—The following table shows the character of the different samples of water:

Locality.	Spring.	Temperature.	Initial activity, volts per hour-litre.
Puertollano	Fuente de San Gregorio	16.25°	138.1
„	Los Baños	20°	44.7
Castromonte	—	—	73.5

W. A. D

Ionisation Phenomena Produced by Snow. G. COSTANZO and C. NEGRO (*Jahrb. Radioaktiv. Elektronik.*, 1908, 5, 120—124).—In the expectation that the emanation emitted by the earth's surface would give rise to an abnormally large ionisation of the air contained in layers of fallen snow, the authors have examined such air electroscopically. Whereas the normal fall of potential amounted to 0.2 volt in five minutes, the voltage drop when the air from 25 grams of collected snow was allowed to circulate through the apparatus amounted to 3.5 volts in the same interval. After sixteen hours, when the snow was melted, the fall of potential under the same conditions was 0.5 volt in five minutes. The ordinary air after the snow-fall was found to contain relatively few ions; this is supposed to be due to the ions previously present having acted as centres of condensation.

H. M. D.

Distribution of the Radiation of Radioactive Substances. H. GREINACHER (*Physikal. Zeitsch.*, 1908, 9, 385—392).—The darkening of photographic plates subjected to the action of metallic uranium, which is cut so as to give plane geometrical figures, shows a peculiar distribution. In general, the darkening extends beyond the uranium itself, but at each angle the plate shows a region where the effect is very greatly reduced. The contrast is greater in the case of acute angles than for angles which are obtuse. Experiments are described which show that the phenomenon cannot be attributed to total reflection or to mutual action of the β - and γ -rays resulting in deflexion. Geometrical figures cut from a hardened mixture of uranium oxide and gypsum show the effect described with the same sharpness, and when minium, which readily absorbs β -rays but radiates secondary rays in large quantities, is added to the mixture of uranium oxide and gypsum, very sharply-defined images are obtained. The phenomenon is supposed to be due to secondary rays produced by the β - and γ -rays, and it is shown that the images produced on the photographic plates are displaced under the influence of a strong magnetic field.

H. M. D.

Life of Radium. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1908, [iv], 25, 493—506).—The growth of radium in solutions of ionium has been examined by measuring the emanation contained in the solutions at different times. Five different solutions of ionium were used in the experiments. The first two were obtained from carnotite, the third from Joachimsthal uraninite, the fourth from secondary uranium minerals, chiefly gummite and uranophane, and the fifth from a specimen of very pure uraninite from North Carolina. The amounts of radium produced by the separated ionium in known periods are compared with the quantities of radium originally associated with the quantities of the various minerals operated on, and from these data the disintegration constant of radium is calculated to be 3.48×10^{-4} (year)⁻¹. The separate values obtained for the five different solutions are in good agreement, and the half-value period corresponding with this constant is about 2000 years.

H. M. D.

Distribution in Electric Fields of the Active Deposits of Radium, Thorium, and Actinium. SIDNEY RUSS (*Phil. Mag.*, 1908, [vi], 15, 601—614).—A rod charged either positively or negatively to 300 volts is exposed to a definite quantity of the emanation of radium, thorium, or actinium mixed with another gas, and the quantities of active deposit compared when the pressure of the admixed gas is varied. With radium emanation in air, the activity of the negative rod diminishes slowly with the pressure at about 100 mm., but much more rapidly at lower pressures, whilst that of the positive rod increases slightly. The ratio of the activities is about 20 at atmospheric pressure, and about 2.5 at 0.01 mm. In sulphur dioxide the difference of activity is much greater, whilst in hydrogen there is no difference at all up to 1 mm. pressure. With thorium emanation in air, the ratio of the activities of the negative and positive rods is about 200 : 1 at atmospheric pressure, and about 25 : 1 at 2 mm., the change being due to a diminution in the activity of the negative rod. With actinium, the ratio is 2 : 1 at atmospheric pressure, but at 2 mm. pressure it is 22.1, the activity of the negative wire increasing. The ratio in the case of actinium increases, however, as the distance of the electrodes from the actinium becomes smaller. The experiments confirm Rutherford's view that the molecules of the active matter are moving too fast to be directed by the electric field unless they are stopped by numerous collisions with other gas molecules. The experiments with actinium indicate that the sign of their electric charge depends on the distance they have travelled through the gas. T. E.

Determination of the Molecular Weight of Radium Emanation by the Comparison of its Rate of Diffusion with that of Mercury Vapour. P. B. PERKINS (*Amer. J. Sci.*, 1908, [iv], 25, 461—473).—An apparatus is described by means of which the rates of diffusion of mercury vapour and radium emanation have been compared at temperatures of 250° to 275°. The tendency of mercury to oxidise at this temperature made it necessary to carry out the diffusion experiments in an atmosphere of hydrogen. The porous plugs through which the gases diffused were made by boring a large number of cup-shaped holes, 1 mm. in diameter, through an iron tube which divided the apparatus into two chambers; these holes were then filled with fine asbestos fibre. The quantities of diffused emanation were measured by determining the amounts of the induced activity on a negatively charged electrode.

It is pointed out that Graham's law can only be applied with accuracy to the determination of molecular weights when the molecular complexity of the two gases compared is the same, and when the molecular weights do not differ very much from one another. These conditions are fulfilled in the comparative experiments made by the author.

From a number of experiments at 250°, the molecular weight of the emanation is found to be 235; from the experiments at 275°, the calculated value is 234. The author concludes that there can be no

doubt that the molecular weight of the emanation is not very different from that of radium.

H. M. D.

Different Kinds of γ -Rays of Radium and the Secondary γ -Rays which they Produce. R. D. KLEEMAN (*Phil. Mag.*, 1908, [vi], 15, 638—663).—When the γ -rays of radium fall on a substance, secondary γ -rays are given off. It is shown that the primary γ -rays consist of at least three groups of rays. Group *A* is most readily absorbed by lead and mercury, group *B* by zinc, copper, iron, sulphur, and aluminium, and group *C* by carbon. The secondary γ -rays radiated from these substances consist mainly of the two groups which are least absorbed by the substance. The best absorbed group of primary rays produces secondary rays, which are still more readily absorbed, and so do not escape from the substance. The explanation of the phenomena on the hypothesis that γ -rays are pulses in the ether produced by changes in the velocity of corpuscles is discussed.

T. E.

The Range of the α -Rays. WILLIAM DUANE (*Compt. rend.*, 1908, 146, 958—960).—It is well known that the ionising, phosphorescent, and photographic activities of α -rays are completely destroyed when the rays traverse a few centimetres of air or an equivalent thickness of some other substance. Rutherford found that the velocity of the α -rays near the end of their course is reduced to 60% of its initial value. The quantity of positive electricity carried by the α -rays of radium is now shown to be similarly affected by the interposition of air.

The apparatus employed consisted of an electrode contained in a cylindrical brass box which could be evacuated. The α -rays were allowed to enter the end of the box through a window made of extremely thin mica supported on copper gauze. The gauze was insulated from the box and electrode, and connected to a battery, so that the ionising effect of the rays could be measured by the conductivity of the air between the window and the electrode.

For ionisation measurements, a minute quantity of radium chloride was purified from emanation and from induced activity by dissolving in water twice, and was finally dried on a piece of platinum foil. The foil bearing the radium was placed at a known distance from the mica window of the box, and the current carried between the charged gauze and the electrode by the ionised air was measured by a quadrant electrometer. Practically the whole ionisation of the air within the box ceased when the radium was removed 2 cm. from the window. The small ionisation which persists even at longer ranges was attributed to traces of induced activity and emanation remaining in the radium chloride. When the chloride was left for two days so that emanation and induced activity accumulated, it produced considerable ionisation in the box even when 4 cm. from the mica window.

A much larger quantity (almost 0.002 gram) of radium chloride, purified by solution in water as before, was employed to measure the quantity of electricity transported to the electrode by the α -particles.

The box containing the electrode was now evacuated, so that no ionisation current could pass between the window and the electrode, and the charge carried by the α -rays themselves to the electrode was measured with a Wilson electroscope. Secondary radiation towards the electrode was suppressed by placing the apparatus in a strong magnetic field parallel to the electrode. It was found that if the radium was more than 2 centimetres from the mica window, no charge was carried through to the electrode. If the radium was not free from emanation and induced activity, however, the charge could be detected at much greater distances, but could not be attributed to the α -particles.

The charge of the α -particles and their ionising effect are stopped by practically the same thickness of air, namely, 2 centimetres.

R. J. C.

Secondary Rays from the α -Rays. WILLIAM DUANE (*Compt. rend.*, 1908, 146, 1088—1090).—It has been shown previously (preceding abstract) that the charge carried by the α -rays of radium stops at the place where the ionising, photographic, and phosphorescent effects disappear. The experiments now described indicate that the α -rays lose their power of producing secondary rays at the same point. The brass box, containing an electrode and fitted with a mica window, described in the first paper, was again employed. When the radium salt is sufficiently near to the mica window, the α -rays pass through the latter and strike the electrode, producing secondary rays on the surfaces both of the mica and of the electrode. The charge of these secondary rays can be readily measured by evacuating the box and determining the potential of the electrode by means of a Wilson electroscope. If a is the positive charge carried to the electrode per second by the α -rays, s_1 the negative charge removed from the electrode per second by the secondary rays leaving its surface, and s_2 the negative charge carried to the electrode by the secondary rays from the mica window, then the total current i towards the electrode is $i = a + s_1 - s_2$. A large enough magnetic field parallel to the surface of the electrode suppresses s_1 and s_2 , whilst an electric field produced between the mica window and the electrode stops either s_1 or s_2 according to its sense. Thus, in order to determine the current s_1 due to the secondary rays leaving the electrode, it is sufficient to measure, firstly, the current $(a + s_1)$, s_2 being eliminated by an electric field, and, secondly, the current a , s_1 and s_2 being suppressed by a magnetic field.

When the radium is placed 1.4 cm. below the mica window, and the latter is charged at different potentials, the current obtained does not increase after the potential has risen to 85 volts, showing that this is sufficient to stop all the secondary rays s_2 ; moreover, the high potential required for this purpose indicates that the currents are not due to ionisation of the gas remaining in the apparatus.

Radium almost free from emanation and induced activity (as in the former experiments) was placed at different distances below the window, and the currents measured (1) with the window at a potential of +85 volts, and (2) with a magnetic field of 2800 gauss. The difference

of these two currents, representing the charge of the secondary rays, is plotted as a function of the distance of the radium, and the curve obtained shows that the production of secondary rays ceases almost completely when the radium is more than 2 cm. below the mica, that is, the distance at which the other effects of the α -rays disappear.

Similar experiments with polonium gave inconclusive results, owing to the minuteness of the currents produced. E. H.

Method of Counting the Number of α -Particles from Radioactive Matter. ERNEST RUTHERFORD and H. GEIGER (*Mem. Manchester Phil. Soc.*, 1908, 52, No. 9, 1—3).—It should be only just possible with very sensitive apparatus to detect the ionisation of a gas produced by a single α -particle, but by making use of the property of ions moving in a strong electric field in a gas at low pressure of producing a number of fresh ions by collision with the gas molecules, the authors have succeeded in automatically increasing the electrical effect several thousand times and rendering it easily observable. The testing vessel was a long brass tube, along the axis of which a thin insulated wire passed which was connected to the electrometer, the gas pressure being about 2 cm. A potential difference of about 1000 volts between the brass tube and the wire was required. From a film of active matter contained in an exhausted tube, which is a prolongation of the testing vessel, the α -particles were fired through a small hole covered by a mica plate at the rate of from six to ten per minute. The effect of the α -particle entering the testing vessel was shown by a sudden throw of the electrometer needle, and by observing the number of throws it was found that the number of α -particles counted by this method is of the same order as the calculated number. By counting at intervals the number of α -particles expelled per minute, the curves of decay of activity of a plate coated with radium-*C* or actinium-*B* have been obtained. The time interval between the entrance of successive α -particles has been observed over a long interval, and the results show that the distribution curve with time is similar in general shape to the probability curve of distribution of the velocity of molecules in a gas. Further observations are in progress.

J. V. E.

Changes in Velocity in an Electric Field of the α , β , and Secondary Rays from Radioactive Substances. A. S. EVE (*Phil. Mag.*, 1908, [iv], 15, 720—737. Compare Abstr., 1905, ii, 4; H. W. Schmidt, Abstr., 1907, ii, 520).—The author withdraws his previous statement that the secondary rays from substances acted on by the β - and γ -rays of radium are homogeneous. Corrected values for the coefficients of absorption by aluminium of the secondary rays emitted by different substances are given. The experimental data for lead, iron, brick, and carbon indicate that the rays from the lighter substances are more easily absorbed, especially at first. The lighter the substance the less is the secondary radiation, and the smaller the group velocity of the secondary rays the more quickly are these absorbed by the screens. The secondary rays from lead are very similar to the primary radium rays which produce them.

Certain substances, such as brick, slate, wood, paper, and carbon, give rise to very penetrating secondary rays, which originate from layers of the radiator several centimetres deep; these appear to be secondary γ -rays or high velocity negative rays.

It is shown that the velocity of the α , β , and secondary rays can be increased or diminished in a strong electric field the lines of force of which are parallel to the direction of motion of the rays. In the case of the α -particles, there also appears to be a small change in the range of the particles. Experiments on the influence of the electric field on the secondary radiations emitted by different radiators show that these are influenced to varying extents. The changes produced in the group velocity of the secondary rays on reversal of a given field increase as the coefficient of absorption by aluminium increases, and, in consequence, as the density of the radiator diminishes.

These results indicate that the secondary rays are in the main intrinsic, and are emitted with distinctive group velocities depending on the density of the radiator. They are not due to dispersed primary rays, although it is not improbable that a certain fraction of the secondary radiation may consist of such primary rays. H. M. D.

Experimental Investigation of the Nature of γ -Rays. WILLIAM H. BRAGG and J. P. V. MADSEN (*Phil. Mag.*, 1908, [iv], 15, 663—675).—An ionisation chamber is closed above by super-imposed plates of different metals (for example, lead and aluminium), the bottom being made of a similar pair of plates. A pencil of γ -rays traverses all four plates, entering at the top. Reversing the top pair of plates makes very little difference in the ionisation in the chamber; reversing the bottom pair, increases it in a very marked way when the lead plate is uppermost. The ionisation is mainly due to secondary radiations from the metal surfaces within the chamber. On the ether pulse theory, the radiation set up by a pulse entering a substance should be the same as that produced on leaving it. The experiment shows that this is not so. The authors propose the hypothesis that γ -rays are material, and consist of neutral pairs formed from β -rays by taking up a positive charge. The secondary radiation, which is known to contain β -rays, would be produced by the γ -ray losing its positive charge again. The same hypothesis applies to X -rays. T. E.

Electrical Charge of the Active Deposit of Actinium. SIDNEY RUSS (*Phil. Mag.*, 1908, [iv], 15, 737—745).—It has been found that the relative activities of positively and negatively charged plates which are symmetrically exposed to the action of actinium emanation depend on the distance between the actinium and the charged plates, and also on the pressure.

At 760 mm. pressure, the ratio of the activity of the negative to that of the positive plate diminishes as the distance of the plates from the actinium increases; at 2 mm. pressure, the opposite relationship holds good. At the higher pressure, the active matter deposited on the negative plate decreases regularly with increasing distance from the actinium, whereas that deposited on the positive plate

increases at first and then decreases. At the lower pressure, the active matter on the negative plate increases with the removal of the plate from the actinium, whilst that on the positive plate shows a steady decrease.

Experiments with an apparatus which permitted of measurements at longer distances were made at a pressure of 12 mm. It was found in these circumstances that the ratio of the negative to the positive activity first increases and then diminishes.

The author concludes that the electrical charge exhibited by the active deposit particles is mainly determined by the collisions between these particles and the ions or molecules of the gas with which they are in contact.

H. M. D.

Number of Quasi-elastic Bound Electrons in the Helium Atom. H. ERFLE (*Ber. deut. physikal. Ges.*, 1908, 6, 331—338).—From Herrmann's measurements of the dispersion of helium, the author calculates a lower limiting value (p) for the number of quasi-elastic bound electrons in the helium atom. It is shown that there is probably only one type of electron with a vibration frequency corresponding with the ultra-violet region. The corresponding wavelength is $113 \mu\mu$, and the calculated limiting value of the number of the electrons under consideration represents in this case the actual number. Since p is equal to 0.25, it follows that the number of helium atoms in a given volume of the gas is four times as large as the number of quasi-elastic bound electrons in the same volume.

H. M. D.

Meso-thorium. OTTO HAHN (*Physikal. Zeitsch.*, 1908, 9, 392—402).—An account of work, most of which has been already published (compare Abstr., 1907, ii, 359, 664). The changes observed in the activity of commercially-purified thorium preparations, from which meso-thorium is separated by the processes of purification, depend on whether the changes are followed by measurements of the quantity of emanation emitted, or whether the α -rays are examined. The difference is traced to the fact that thorium itself emits α -rays. When the constant α -radiation of thorium is taken into account, the activities of thorium preparations of different ages, measured by both methods, are in good agreement with the activities calculated on the basis of the constants of meso-thorium and radio-thorium.

The α -ray activity of meso-thorium, free from radio-thorium, has been observed during a period of one and a-half years. The observed increase in the activity agrees with that required by the known constants of meso- and radio-thorium. All the later experiments confirm the previous statement that meso-thorium emits β -rays but not α -particles.

H. M. D.

Electrical Conductivity of Alloys and their Temperature Coefficients. W. GUERTLER (*Physikal. Zeitsch.*, 1908, 9, 404—405).—Polemical against Rudolphi (*Physikal. Zeitsch.*, 1908, 9, 198).

H. M. D.

Aluminium in the Potential Series. CHARLES M. VAN DEVENTER and H. VAN LUMMEL (*Chem. Weekblad*, 1908, 5, 359—363; JOHANNES J. VAN LAAR, *ibid.*, 383, 390).—Polemical (compare van Deventer and van Lummel, this vol., ii, 12; van Laar, this vol., ii, 248).

A. J. W.

Galvanic Self-induction of Metals. CHARLES M. VAN DEVENTER and H. VAN LUMMEL (*Chem. Weekblad*, 1908, 5, 349—356. Compare van Deventer and van Lummel, this vol., ii, 12).—The authors describe experiments with zinc, cadmium, tin, lead, nickel, copper, silver, and platinum in support of their theory of the "leaking insulator."

A. J. W.

Dielectric Constants of Gases at High Pressures. KARL TANGL (*Ann. Physik*, 1908, [iv], 26, 59—78).—The dielectric constants of hydrogen, nitrogen, and air have been measured at pressures varying from 20 to 100 atmospheres. The values for 20, 40, 60, 80, and 100 atmospheres are for hydrogen at 20°: 1.00500, 1.00986, 1.01460, 1.01926, and 1.02378; for nitrogen at 20°, 1.01086, 1.02185, 1.03299, 1.04406, 1.05498, and for air at 19°, 1.01080, 1.02171, 1.03281, 1.04386, and 1.05494 respectively.

The Clausius-Mossotti formula holds good up to 100 atmospheres; the extrapolated value of the dielectric constant for 1 atmosphere and 0° is equal to the square of the refractive index for infinitely long wave-lengths in the case of all three gases examined.

The dielectric constant of mixtures of hydrogen and nitrogen (D_m) is given by the equation $D_m - 1 = (D_H - 1) + (D_N - 1)$, where D_H and D_N are the dielectric constants for the two gases at the pressures in which they are contained in the mixture.

H. M. D.

Reactions in the Iron-Nickel Peroxide Accumulator. II. Behaviour of the Electrolyte. FRITZ FOERSTER (*Zeitsch. Elektrochem.*, 1908, 14, 285—298. Compare this vol., ii, 146).—The potassium hydroxide solution, which forms the electrolyte in the iron-nickel peroxide accumulator, becomes more concentrated during discharge and vice versa. The change of concentration is almost complete as soon as the charge or discharge is ended; in both cases, the large change is followed by a small gradual increase of concentration, due to decomposition of water by the finely-divided iron of the cathode. The change is therefore due to combination of water with the nickel peroxide electrode during discharge; the quantity taken up is between 1 and 2 molecules for each faraday given out by the cell. The *E.M.F.* of the cell decreases as the concentration of the electrolyte increases; the change is very small (2.8 millivolts when the concentration increases from 2.8*N* to 5.3*N*, for example). A calculation of the change to be expected, based on the vapour pressures of the solutions, gives values of the same order of magnitude as those observed.

T. E.

Explanation of Supertension. II. FELIX KAUFLEDER (*Zeitsch. Elektrochem.*, 1908, 14, 321—326. Compare Abstr., 1907, ii, 924).—The resistance of an electrolytic cell with lead electrodes and sulphuric

acid of maximum conductivity as electrolyte is measured during the passage of a current. In these circumstances, there is a "supertension" at the cathode, that is, the apparent fall of potential between cathode and electrolyte is greater than that corresponding with the reversible decomposition of water into oxygen and hydrogen at atmospheric pressure. The addition of a trace of copper sulphate removes this supertension. It is found that the resistance of the cell with copper sulphate is the same as that calculated from the resistance of the sulphuric acid and the dimensions of the cell, but when "supertension" exists it is greater. There is therefore a high resistance film at the surface of the cathode; possibly this is a hydride of lead, the rate of decomposition of which is much accelerated by traces of platinum or copper.

Further experiments are made in the same way as before with a platinised platinum cathode (or anode), which is heated to a higher temperature than the electrolyte by means of a current of electricity. Here there is practically no supertension, and yet reactions (reduction of benzophenone; oxidation of *p*-nitrotoluene) take place at it which usually are observed only at electrodes showing supertension. The author believes that supertension is not the cause, but a symptom, of a reaction. When a finite current is flowing, the electrolytic changes are always irreversible, and the electrode potential, therefore, higher than that corresponding with the main reaction. Traces of substances of higher potential may therefore be formed, and these condition the potential of the electrode.

T. E.

Transport Number for Dilute Hydrochloric Acid. KARL DRUCKER and B. KRŠNJAVI (*Zeitsch. physikal. Chem.*, 1908, 62, 731—742. Compare Jahn, Abstr., 1901, ii, 540; Noyes and Sammet, Abstr., 1903, ii, 126; Noyes and Kato, this vol., ii, 346).—The authors have made a very careful determination of the transport number for chlorine in a solution of hydrochloric acid, special attention being directed to the purity of the materials used and to the accuracy of the analyses. The apparatus employed was essentially that due to Loeb and Nernst, the bulk of solution being large enough to permit the analysis of five sections of the conducting column in addition to the solutions round the electrodes. These were both made of palladium, the anode being charged with hydrogen.

For the transport number of chlorine at 18°, the authors deduce the value 0.1697 from analysis of the anode solution, and 0.1647 from analysis of the cathode solution. The cause of the divergence of these numbers cannot be traced.

Discussion of their own and others' results leads the authors to the conclusion that the transport number for chlorine in highly diluted hydrochloric acid is at least 0.170 at 18°, and that the ionic conductivity of hydrogen at the same temperature is not more than 313.

J. C. P.

Electrochemical Equivalents of Oxygen and Hydrogen. ROBERT A. LEHFELDT (*Phil. Mag.*, 1908, [vi], 15, 614—627).—A form of electrolytic gas voltameter is described wherein the gas is measured

by displacement of mercury, which is weighed. The errors of the measurements of electricity, time, volume of gas, pressure, and temperature are fully discussed; the results are probably correct to less than 1 part in 1000. Solutions of sulphuric acid, sodium hydroxide, sodium sulphate, sodium thiosulphate, disodium hydrogen phosphate, sodium chromate, potassium iodide, potassium dichromate, sodium oxalate, sodium arsenate, sodium nitrate, and sodium chlorate were tried. Of these, sodium sulphate and potassium dichromate give correct results, but the other substances give too little gas; even with sodium hydroxide the quantity of gas obtained varied from 98.5% to 99.8% of the theoretical quantity. The mean of sixteen experiments with sodium sulphate and potassium dichromate was 0.17394 c.c. of gas (under normal conditions) per coulomb, from which it follows that the quantity of electricity required to decompose an equivalent of water (1 faraday) is 96590 coulombs.

T. E.

Amphoteric Electrolytes. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1908, 62, 726—730. Compare Bredig, *Zeitsch. Elektrochem.*, 1899, 6, 34; 1904, 10, 245; Walker, Abstr., 1904, ii, 309; 1905, ii, 138; 1906, ii, 735; Lundén, Abstr., 1906, ii, 265, 828; Johnston, Abstr., 1906, ii, 733; Cumming, Abstr., 1906, ii, 734).—The hydrogen ion concentration in solutions of various amphoteric electrolytes (*o*-, *m*-, and *p*-aminobenzoic acids, *d*-aspartic acid, and *d*-glutamic acid) has been determined by the ethyl diazoacetate catalysis (see Bredig and Fraenkel, Abstr., 1905, ii, 692; Fraenkel, Abstr., 1907, ii, 746). The values so found are in good agreement with the calculated values.

J. C. P.

Electrolytic Valve Action of Zinc, Cadmium, Silver, and Copper. GÜNTHER SCHULZE (*Ann. Physik.*, 1908, [iv], 26, 372—392. Compare Abstr., 1907, ii, 842; this vol., ii, 350).—Zinc and cadmium exhibit electrolytic valve action in a solution of potassium carbonate. The normal effect is not obtained in the case of zinc for solutions containing less than 10% of carbonate; at this concentration the maximum voltage is 83V. Cadmium shows the normal valve action in a 1% solution, the maximum voltage for this concentration being 126V. For both metals the maximum voltage decreases rapidly with increasing concentration of the electrolyte. For a given concentration the maximum voltage is much higher for zinc than for cadmium, and this voltage is reached at a much smaller current density in the case of zinc. The diminution of the maximum voltage with rise of temperature is much less rapid for zinc than for cadmium.

Electrolytic valve action is also exhibited by silver in solutions of hydrochloric, hydrobromic, and hydriodic acids, and by copper in a solution of hydrofluoric acid. In these cases the phenomenon appears to be due directly to the formation of a layer of solid on the surface of the anode.

Summarising the results obtained with different metals, the author points out that the faculty of a metal to give rise to electrolytic valve action depends on the particular group of the periodic system to which the metal in question belongs.

H. M. D.

Influence of the Silent Discharge on Explosive Gaseous Mixtures. HEINRICH FASSBENDER (*Zeitsch. physikal. Chem.*, 1908, 62, 743—759).—When a mixture of carbon monoxide and oxygen is exposed to the silent discharge, the rate of explosion is increased. This result, however, is shown to be due to the presence of ozone produced by the discharge. In this connexion, it is noteworthy that when a mixture of carbon monoxide and oxygen is exploded, a piece of potassium iodide-starch paper exposed to the gases is turned blue by the ozone formed in the explosion.

The velocity of explosion of a dry mixture of hydrogen and chlorine is not increased by previous exposure of the mixture in an alternating field. The author's experiments show, however, that during such an exposure the slow combination of hydrogen and chlorine is accelerated. A similar slow combination of carbon monoxide and oxygen is promoted by the influence of an alternating field, but in this case the field must be much more powerful in order to produce the result.

From these experiments it appears that in an explosive gaseous mixture, ionisation and dissociation result from the action of an alternating field, but that this state of dissociation does not persist, the dissociation products combining forthwith to form new neutral molecules. Such a formation of dissociation products and their subsequent combination under the influence of the silent discharge is sometimes so vigorous as to lead to the ignition of the gaseous mixture. This phenomenon was observed especially with mixtures of carbon monoxide and oxygen, a case in which the heat of combination is very great.

J. C. P.

Is the Fixation of Atmospheric Nitrogen in the Electric Discharge to be Regarded as a Purely Thermal Effect? G. BRION (*Zeitsch. Elektrochem.*, 1908, 14, 245—251).—The electric discharge through a gas is carried by a comparatively small number of ions, which have a very much larger kinetic energy than the majority of the molecules. The distribution of energy in the gas is therefore quite different from that in a gas of the same average temperature through which no discharge is passing. The application of the ordinary laws of chemical equilibrium does not, therefore, appear to be justified. The yields of nitric oxide actually obtained in practice are explicable on the assumption of an "electrical" temperature of about 4000° for the molecules which carry the current, but, on the other hand, the small yields obtained with small currents in the glow discharge are not in harmony with this view.

T. E.

Difference of Potential and the Stability of the Alternating Arc between Metals. CHARLES E. GUYE and A. BRON (*Compt. rend.*, 1908, 146, 1090—1093).—The authors find that the difference of potential measured depends within wide limits on the degree of stability of the arc, so that any cause (gas pressure, cooling, air currents, diminution in the self-induction, or the resistance of the circuit, &c.) which tends to diminish this stability, that is, to prolong the duration of the extinction, immediately results in an increase of

the efficacious difference of potential at the electrodes. Similar lack of stability, by producing momentary extinctions, will vitiate experiments with the continuous current arc. By the disposal of a very large reserve tension in the open circuit (20,000 volts) and heating the electrodes almost to their melting point, arcs are obtained of extreme stability. Under these conditions, the extinction period becomes negligible, and the experimental results can be easily interpreted conformably with the views on the mechanism of the arc. The authors show that, other conditions being equal, the potential difference tends towards an inferior limit which is approximately the same for all metals, provided they are only slightly volatile. As the result of experiments in air at 40 cm. pressure for a distance between the electrodes of 4 mm. and an alternating intensity of 0.1 ampere (frequency 50), the limit for platinum, gold, palladium, silver, copper, nickel, iron, and aluminium is found to be approximately 475 volts. For volatile metals the limit is lower.

In the case of long arcs of small intensity between non-volatile metals, the medium between the electrodes (the latter must be incandescent in order to emit the electrons required to maintain the arc), which is ionised by the electrons and which is principally concerned in the difference of potential, is almost wholly air in every case. This accounts for the fact that the potential difference is independent of the nature of the metal. When the ionised medium contains metallic vapours, as in the case of short intense arcs, or with volatile electrode metals, this independence, of course, no longer is observed.

The minimum potential difference obtained as the gas pressure diminishes, already observed with short intense arcs, is also found with the arcs here experimented with. The gas pressure corresponding with this minimum is 5—7 cm.

Thus it seems that below a certain pressure the number of gaseous molecules interposed between the electrodes is insufficient for the normal ionisation, an increase in the potential difference then becoming necessary in order to maintain the same current.

Under the conditions of extreme stability, the law of the decrease of the potential with the pressure is a linear one. E. H.

Theory of Dulong and Petit's Law. I. FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1908, 58, 356—374).—A theoretical paper, which contains a summary of the author's work on this subject published at intervals during the last fifteen years (compare Abstr., 1893, ii, 404). A simple proof is given of the well-known result that the atomic heat of a gas at constant volume is 3. Further, on certain assumptions, based mainly on atomic considerations, it is shown that the atomic heat of solid elements at constant volume is constant and equal to 6.012. The atomic heat at constant pressure is greater, owing to the work done in overcoming the attraction of the atoms, and varies from 6.072 to 6.914 for different elements. The theory also accounts satisfactorily for the fact that some elements have exceptionally low atomic heats (compare Behn, Abstr., 1900, ii, 259).

G. S.

Thermal Expansion and Specific Heat of Metals. E. GRÜNEISEN (*Ann. Physik.*, 1908, [iv], 26, 211—216).—From a comparison of the true coefficients of expansion and the true specific heats of aluminium, iron, nickel, copper, palladium, silver, iridium, and platinum within wide limits of temperature, it is shown that the quotient of the coefficient of expansion by the specific heat is almost independent of the temperature. Except in the case of iridium and platinum, for which the values of the quotient are very nearly constant, the ratio of the two numbers appears to increase slightly with the temperature. For those intervals of temperature in which molecular changes take place, the relationship does not hold. The author supposes that the variations of the expansion and the specific heat with temperature are due to the operation of the same cause, and reference is made to the hypothesis of Richarz relating to the influence of temperature on specific heat.

H. M. D.

Relationship between Compressibilities, Thermal Expansions, Atomic Volumes, and Atomic Heats of the Metals. E. GRÜNEISEN (*Ann. Physik.*, 1908, [iv], 26, 393—402).—The fact that the compressibility of the elements exhibits periodicity has led the author to inquire into the relationship between this and other physical properties for which a similar periodicity has been established. Denoting the compressibility by K , the thermal expansion by 3α , the volume of a gram atom by v , and the atomic heat at constant pressure by C_p , and applying the kinetic theory to the metals which are supposed to be monatomic in the solid state, it is shown that $3\alpha v/K$ and $3\alpha v/KC_p$ should be constant. For twenty metals, the values of these expressions are shown to be in fairly close agreement; antimony and bismuth show the largest deviations from the mean value. The assumption that the solid metals and liquid mercury are monatomic is in consequence considered to be justified. The relationships involved may be used for the deduction of the compressibilities of metals which have not been subjected to direct measurement. For silicon and liquid chlorine, the expression $3\alpha v/K$ is found to have the same value as it has for metals.

H. M. D.

Change of Density and Specific Heat of Platinum and Nickel after Treatment, and the Dependence of the Specific Heat on the Temperature. WILHELM SCHLETT (*Ann. Physik.*, 1908, [iv], 26, 201—210).—The changes which take place in the density and specific heat of platinum and nickel after various kinds of mechanical treatment, such as hammering, rolling, and cold-drawing, and also after heating to a high temperature, have been examined. In both cases the more dense form of the metal has the smaller specific heat, a relationship already pointed out for the allotropic modifications of the non-metals. From a comparison of the variations of the specific heat with the temperature and with the density, the conclusion is drawn that a rise of temperature causes molecular changes to take place which are very different from those brought about by mechanical treatment.

The true specific heat of nickel between 0° and 300° is given by

$C_t = 0.10280 + 0.0000941t$, and that of platinum by $C_t = 0.030456 + 0.00002972t + 0.0000000561t^2$.
H. M. D.

Practice of Cryometric Measurements. PODA (*Zeitsch. angew. Chem.*, 1908, 21, 1066—1069).—A freezing-point apparatus is described by means of which accurate determinations can be carried out rapidly. The vessel in which the liquid is contained consists of a double-walled tube expanded to form a bulb in the lower half; by means of a tube sealed on to the bulb, the space between the two walls communicates with a levelling tube through a piece of thick-walled rubber tubing. By raising or lowering the levelling tube, the space between the walls of the freezing vessel can be filled with mercury or exhausted; by this means ice which has separated out from an aqueous solution can be quickly melted, or during a measurement the loss of heat by radiation can be reduced to a small value. A simple form of stirrer is also described, and numbers are recorded for the freezing points of sucrose and potassium chloride solutions.

H. M. D.

Stand for Apparatus for Cryoscopic Measurements. ROBERT LESPIEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 613—617).—A stand is described provided with (1) a small platform on which the refrigerator vessel and its contents can be placed, (2) a driving-wheel by which the thermometer suitably provided with a pulley can be caused to rotate in the solution under examination, and (3) a support in which the thermometer rotates. The stand is figured in the original.

T. A. H.

Calculation of Thermochemical Constants. H. STANLEY REDGROVE (*Chem. News*, 1908, 97, 253—255, 266—268. Compare Abstr., 1907, ii, 604; this vol., ii, 463).—The molecular heats of combustion and molecular heats of formation of eight ethers, nine primary, one secondary, and two tertiary alcohols, three aldehydes, two ketones, nine esters, three organic acids, and one organic anhydride have been calculated by means of the author's system of "fundamental constants." For thirty-four substances out of the thirty-eight up to the present considered, the results are in excellent agreement with those values actually found by Thompsen. A table of the "Fundamental Molecular Heat of Combustion and Formation, Oxygen Constants" is also given.

J. V. E.

New Method for Determining Vapour Densities. III. PHILIP BLACKMAN (*Ber.*, 1908, 41, 1588—1591; 2487—2488. Compare Abstr., 1907, ii, 931; this vol., ii, 157).—A small error in the author's method of determining vapour densities, caused by air bubbles trapped in the mercury column, is overcome by heating the mercury and re-reading the gas volume after the temperature has again reached that of the laboratory. Details are quoted of vapour density determinations with a number of substances to illustrate the accuracy of the method.

G. Y.

Application of a Deduction from the Boyle-Mariotte Law. H. REBENSTORFF (*Chem. Zeit.*, 1908, 32, 570).—From the equation for isothermal alteration of a closed volume of a gas, the expression $\Delta v/v' = \Delta p/p$, as also $\Delta v/v = \Delta p/p'$, has been arrived at; this is called the "*alteration law*," and states that the alteration of volume is to the one volume as the alteration of pressure is to the other pressure. Use is made of this relationship for finding the volume of large air vessels in a rapid and convenient manner. The vessel the capacity of which is to be measured is connected by a rubber tube carrying a pinch clip to a graduated glass tube filled with water, and covered at its lower end with a piece of fine muslin. On opening the pinch clip, water flows out of the tube, giving a measure on the scale of the alteration of volume Δv of the unknown volume v , and at the same time a measure of the decrease of pressure Δp from the original atmospheric pressure p' . From this, the unknown volume of the vessel may be calculated from the equation above. By lowering a weighted bottle, the mouth of which is covered by muslin, into water and measuring the water that has been forced into the bottle by the increased pressure, an approximate estimation of the depth of the water may be obtained.

J. V. E.

Molecular Aggregations Produced in Gases by Sudden Cooling. GWILYM OWEN and A. LL. HUGHES (*Phil. Mag.*, 1908, [vi], 15, 746—761. Compare Abstr., 1907, ii, 843).—The previous experiments on the production of condensation nuclei by cooling gases to low temperatures have been extended. It is now found that the effect depends to a large extent on the rapidity of the cooling process. By cooling rapidly, condensation nuclei are formed in air at temperatures considerably higher than the maximum temperature in the case of slow cooling. At a given temperature below this maximum, the number of nuclei produced is much greater when the air is cooled very quickly than when slow cooling takes place. The so-called "nucleating temperature" also varies with the size of the apparatus into which the gas to be cooled is admitted, but this phenomenon is supposed to be simply due to a difference in the rate of cooling which is attainable when cooling vessels of different sizes are employed.

Carbon dioxide can be cooled to its condensation temperature without nuclei being produced; when the condensed solid sublimes, large nuclei are, however, formed. Ethylene does not show a "nucleating temperature," but with methane results are obtained similar to those met with in the case of air. The phenomena in mixtures of these gases can be accounted for when the partial pressures of the components are taken into consideration.

Experiments made to determine the influence of temperature on the persistency of the nuclei show that rise of temperature increases the rate of disappearance. The nuclei are not electrically charged.

H. M. D.

Osmotic Pressure. ISIDOR TRAUBE (*Pflüger's Archiv*, 1908, 123, 419—432).—The direction of osmosis is determined by the difference of surface tension towards air of the liquids separated by the membrane. This difference is termed the "surface pressure," and is regarded,

instead of the osmotic pressure, as the directing force governing osmosis. The membrane also plays some part in the process, for, according to Willard Gibbs, substances which lower the surface tension of a solvent have a tendency to collect on the surface. The dissolved substance also has an influence on the solvent, exerting what is termed a cohesion pressure; the more a substance lowers the surface tension of a solvent the smaller is this cohesion pressure.

The smaller the cohesion pressure exerted by a substance the more readily will it tend to be eliminated from the solution, and the more readily will it be dissolved or adsorbed by a second liquid or solid phase in contact with the solution.

A simple relationship can be deduced between the lowering of surface tension, adsorption, and the coefficient distribution of a substance between two solvents.

In the above theory, the cohesion pressure of a substance in the separating membrane will also exert influence on the rate and direction of diosmosis.

This theory, too, which takes into account the cohesion pressure, is capable of explaining facts which are not explicable by Overton's theory of the distribution of substances between lipoids and non-lipoids, as, for example, the absorption of peptones which are not readily soluble in lipoids.

It has been applied to explain this, and other absorption phenomena in the digestive tract, and also the action of the kidneys, where it can be shown that there is an intimate relationship between the functional capacity and the surface tension of the urine. The theory has also been applied to explain the action of lymphagogues and certain phenomena of parthogenesis, also hæmolysis, narcosis of the ganglia, plasmolysis, &c.

S. B. S.

Relation between the Diffusion Constant, Internal Friction, and Electrical Conductivity. LEO PISSARJEWSKY and E. KARP (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 599—611*).—After discussing the work of Jones and Lindsay (Abstr., 1903, ii, 55), Jones and Carroll (Abstr., 1905, ii, 73), Pissarjewsky and Lemcke (Abstr., 1905, ii, 684), and Walden (Abstr., 1906, ii, 335), the authors give the results of their own determinations of the diffusion constant, internal friction, and electrical conductivity of solutions of sucrose, sodium chloride, sodium hydroxide, ammonia, and acetic acid in water or aqueous alcohol.

When the diffusing substance is a non-electrolyte, such as sucrose, the product of the diffusion constant and the internal friction, $D\eta$, is a constant, and for acetic acid this product also remains comparatively constant.

In the case of electrolytes, the values of $D\eta$ vary as much as 30%. If this variation depends on differences in the degree of dissociation, the value of $D\eta/a$ should exhibit greater constancy than $D\eta$. It is first shown that $D\eta/a = D\mu_v/\mu'_v$, where μ_v and μ'_v are the molecular conductivities of the substance in water and the given solvent respectively, and then found by conductivity measurements of aqueous

* and *Zeitsch. physikal. Chem.*, 1908, 63, 257—268.

and aqueous alcoholic N -sodium chloride and of $4/7N$ solutions of sodium chloride in water and sucrose solutions that $D\mu_v/\mu'_v$ is constant.

It also seems probable that for all electrolytes in all solvents, $D\eta\sqrt{M}/\alpha$ is constant. When D and η are given, this relation renders it possible to calculate α , and then, having determined μ_v and η_v , to calculate μ_∞ for the given electrolyte in the given solvent according to the formula $\alpha = \mu_v \cdot \eta_v / \mu_\infty \cdot \eta_\infty$.

When the dilution is such that α has the value unity, the above relations become $D\eta = \text{constant}$ and $D\eta\sqrt{M} = \text{constant}$, and as, also, $\mu_\infty \eta$ is constant, we have $D/D' = \mu_\infty / \mu'_\infty$, that is, the ratio of the diffusion constant of any given electrolyte to its molecular conductivity at infinite dilution is constant for different solvents. T. H. P.

Time Taken by Substances in Dissolving. GASTON GAILLARD (*Compt. rend.*, 1908, 146, 1020—1022. Compare Abstr., 1905, ii, 241).—In the experiments described, given weights of various substances (sodium thiosulphate, sodium sulphate, sucrose) were introduced into fixed quantities of solvent at a known temperature and agitated by a turbine-driven stirrer regulated to a constant known velocity, and the time elapsing between the addition and the total disappearance of the substance observed. Only the results of experiments in which portions of the same sample of substance and the same rate of stirring were employed can be compared, since the size of the crystals and the rapidity of diffusion have considerable influence on the time of dissolution. The following results are obtained: (1) With increasing quantities of the same substance, the ratio of the time to the concentration obtained is (within the limits of the experiments) at first practically constant, and then increases. (2) In certain cases the curve, obtained by plotting reciprocals of the times against the corresponding temperatures, is comparable with the solubility curve. But salts of equal solubility may take widely different times to dissolve, and the variation of the time with the temperature does not always follow that of the solubility. (3) For some mixtures of salts (potassium chromate and sulphate, ammonium and potassium nitrates, sodium chloride and potassium nitrate) the variation in the time is in the same sense as the modification in the solubility, but these variations are small. (4) A table is given showing the increase in the times required for the dissolution of successive equal quantities of sodium chloride or sucrose in the same quantity of solvent, each addition being made immediately after the disappearance of the preceding quantity of substance. E. H.

Influence of Temperature on Complex Formation in Solution. ALFRED BENRATH (*Zeitsch. anorg. Chem.*, 1908, 58, 257—264. Compare Abstr., 1907, ii, 694).—From the results of ebullioscopic, and in some cases of cryoscopic, determinations with mixtures of two salts in water and in alcohol as solvents, it is shown that when there are deviations from additive behaviour, they are greater at the freezing point than at the boiling point. This is best accounted for on the

view that complexes of the two salts partly decompose as the temperature is raised.

Cobalt and cupric chlorides do not appear to combine with sodium chloride in aqueous solution at 100° even when the concentration of the latter salt is high, but in alcoholic solution the elevation of the boiling point for mixtures of lithium chloride with cobalt and cupric chlorides respectively is smaller than the sum of the effects due to the salts separately. Mixtures of nitrates which give an abnormally small freezing-point depression behave normally at the boiling point. Cadmium chloride does not combine appreciably with sodium chloride at the boiling point of the aqueous solution. Experiments have also been made with mixtures of mercuric chloride and potassium and sodium chlorides respectively. G. S.

Influences of Solubility. GIUSEPPE KERNOT, E. D'AGOSTINO, and M. PELLEGRINO (*Gazzetta*, 1908, 38, i, 532—554).—The authors have studied the influence of increasing proportions of (1) potassium chloride on the solubility of calcium hydroxide, (2) ammonium chloride on the solubility of barium carbonate, and vice versa. The results, which are given in the form of both tables and curves, are briefly as follows.

In presence of increasing quantities of potassium chloride, the solubility of calcium hydroxide at first increases and afterwards diminishes, becoming less than the solubility in water alone (compare Rothmund, *Abstr.*, 1900, ii, 467; Rothmund and Wilsmore, *Abstr.*, 1902, ii, 447; Hoffmann and Langbeck, *Abstr.*, 1905, ii, 374).

The solubility of barium carbonate rises continuously as the amount of ammonium chloride present increases, and at 25°, when the solution contains about 5 mols. of the chloride, the solubility curve assumes an upward inflexion, which is probably due to the formation of a double chloride of barium and ammonium. The relation of the solubility of ammonium chloride to the proportion of barium carbonate present is represented by a curve perfectly analogous to the preceding one.

Conductivity curves indicate that the degree of dissociation of potassium chloride is not altered by the presence of calcium hydroxide, or that of ammonium chloride by the presence of barium carbonate. The conductivity of the mixed solution may be regarded as the sum of the conductivity of the saturated solution of the substance influenced and that of the solution of the influencing substance, so that the amount of the substance influenced which is brought into solution or expelled therefrom by the influencing substance does not participate in the formation or destruction of the electric molecules.

In order to obviate difficulties in the analysis of the mixed solutions, the authors have made use of the following method, which reduces all the determinations to simple weighings. The two substances are weighed, one after the other, into the same vessel, which is placed in a thermostat in which it can be rotated. Water is then gradually added to the vessel, avoiding contact with the air, until the two substances are completely dissolved. This may be effected con-

veniently by means of two flasks, one inverted above the other, the two being connected by means of a glass tube passing through rubber stoppers in the two flasks and having its lower end drawn out to a fine point. The upper flask is filled to the extent of about $19/20$ with water, which may be forced into the lower flask in quantities as small as desired by gently warming the air in the upper flask.

T. H. P.

Solubilities in Mixed Solvents. WALTER HERZ and F. KUHN (*Zeitsch. anorg. Chem.*, 1908, 58, 159—167. Compare Abstr., 1904, ii, 709; 1905, ii, 510, 709; 1907, ii, 159, 848).—The solubility of mercuric chloride, bromide, iodide, and cyanide in mixtures of methyl and ethyl alcohol in varying proportions has been determined at 25° , and the density and viscosity of the solutions have also been determined.

For the bromide, iodide, and cyanide, $L-l$ (L =observed solubility, l =solubility calculated on the assumption that the components exert their effect independently) is small, and may be positive or negative. The solubilities and densities increase, and the viscosities decrease, throughout as the proportion of methyl alcohol increases. For mercuric chloride, $L-l$ is fairly large for intermediate concentrations, and is positive throughout; the different behaviour in this case is probably to be ascribed to the fact that the salt combines with methyl alcohol (McIntosh, Abstr., 1897, ii, 372). For the chloride, bromide, and cyanide, $L-l$ attains its maximum value for the mixture containing the components in equivalent proportions.

G. S.

[Vapour Pressure of Dry and of Ordinary Sal Ammoniac.] JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1908, 62, 678—680. Compare this vol., ii, 353).—A further criticism of Abegg's views (this vol., ii, 157, 466).

J. C. P.

Thermodynamics of the Sulphuryl Chloride Equilibrium $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$. MAX TRAUTZ, E. BAISCH, and ALFRED VON DECHEND (*Zeitsch. Elektrochem.*, 1908, 14, 271—280).—In order to calculate the equilibrium between sulphuryl chloride, sulphur dioxide, and chlorine, it is necessary to know the vapour-pressure curve of sulphuryl chloride, its heat of evaporation, and the specific heat of the vapour. Details of the methods used in determining these quantities are given. The results obtained are: vapour pressure (in mm. of mercury) at -78° , 0.2; 0° , 40.92; 17.99° , 95.2; 34.73° , 209.6; 40.13° , 263.9; 45.26° , 322.1; 50.42° , 292.1; 55.25° , 467.8; 60.09° , 555.9; 64.94° , 656.2; 69.62° , 766.9. Many other points on the curve were determined. The heat of evaporation (per molecule) at pressure p and absolute temperature T is given by $\lambda = (1 - p/55)(8940 + 3.5T - 0.02845T^2)$. The molecular heat of the vapour at 43 mm. pressure between 16° and 99° is 15.5.

T. E.

Equilibrium Between Metals and Solutions of Metallic Salts. EMIL BOSE (*Zeitsch. Elektrochem.*, 1908, 14, 314—316).—By means of the apparatus already used for silver and gold (Abstr.,

1907, ii, 735 ; this vol., ii, 264), it is now shown that platinum is more soluble in a hot concentrated solution of platinum tetrachloride than in a cold one. The difference is very small, and prolonged circulation is required in order to obtain a precipitate of platinum in the cold tube. The equilibrium is $\text{Pt} + \text{Pt}^{++++} \rightleftharpoons 2\text{Pt}^{++}$. A bibliography of investigations dealing with equilibria of this kind is given. T. E.

Influence of the Solvent on the Equilibrium Constant. LEO PISSARJEWSKY and A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 611—623).—The influence of the solvent on the equilibrium constant is often very considerable. Thus, K of the reaction $\text{CaSO}_4 + 2\text{OH}' \rightleftharpoons \text{SO}_4'' + \text{Ca}(\text{OH})_2$ in 10.5% aqueous mannitol solution is eleven times, and in 23.7% aqueous glycerol solution nineteen times, as small as in water, whilst K of the reaction $\text{Ag}' + \text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++} + (\text{Ag})$ in 10.5% mannitol solution is about sixteen times as small as in water. Comparison of the changes of free energy in the reaction $\text{CaSO}_4 + 2\text{OH}' \rightleftharpoons \text{SO}_4'' + \text{Ca}(\text{OH})_2$ in water and in equal molecular aqueous solutions of methyl and ethyl alcohols, ethylene glycol, glycerol, and erythritol leads to the empirical relation $A = A_b - 100B\cdot\eta$, where A and A_b are the changes of free energy in the alcoholic solution and water respectively, B the number of hydroxyl groups in the alcohol employed, and η the relative internal friction of the alcoholic solution. In all cases where the degrees of dissociation of the reacting substances in the various solvents are identical, it seems probable that the product $A\eta$ is a constant. By the gradual addition of glycerol to water, the change of the free energy of the reaction $\text{CaSO}_4 + 2\text{OH}' \rightleftharpoons \text{SO}_4'' + \text{Ca}(\text{OH})_2$ diminishes in such a manner that the product of the free energy into the number of mols. of added glycerol is constant. The marked influence of the solvent on the equilibrium constant may also be applied to the determination of the change of free energy of non-reversible reactions. T. H. P.

Transition Concentrations. I. Conversion of Lanthanum Oxalate into Sulphate by Sulphuric Acid. F. WIRTH (*Zeitsch. anorg. Chem.*, 1908, 58, 213—227).—The equilibrium in the condensed system lanthanum oxalate and sulphate and the free acids has been investigated in the usual way by solubility measurements at 25°, and the relations are discussed on the basis of the phase rule.

The solubility of oxalic acid in water diminishes on progressive addition of sulphuric acid, at first rapidly, and then, beyond 12% of acid, comparatively slowly. The solubility of lanthanum oxalate in water increases with the concentration of sulphuric acid up to 1.9 mols. of the latter in 1000 grams of solution, at which point the solution contains 0.0264 mol. of lanthanum oxide in 1000 grams. As the concentration of sulphuric acid is further increased, the lanthanum oxalate is gradually converted into sulphate along the "transition curve," the proportion of lanthanum oxide in solution at the same time steadily decreasing. The transition curve oxalate \rightarrow sulphate meets the two solubility curves of lanthanum oxalate and sulphate respectively in sulphuric acid in the presence of solid oxalic acid at a triple point at which the solution is in equilibrium with the

three solid phases. At this point, the solution contains about 2.5 mols. of sulphuric acid and 0.011 mol. of lanthanum oxide in 1000 grams. The solid salts in equilibrium with the solution at the triple point are $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$ and $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. G. S.

Equilibria in Quaternary Systems. FRANZ A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 817—823).—The equilibria in certain quaternary systems have been investigated by solubility measurements in the usual way, and the results are represented on projected space diagrams.

The systems water, methyl and ethyl alcohols and ammonium nitrate; water, methyl and ethyl alcohols and potassium nitrate, and water, ethyl alcohol, ammonium and silver nitrates, have been investigated at 30°. The latter system is the most complicated, as a double salt, $\text{NH}_4\text{NO}_3 \cdot \text{AgNO}_3$, exists, which is soluble without decomposition in water and in 71% alcohol, but is decomposed by 91% alcohol. Equilibria similar to the last named occur at 30° in the systems water, ethyl alcohol, silver nitrate and potassium nitrate, and water, alcohol, benzoic acid and ammonium benzoate; in the latter case, a double compound of benzoic acid and ammonium benzoate is formed.

The equilibria in the system water, ethyl alcohol, ammonium and manganese sulphates are very different at 50° and 25°; at the former temperature, an anhydrous double salt, $2(\text{MnSO}_4)_2 \cdot (\text{NH}_4)_2\text{SO}_4$, and the hydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, are stable, and at the latter temperature the compound $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. G. S.

Reactions in Solutions of Different Salts, but with the Same Ions. ALBERT J. J. VANDEVELDE (*Chem. Zentr.*, 1908, i, 1360; from *Rev. gén. Chimie*, 1908, 11, 57—59).—It has been shown previously (*Abstr.*, 1907, ii, 609) that the velocity of reaction is not influenced by the substitution of copper for zinc in copper sulphate solution, but depends on the nature of the ions present; Cl ions increase and SO_4 ions retard the reaction. The production of the copper solution is effected equally well from $\text{CuSO}_4 + \text{NaCl}$ or $\text{CuCl}_2 + \text{Na}_2\text{SO}_4$; the same applies to acid solutions, for example, $\text{H}_2\text{SO}_4 + 2\text{NaCl}$ and $2\text{HCl} + \text{Na}_2\text{SO}_4$, &c. J. V. E.

Estimation of the Concentration of Hydrogen Ions by Indicators. LEONOR MICHAELIS and PETER RONA (*Zeitsch. Elektrochem.*, 1908, 14, 251—253).—A simple way of estimating the concentration of the hydrogen ions in a solution (between 0.0005 and 0.01*N*) is to add Congo-red to the solution, and compare this colorimetrically with a solution containing a known quantity of hydrochloric acid. The authors find, however, that the colour is changed by neutral salts, the acidity apparently decreasing. Salts of the alkali metals have the same effect, those of bivalent metals a greater effect, and those of trivalent metals a still greater one. Measurements of the *E.M.F.* of concentration cells with hydrogen electrodes show that no change occurs in the concentration of the hydrogen ions. The change of colour is the first stage in the precipitation of the colouring matter, and is analogous to the change of colour of a colloidal solution

of gold which precedes coagulation. Methyl-violet behaves in a similar way, the change of colour being, however, in the opposite direction. Phenolphthalein and methyl-orange also exhibit colour changes when very large quantities of neutral salts are used.

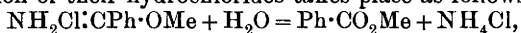
T. E.

Kinetics of the Sulphonation Reaction. HAAVARD MARTINSEN (*Zeitsch. physikal. Chem.*, 1908, 62, 713—725. Compare Abstr., 1905, ii, 149; 1907, ii, 609).—The author has studied the rate at which *p*-nitrotoluene undergoes sulphonation when dissolved in sulphuric acid. The possibility of following the course of the reaction depends on the fact that *p*-nitrotoluene is nitrated with great rapidity by nitric acid, whereas this reagent has no appreciable effect on *p*-nitrotoluene-sulphonic acid. A determination therefore of the quantity of nitric acid used up by a given volume of the reaction mixture serves to indicate the extent to which sulphonation has proceeded at any selected time. As in the earlier work (*loc. cit.*), the nitrometer was employed in the determination of unused nitric acid.

One of the reagents, namely, the sulphuric acid, was always present in large excess, and it was therefore expected that sulphonation would proceed according to the formula for a unimolecular reaction. This is borne out generally by the experimental results, which, however, bear evidence also to the marked influence of traces of water, even the small amount produced in the reaction leading to a decrease of the velocity-coefficient as time goes on. Three solvent media were used, namely: (1) absolute sulphuric acid containing 2.4% SO_3 ; (2) absolute sulphuric acid; (3) an acid containing 99.40% H_2SO_4 and 0.49% H_2SO_3 . The values of the velocity-coefficient observed in these three media were respectively 0.003, 0.0004, and 0.0000005. The temperature-coefficient of the velocity is 2.0—2.5 for a rise of 10° .

J. C. P.

Catalysis. V. Catalysis of Imino-esters. WILLIAM MCCrackEN (*Amer. Chem. J.*, 1908, 39, 586—613. Compare Derby, this vol., i, 419).—Stieglitz (this vol., ii, 167, 168) has given an account of the catalysis of imino-esters, and has stated that the decomposition of their hydrochlorides takes place as follows:



and that it proceeds most rapidly with the salts of those imino-esters which are the weakest bases.

An investigation of this decomposition has now been carried out with the object of ascertaining whether it is the salt or the free base which undergoes the change into ester and ammonia, and also of determining whether there is any general relation between the velocity of decomposition of the salts and the affinity constants of the bases. The velocity of reaction and the hydrolysis constants have been determined with the hydrochlorides of ethyl, *isobutyl*, and *isoamyl* iminobenzoates, ethyl imino-*p*-toluate, methyl imino-*o*-toluate, ethyl iminophenylacetate, ethyl imino-*m*-nitrobenzoate, ethyl imino-*m*-bromobenzoate, and ethyl imino- β -naphthoate.

The results show that the velocity of decomposition of these imino-

esters by water is proportional to the concentration of the salt formed with the acid, that is, of the positive ester ions. The whole salt does not undergo decomposition, but only its positive ions. The presence of an excess of hydrochloric acid decreases the velocity of reaction by reducing the degree of ionisation of the imino-ester salt, thus diminishing the active mass of the positive ester ions, and simultaneously tends to increase the velocity by a "salt effect." The acceleration due to the "salt effect" is practically the same for the same excess of acid acting on the salts of two imino-esters, of which the velocities of decomposition are as 10:1. This fact confirms the view that the "salt effect" is not due to a primary action on the salt, but to an effect on the active mass of water involved in the reaction. With two exceptions, the velocity constants were found to decrease as the strength of the imino-esters as bases increased. E. G.

Artificial Peroxydiastases. JULES WOLFF (*Compt. rend.*, 1908, 146, 1217—1220. Compare this vol., i, 490).—The oxidation of pyrogallol under the combined influence of hydrogen peroxide and a colloidal solution of iron ferrocyanide has been studied in detail. The colloidal ferrocyanide solution used contained 0.0023 mg. of iron per drop, and the hydrogen peroxide solution 7mg. of active oxygen per drop. The total volume of solution in each experiment was 40 c.c., and the amount of pyrogallol present was 1.2 grams.

With a constant quantity of hydrogen peroxide (eight drops) and increasing quantities of ferrocyanide, the yield of purpurogallin is proportional to the amount of peroxydiastase until the latter reaches ten drops, after which the amount of purpurogallin increases more and more slowly.

In the presence of a fixed amount of ferrocyanide, the quantity of purpurogallin formed rises regularly as the amount of hydrogen peroxide present increases to nine drops, after which the increase in yield becomes less and less.

In experiments in which twenty drops of ferrocyanide, solution and five drops of hydrogen peroxide solution were used, addition of 2.5 mg. and 5.0 mg. of sulphuric acid reduced the yield of purpurogallin 17% and 62% respectively, whilst 0.85 mg. of ferrous sulphate or 0.89 mg. of copper sulphate produced a 70% reduction, but 0.84 mg. of manganese sulphate had very little effect. A similar prejudicial action of ferrous sulphate has been observed by Stoecklin (*Thesis*, Geneva, 1907) in the case of the natural peroxydiastase.

Amongst salts, potassium dihydrogen phosphate has a markedly noxious effect.

The conclusion is drawn that this colloidal ferrocyanide acts in all its essential respects like a natural enzyme. E. H.

[Deduction of the Stoicheiometric Laws.] EMIL BAUR (*Zeitsch. physikal. Chem.*, 1908, 62, 760—761).—A reply to de Vries (this vol., ii, 366). J. C. P.

Commensurability of Atomic Weights. GUSTAVE D. HINRICHS (*Compt. rend.*, 1908, 146, 971—973).—In a previous paper (*Abstr.*, 1907, ii, 945), it was assumed that a perpendicular from the origin of

co-ordinates upon the graph of the equation of condition in a given determination of atomic weight was equal to the deviation of the atomic weight from the "absolute" (round number) value. This is now said to be true only if the values of the analytical excess " e " in the equations of condition are distributed about the origin conformably with the laws of probability. Otherwise, a more detailed discussion of the experimental errors is necessary in order to determine the deviation of an atomic weight from the round number.

The atomic weight of silver is calculated from the synthesis of silver nitrate to be $(108 - \frac{1}{8}) = 107.875$. Hydrogen is calculated to be $16/(16 - \frac{1}{8}) = 1.00787$, whilst chlorine is given as $(35.5 - \frac{1}{8} \times \frac{1}{8}) = 35.458$.

The author claims that his results lend support to the hypothesis of the unity of matter, but the differences between successive elements must be expressed in terms of a smaller unit than hitherto.

R. J. C.

Atomic Weights of Sixteen Chemical Elements. GUSTAVE D. HINRICHS (*Chem. Zentr.*, 1908, i, 1240; from *Mon. Sci.*, 1908, [iv], 22, i, 155—172).—From the published data, the author has calculated the atomic weights of the following elements by the method previously suggested (*Abstr.*, 1893, ii, 317): bismuth, lead, mercury, iron, tellurium, potassium, bromine, iodine, manganese, cadmium, cobalt, indium, platinum, didymium, terbium, and radium. The difference of the calculated atomic weights from whole numbers is found to be decreased and often is due to experimental error. The probability of these values being whole numbers is raised to $10^{148}:1$ for the 28 elements up to the present considered.

J. V. E.

Non-Metallic Elements in Connexion with Valency and Specific Gravity. GEORGE WOODIWISS (*Chem. News*, 1908, 97, 265. Compare this vol., ii, 368).—From a consideration of the relationship existing between the valency and specific gravity and specific gravity and atomic weight of the non-metallic elements immediately preceding in Mendeléeff's table the elements of the argon group, evidence is advanced for the valency of these inert elements being 0.5 and not zero. When the quotients of specific gravity divided by the square root of the assumed valency (0.5) of the elements argon, krypton, and xenon are plotted against their atomic weights, it is found that they are in close agreement with other non-metallic elements.

J. V. E.

Valency on an Atomistic Electrical Basis. JOHANNES STARK (*Jahrb. Radioaktiv. Elektronik.*, 1908, 5, 124—153).—A theoretical paper, part of which has been published previously (compare this vol., ii, 138). An attempt is made to account for chemical action by assuming that the atoms consist of positively charged spheres on the interior surface of which are the relatively minute negative electrons. The forces which operate in the union of two different atoms are entirely of electrical nature, and combination takes place as the result of the partial displacement of the lines of force of such a superficial negative electron (termed a valency electron) from the positive sphere

of the atom to which it originally belonged to the positive sphere or spheres of neighbouring atoms. Three kinds of electrons, depending on the way in which the lines of force from the electron are related to the positive spheres of neighbouring atoms, are distinguished. These are classified as unsaturated, saturated, and displaced electrons. On the basis of these three types, the various kinds of dissociation which give rise to the phenomenon of electrical conductivity are explained. The banded spectra of compounds are discussed in reference to the properties of the saturated and the displaced electrons. The line spectra are supposed to be due to internal electrons and not to the valency electrons. Finally, an interpretation of the variation of the valency of the elements along the vertical groups and horizontal series of the periodic table is given.

H. M. D.

Steam Distillation under Reduced Pressure. WILHELM STEINKOPF (*Chem. Zeit.*, 1908, 43, 517).—The author suggests the use of this method for separating a substance volatile in steam which is itself decomposed by it, or a substance volatile in steam from substances decomposed at the ordinary temperature by such treatment. Toluene is found to distil with steam at $27.5^{\circ}/27$ mm., aniline at $23^{\circ}/20$ mm., nitrobenzene at $22.5^{\circ}/19$ mm., and a 40% yield of benzoyl chloride is obtained at $21^{\circ}/16$ —17 mm.

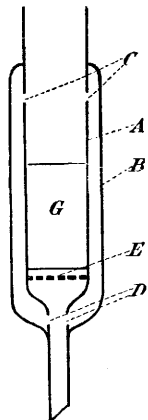
J. V. E.

Receiver for Vacuum Distillation. GUSTAV KOLBE (*Chem. Zeit.*, 1908, 32, 487).—A modification of Lothar Meyer's apparatus (*Abstr.*, 1887, 884), the valve plug being made of glass rod instead of glass tubing; the exhaust tube is placed in such a position that none of the distillate can be drawn up into it. By means of a special device, it is possible to exhaust the receiver independently of the rest of the apparatus.

P. H.

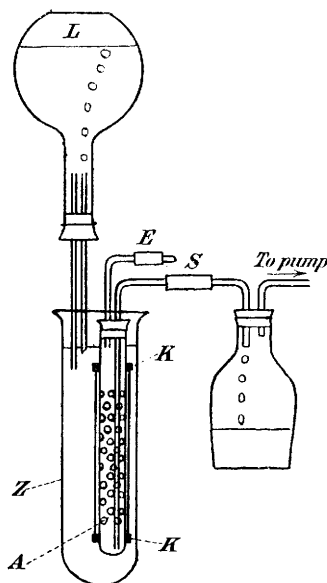
Apparatus for Simultaneously Extracting a Solid and Filtering the Solution So Obtained.

FREDERICK RECORD (*Chem. News*, 1908, 97, 280).—An apparatus devised to obviate the loss of substance which occurs in the course of filtration subsequent to the extraction of solids with such solvents as ether and alcohol. It consists of an inner tube, *A*, sealed to a shorter concentric jacket, *B*, and in that portion of *A* which is within *B* there are two pairs of holes, *C* and *D*. The substance to be extracted, *G*, is placed above a filter disk, *E*, and covered with filter paper and asbestos. A reflux condenser is attached to the upper part of the apparatus, and a flask containing the solvent to the lower end. The vapour from the boiling solvent rises through apertures *D* and *C* into the condenser, from which the liquid drops upon the substance to be extracted, and percolates through to the flask again.



J. V. E.

Filter for Filtering Solutions of Definite Concentration at a Temperature Either Above or Below that of the Surrounding Medium. A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 623—624).—The author has devised a filtering apparatus which may be employed with advantage in cases where the change of concentration occurring when an open filter is employed is to be avoided. Over one end of a glass tube, 4 cm. long and having an internal diameter of about 6 mm., three or four glass fibres, about 1/3 mm. thick, are soldered parallel to one another so as to form a kind of grating. Over this grating is placed a filter paper, which also extends some distance along the tube, and is kept in position by a piece of rubber tubing, the latter serving also to connect the glass tube with a similar shorter piece. The pipette containing the liquid to be filtered may be connected with the filtering apparatus by means of rubber tubing. Suction may be employed to hasten the filtration. T. H. P.



Filtration Apparatus. HANS WISLICENUS (*Chem. Zentr.*, 1908, i, 1238; from *Zeitsch. Chem. Appar.*, 3, 89—93).—The inner tube *A* is of porcelain or glass, and is perforated by a number of small holes. Over this is wound a broad strip of moistened filter paper, which is kept in position by two indiarubber bands *K.K.* A double bored indiarubber stopper fitting into the mouth of *A* carries two tubes, one of which, *S*, is a suction tube and extends to the bottom of *A*; the other, *E*, reaches only just below the stopper, and is closed during the process of filtration by means of a glass plug on the outside. For ordinary use with cold solutions, the part of the apparatus described is supported in a wide cylinder, *Z*; but when filtra-

tion is required to be carried out at a higher or a lower temperature, the cylinder *Z*, containing the tube *A*, is placed in a heating or cooling bath. The liquid in *Z* to be filtered is best maintained at a constant level by the arrangement indicated by *L*. This apparatus has been found most useful when dealing with slimy or colloidal extracts. J. V. E.

Inorganic Chemistry.

Condition of Steam. EMIL BOSE (*Zeitsch. Elektrochem.*, 1908, 14, 269—271).—The high density of steam is most readily explained by assuming it to contain single and double molecules in equilibrium, $(\text{H}_2\text{O})_2 \rightleftharpoons 2\text{H}_2\text{O}$. The density (air = 1) should then be $\Delta = \delta - K/p(\sqrt{1 + \delta p/K} - 1)$, where δ is 1.2432, the theoretical density for $(\text{H}_2\text{O})_2$, p is the pressure, and K is the equilibrium constant at any temperature T . Using determinations of the density made by Kornatz (*Diss.*, Königsberg, 1908), the author calculates $\log K = -4857.1/T + 21455$. The values of the density calculated by these equations show a mean deviation from the experimental results of 0.4%. Regnault showed that the deviations of the vapour density of steam from the theoretical value are a function of the degree of saturation of the steam, that is, of the ratio p/P , where P is the pressure of saturated steam, whereas the author represents them as a function of p/K . It is shown that P is approximately proportional to K , so that formally either ratio may be used. T. E.

Atomic Weight of Chlorine. E. C. EDGAR (*Mem. Manchester Phil. Soc.*, 1908, 52, No. 7, 1—2).—The method used to redetermine this constant was to burn pure dry chlorine at the tip of a quartz jet in an atmosphere of pure dry hydrogen in a quartz combustion vessel, the hydrogen chloride formed being condensed in a limb of it by means of liquid air.

The mean of eight determinations gave the atomic weight of chlorine, calculated from the ratio weight of chlorine burnt/weight of hydrogen burnt, to be 35.194, and from the ratio weight of hydrogen chloride caught—weight of hydrogen burnt/weight of hydrogen burnt, to be 35.193 (at. wt. of hydrogen = 1). If the atomic weight of oxygen is taken as 16, that of chlorine becomes 35.462 and 35.461 respectively, numbers which differ appreciably from that accepted by the International Committee on Atomic Weights, but in close agreement with 35.463 found by Dixon and Edgar and 35.461 found by Guye. J. V. E.

Study of the Oxidation Phenomena Produced by Iodic and Bromic Acids. HENRI BAUBIGNY (*Compt. rend.*, 1908, 146, 1097—1100 *).—An ammoniacal solution of silver chloride or bromide when heated at 100° with iodic acid, contrary to the statements in certain text-books, does not give any deposit of silver iodide. The latter is only formed when the temperature has been raised to 200°, and in this case a slight excess pressure in the cooled tube indicates the evolution of a small quantity of gas.

* and *Bull. Soc. chim.*, 1908, [iv], 3, 767—771.

When 45 c.c. of ammonia (D 0.926) are heated with 1.1 grams of iodic acid in a sealed tube at 210° for five hours, a small amount of gas is evolved and an appreciable quantity of ammonium iodide formed. At 150° very little iodide is produced. In three experiments similar to the above, to each of which 0.256 gram of silver bromide was added, 0.0006 gram of silver iodide was formed at 100° , 0.0021 gram at 150° , and 0.1760 gram at 210° .

The conclusion is drawn that the iodic acid oxidises the ammonia, $\text{NH}_4\text{IO}_3 + 2\text{NH}_3 = \text{NH}_4\text{I} + 3\text{H}_2\text{O} + \text{N}_2$, giving water, nitrogen, and ammonium iodide, of which the latter reacts with silver bromide, giving the less soluble silver iodide.

Entirely similar results are obtained with bromic acid, which is not completely destroyed in the experiment, showing that it has a certain stability under these conditions. Since therefore no bromic acid could be detected in the mother liquors of the three experiments described above, it is concluded that none is formed (contrary to the assertions of text-books). Similarly, with silver chloride at 210° , no chloric acid is produced.

E. H.

Origin of Atmospheric Ozone, and Causes of the Variation of Carbon Dioxide in the Air. H. HENRIET and BONYSSY (*Compt. rend.*, 1908, 146, 977—978).—A preliminary note, in which the authors summarise the conclusions drawn from a series of experiments on the origin of atmospheric ozone, and the causes of the variation of carbon dioxide in the air. Ozone is formed at the expense of the oxygen of the high regions of the atmosphere under the influence of the ultra-violet rays of the sun; it is carried to the lower layers of the air by winds and rain; the proportion of ozone in the air is at a maximum during a West or South-west wind and at a minimum during an East wind, and it is also increased during clear, calm weather by the direct action of the solar radiations on the lower layers of air. The amount of carbon dioxide in the air varies inversely with that of the ozone for values below the normal; for values above the normal, the variation of carbon dioxide is due to local phenomena, such as fog, animal respirations, combustions, &c.

M. A. W.

Vapour Pressure of Sulphur at Low Temperatures. OTTO RUFF and HUGO GRAF (*Zeitsch. anorg. Chem.*, 1908, 58, 209—212).—The authors' results for the vapour pressure of sulphur at low temperatures (Abstr., 1907, ii, 947) are considerably higher than those given by Gruener (Abstr., 1907, ii, 860); this is ascribed to the inaccuracy of the method employed by the latter observer. Some fresh determinations at 0° and 49.7° have been made by the method previously used, with the slight modification that a second condensing tube, cooled to -185° , was employed. Hydrogen was used as indifferent gas. The results previously given have to be corrected by adding the vapour pressure of sulphur at $0^{\circ}/00013$ mm. Results are given for temperatures between 49.7° and 211.3° . At 49.7° , 131.9° , and 211.3° , the corrected pressures are 0.00034, 0.081, and 3.14 mm. respectively.

G. S.

Hydrogen Persulphides. I. Historical. Crude Hydrogen Persulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1908, 41, 1961—1971).—The authors give a historical account of the polysulphides of hydrogen from their discovery in 1777. By heating sodium sulphide with varying amounts of sulphur in an atmosphere of hydrogen for three hours on the water-bath and dissolving the products in water, the authors obtain solutes of the composition Na_2S_2 , Na_2S_3 , Na_2S_4 , and Na_2S_5 . When the solutions are allowed to flow into mixtures of equal parts of ice and hydrochloric acid (D 1.19) cooled in a freezing mixture, crude hydrogen persulphide is obtained as a yellow, oily liquid with the odour of sulphur chloride and camphor. It is decomposed instantaneously by alkalis, and therefore it is essential that all apparatus used in the preparation should be washed with an acid. The oil can be kept for an hour without visible decomposition. Water decomposes it, but dilute acids, particularly hydrochloric acid, act as preservatives. A criterion of purity is the fact that the freshly-prepared persulphide yields a clear solution in benzene. Alcohols, ether, ethyl acetate, and acetone decompose the oil more or less rapidly, whilst with aldehydes and ketones condensation occurs, yielding substances rich in sulphur. Estimations of the hydrogen and sulphur alone do not suffice to fix the composition of the persulphide, but from the amount of hydrogen sulphide liberated by heating, the authors prove the incorrectness of Rebs' statement (*Abstr.*, 1888, 1155) that the hydrogen persulphide obtained by the decomposition of polysulphides by acids always has the composition H_2S_5 . C. S.

Hydrogen Persulphides. II. Hydrogen Trisulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1908, 41, 1971—1975).—Crude hydrogen persulphide (preceding abstract) is distilled under reduced pressure. In order to prevent the deposition of sulphur during the distillation, it is necessary to pass dry hydrogen chloride through the apparatus before it is evacuated. The fraction passing over at $69^\circ/2$ mm. is collected in three portions, and the middle one analysed. The estimations and the molecular weight in benzene by the cryoscopic method point to the composition H_2S_3 .

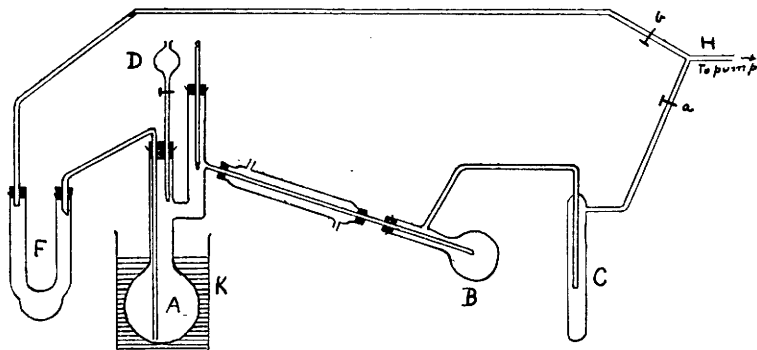
Hydrogen trisulphide, H_2S_3 , m. p. -52° to -53° , D^{15}_4 1.496, is a pale yellow oil, which becomes colourless at lower temperatures. It decomposes slowly in the dark, more quickly in daylight, and rapidly on warming, evolving hydrogen sulphide and depositing rhombic sulphur. It is decomposed slowly by acids, and rapidly by alkalis or alcohols; its solution in ether, benzene, or carbon disulphide is relatively stable. C. S.

Hydrogen Persulphides. III. Hydrogen Disulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1908, 41, 1975—1980).—By means of the apparatus described later, crude hydrogen persulphide has been separated into hydrogen trisulphide and *hydrogen disulphide*, H_2S_2 , b. p. $74-75^\circ$, D 1.376, which resembles the trisulphide in many respects, but differs from it in its greater volatility, greater sensitivity to alkalis, and in the more aggressive character of its vapour. It does not solidify in an ether-carbon dioxide mixture.

The apparatus figured has been designed for the distillation under

reduced pressure of large quantities of a liquid in small portions at a time, the residue being removed after the distillation of each portion without disconnecting the apparatus. Its use in the separation of hydrogen di- and tri-sulphides is as follows.

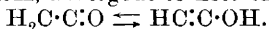
The flask *A*, of 300 c.c. capacity, immersed in the glycerol bath *K*, is connected through the condenser with *B* (150 c.c.), which is attached to the strongly-cooled vessel *C*. By means of a tube reaching to the bottom, *A* is connected with the U-tube *F*. Between *H* and the water pump are vessels containing soda-lime and calcium chloride, and a manometer. The flask *A* can be connected with the pump either through *B* and *C* by means of the stopcock *a*, or through *F* by the



stopcock *b*. To carry out the distillation, the bath *K* is raised to 110–125°, and the apparatus evacuated to about 20 mm., *a* being open and *b* closed. From the dropping funnel *D*, about 15 c.c. of crude hydrogen persulphide is run slowly into *A*. Distillation commences; when it becomes irregular, *a* is closed and *b* opened, whereby the residue in *A* is drawn over into *F*. The distillation is then continued by closing *b*, opening *a*, and introducing another 15 c.c. of hydrogen persulphide into *A* from *D*. The liquid collecting in *B* is mainly hydrogen trisulphide, whilst the more volatile disulphide is found in *C*.

C. S.

Hydrogen Persulphides. IV. Constitution of Hydrogen Disulphide and Trisulphide, and the Chemistry of Sulphur Compounds. IGNAZ BLOCH (*Ber.*, 1908, 41, 1980–1985).—The relationships of hydrogen di- and tri-sulphides (preceding abstracts) with one another and with other compounds of sulphur are discussed. The author points out that the change of colour of the two sulphides with change of temperature is perhaps explicable by an intramolecular change, $\text{H}_2\text{S}_2\text{S} \rightleftharpoons \text{HS:SH}$, analogous to keto-enol tautomerism,



Mendeléeff's conception of a homologous series of hydrogen sulphides, H_2S_n , derived from hydrogen sulphide itself by the successive replacement of H by SH receives favourable consideration.

C. S.

Existence of Compounds of Sulphur and Iodine. FRITZ EPHRAIM (*Zeitsch. anorg. Chem.*, 1908, **58**, 338—352. Compare Smith and Carson, this vol., ii, 32).—The freezing-point curve of mixtures of sulphur and iodine has been determined, and the results indicate that the elements do not enter into chemical combination and only form one series of mixed crystals, containing 7—8% of sulphur. Further, boiling-point determinations with the two elements in carbon disulphide afford no evidence of combination in that solvent. The two compounds described by Schneider (Abstr., 1888, 414) as double compounds of iodides of sulphur with arsenic trisulphide and the compound SnSI_2 respectively do not exist; the former is a mixture of arsenic trisulphide and iodine and the latter of stannic iodide and sulphur. G. S.

Sulphuric Acid Contact Process. LOTHAR WÖHLER, W. PLÜDDemann, and P. WÖHLER (*Zeitsch. physikal. Chem.*, 1908, **62**, 641—677. Compare Wöhler, Foss, and Plüddemann, Abstr., 1906, ii, 846; Wöhler, Plüddemann, and Wöhler, this vol., ii, 290).—The efficiency of any agent in promoting the union of sulphur dioxide and oxygen is measured by the amount of change which it induces under given conditions, such change being expressed as a percentage of the change which would be observed if the system reached its equilibrium position. Numerous experiments have been made in which chromium oxide, copper oxide, cupric and cuprous chromites, aluminium oxide, ferric oxide, thorium, cerium, silicon and titanium dioxides were used as catalytic agents at temperatures up to 900° . In all these cases, it is found that the efficiency, measured in the way already defined, increases regularly as the temperature rises without any sign of a maximum so long as the condition of the catalytic surface is unchanged. The experiments reveal the very marked influence which sintering has in diminishing the efficiency of the catalytic surface, and occasionally observed cases of a temperature of maximum efficiency are shown to be due to this cause.

It appears probable that the relative adsorptive power of variously treated samples of a given catalyst can be taken as a measure of the relative catalytic efficiency of these samples, but there is no such relation between the adsorptive power and the catalytic efficiency of different catalysts.

The authors conclude that the action of catalysts in the sulphuric acid contact process can be equally well explained by supposing the intermediate formation of a solid solution, either of a gas or of a chemical compound, in the surface layer.

In a note added to the paper, the authors discuss the discrepancies between their results (this vol., ii, 290) and those of Keppeler and D'Ans (this vol., ii, 289). J. C. P.

Action of Metals on Aqueous Solutions of the Persulphates. MARIO G. LEVI, E. MIGLIORINI, and G. ERCOLINI (*Gazzetta*, 1908, **38**, i, 583—602. Compare Abstr., 1907, ii, 81).—After discussing the work of Brighenti (*Atti R. Ist. Veneto*, 1905, **64**, ii, 1321) and Turrentine (this vol., ii, 104), the authors give the results of a study of the action of a large number of metals on solutions of potassium and ammonium persulphates.

All the metals examined, except gold and platinum, react with the persulphate solutions, either passing directly into solution or remaining undissolved in the form of oxides or basic salts. In general, the reaction is slower for ammonium than for potassium persulphate, probably owing to the slightly greater degree of dissociation of the potassium salt; in the catalysis with platinum, the tendency is in the opposite direction.

A special case is presented by magnesium, which reacts with extreme violence with ammonium persulphate, causing evolution of ammonia.

In general, those metals go into solution as anions which in their general chemical behaviour exhibit a marked non-metallic character, such as chromium, manganese, selenium, arsenic, molybdenum, &c.; some metals of this type, however, such as antimony, are transformed into insoluble oxides. The general action with these metals is hence oxidation by the persulphate with intervention of water.

Elements which are distinctly metallic in character pass into solution as cations, the persulphate being decomposed, sometimes with evolution of gas. With zinc, nickel, cobalt, &c., no gas is evolved, and in these cases the reaction is probably represented by $\text{Zn} + \text{X}_2\text{S}_2\text{O}_8 = \text{ZnSO}_4 + \text{X}_2\text{SO}_4$, or by (1) $\text{Zn} + \text{X}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2\text{SO}_4 + \text{X}_2\text{SO}_4$ and (2) $\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O}$; according to the latter interpretation, the solution may remain neutral or become acid, this depending on the relative velocities of the reactions (1) and (2). When gas is evolved, this is found to be hydrogen, at any rate for concentrated persulphate solutions.

The reactions studied are, except in the cases of gold and platinum, more chemical than catalytic in nature. They proceed with different velocities for different metals, although the velocity does not always bear any evident relation to the oxidisability of the metal or to its readiness of attack by sulphuric acid. The tendency to form double salts or complexes doubtless plays a part.

T. H. P.

Contact Oxidation of Ammonia and Organic Bases. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 659—660).—When ammonia is oxidised by the author's contact process (this vol., i, 306), it undergoes transformation mainly according to the equation $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$, a small quantity of the nitrogen being also found as nitrous and nitric acids.

Organic bases, such as aniline, toluidine, and pyridine, can also be oxidised in this way.

T. H. P.

Reduction of Hydroxylamine at Copper Cathodes. JULIUS TAFEL (*Chem. Zeit.*, 1908, 32, 135—136).—In reply to Patten (*ibid.*, 44), the author reasserts that hydroxylamine is not reduced at a copper cathode under the conditions expressly stated in his paper (*Abstr.*, 1902, ii, 559). His current researches in conjunction with Hahl (this vol., ii, 175) show that reduction occurs only when the concentration of the sulphuric acid round the cathode falls below a certain value.

C. S.

Electrolytic Reduction of Hydroxylamine. VICTOR ROTHMUND and O. FLASCHNER (*Zeitsch. anorg. Chem.*, 1908, 58, 183—188. Compare Flaschner, Abstr., 1907, ii, 454).—Remarks on Tafel and Hahl's recent paper (this vol., ii, 174). The authors maintain that the use of a stirring arrangement is of great advantage in such investigations.

G. S.

Action of Ammonia on Phosphorus. Observations on the Modifications of Phosphorus. ALFRED STOCK and OTTO JOHANNSEN (*Ber.*, 1908, 41, 1593—1607).—The paper opens with a résumé of the work of various authors on the action of ammonia on phosphorus. As conflicting statements have been made, the question has been re-studied. The present experiments were performed with a specially purified colourless phosphorus, which was freed from traces of arsenic by distillation in a current of steam. The results described show that when colourless phosphorus is treated with liquid ammonia, it is converted more or less completely, depending on the temperature and time of action, into red phosphorus. At the same time, small amounts of a solid hydride and an amide, or imide, of phosphorus are formed; the acid hydride combines with ammonia to form a black salt, which colours the whole mass. When treated with an acid, the red or yellow hydride is liberated, and, on addition of ammonia, again forms the black salt. The amide, when heated, is converted into phosphorus nitride, P_3N_5 .

The red phosphorus, prepared by the action of ammonia on the colourless modification, is identical with Schenck's phosphorus (Abstr., 1904, ii, 117); both have D^{22} 2.02, and are soluble in hot dilute sodium hydroxide. Ordinary red phosphorus, D^{22} 2.17, and Hittorf's phosphorus, D^{22} 2.35—2.37, are insoluble in sodium hydroxide. Both forms of red phosphorus have m. p. 600—615°; Hittorf's phosphorus, m. p. 620—625°; colourless phosphorus, when heated, changes into the red modification, and melts above 600°. All four modifications when heated in sealed tubes form a yellow liquid, which, on cooling, commences to deposit red crystals at about 550°. The relations of the four modifications of phosphorus to each other are discussed.

G. Y.

Action of Ammonia on Phosphorus Chloronitride. ADOLPHE BESSON and ROSSET (*Compt. rend.*, 1908, 146, 1149—1151. Compare Stokes, Abstr., 1895, ii, 217).—By acting on phosphorus chloronitride with liquid ammonia, a white *compound*, PN_3H_4 , is formed according to the equation $PNCl_2 + 4NH_3 = 2NH_4Cl + PN(NH_2)_2$. This substance is very soluble in water, and, when heated at 220° for several days, loses ammonia and yields phospham, $PN(NH_2)_2 = NH_3 + PN_2H$. When dry gaseous ammonia is passed into a solution of phosphorus chloronitride in dry carbon tetrachloride, slender, silky, prismatic needles are obtained having the composition $P_2N_3H_2Cl_3$, and formed according to the equation $2PNCl_2 + 2NH_3 = NH_4Cl + P_2N_2Cl_3 \cdot NH_2$. The *compound* is insoluble in ether or carbon disulphide, but dissolves in water with slow decomposition. The carbon tetrachloride drained from the crude product probably contains a mixture of ammonium

chloride and the compound PN_3H_4 . The action of gaseous ammonia on phosphorus chloronitride may therefore be represented as follows: $3\text{PNCl}_2 + 6\text{NH}_3 = \text{P}_2\text{N}_2\text{Cl}_3 \cdot \text{NH}_2 + 3\text{NH}_4\text{Cl} + \text{PN}(\text{NH}_2)_2$. The chloro-derivative is regarded as an intermediate product, and the compound PN_3H_4 as being formed by using an excess of ammonia. J. C. C.

Polymeric Forms of Metallic Arsenic. HUGO ERDMANN and RUDOLF REPERT (*Annalen*, 1908, 361, 1—31. Compare Abs'r., 1903, ii, 73, 74).—It is found that the transformation of solid, yellow arsenic, As_4 , into metallic arsenic, As , under the influence of light takes place in two stages, grey arsenic, which is considered to have the constitution $\text{As}:\text{As}$, being formed intermediately. The brown modification, D^{20} 3·67—3·69, formed by the action of light on dissolved yellow

arsenic, must have the constitution $\begin{array}{c} \text{As}:\text{As}:\text{As}:\text{As} \\ | \quad | \quad | \quad | \\ \text{As}:\text{As}:\text{As}:\text{As} \end{array}$. This is formed also

when dissolved yellow arsenic is treated with oxygen, arsenious bromide, or acetylene tetrabromide, or is allowed to remain in the dark.

An improved apparatus is described and figured for the preparation of a carbon disulphide solution of yellow arsenic. This modification, As_4 , D^{-50} 2·35, D^{18} 2·026, is unstable in violet or ultra-violet light, but is converted into metallic arsenic only slowly when exposed to red light; radium rays are without effect on the rate of this change.

Grey arsenic, As_2 , D^{20} 4·64, is formed as a by-product in the preparation of the carbon disulphide solution of the yellow polymeride, and is obtained also when the solid yellow arsenic is exposed to light at low temperatures or dissolved yellow arsenic is treated with alcohol or cooled with carbon dioxide and ether or with liquid air. It is stable towards atmospheric oxygen, and is oxidised by nitric acid more slowly than the brown modification or metallic arsenic.

The yellow, grey, and brown polymerides of metallic arsenic do not conduct electricity, whereas metallic arsenic is a conductor. This difference is employed to determine the temperature at which metallic arsenic is formed from its polymerides at a sensible rate. It is found that, when heated, brown arsenic changes into the grey modification, which decomposes into metallic arsenic at about 303° .

When solutions of yellow arsenic and silver nitrate are mixed together, the arsenic, if present in excess, reduces the salt quantitatively to metallic silver, but, if the silver nitrate is in excess, the arsenic is precipitated in the metallic state. Yellow arsenic also precipitates mercury from solutions of mercurous nitrate, and from copper sulphate, a black substance containing 53% to 55% of copper and considerable amounts of arsenic and sulphuric acids. Yellow arsenic therefore is a strong reducing agent, resembling yellow phosphorus, which gives similar reactions. Although isomorphous and chemically closely related, yellow phosphorus and yellow arsenic do not form mixed crystals; this is ascribed to the marked differences in the solubilities. G. Y.

Compounds of Arsenic and Antimony Pentafluoride with Nitrosyl Fluoride. OTTO RUFF [with KURT STÄUBER and HUGO GRAF (*Zeitsch. anorg. Chem.*, 1908, 58, 325—337. Compare Abstr., 1906, ii, 20).—The compound $\text{AsF}_5 \cdot \text{NOF}$ is obtained pure by passing

nitrosyl fluoride, NOF (prepared in the same operation by passing nitrosyl chloride through a platinum tube containing dry silver fluoride and heated to 250—280°), through cooled arsenic trichloride until absorption is complete, the product being finally kept over fused sodium hydroxide in a vacuum for some time to absorb traces of nitrosyl chloride. The compound forms a white, crystalline mass, and is remarkably stable; it is unaffected in dry air even at a high temperature, but decomposes in moist air; it is split up by water, by alkali, and by concentrated hydrochloric acid, but is unacted on by phosphorus trichloride, carbon tetrachloride, silicon, copper, lead, and other substances. On warming gently with antimony pentafluoride, arsenic pentafluoride and the solid antimony compound described below are obtained.

The corresponding antimony compound, $\text{SbF}_5\cdot\text{NOF}$, is obtained in an analogous way by the action of nitrosyl fluoride on antimony pentachloride, but more simply by interaction of nitrosyl fluoride and a solid antimony chlorofluoride, $(\text{SbF}_5)_2\cdot\text{SbCl}_5$. (The latter compound is obtained by the action of chlorine on antimony trifluoride; and will be described later.) The chlorofluoride and nitrosyl chloride are mixed in a tube at -80° , and the mixture allowed to warm up; the tube is then sealed, and kept for one to two hours at room temperature with occasional shaking. The compound occurs in slender, colourless needles, which sublime without decomposition below a red heat; it is very hygroscopic, and is decomposed by water and by alcohol. On warming with arsenic trifluoride, it gives arsenic pentafluoride mixed with excess of the trifluoride, and, on heating with potassium fluoride, it yields nitrosyl fluoride and a compound of antimony pentafluoride and potassium fluoride.

G. S.

Absorptive Power for Air of Certain Varieties of Vegetable Carbon. ARNALDO PIUTTI and G. MAGLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 68—75).—The density and absorptive power for air of different forms of carbon are tabulated in the original. The absorption was carried out at the temperature of liquid air, and the air absorbed driven off by heating the carbon gradually to a temperature of 550° .

The maximum absorption is shown by the carbon of cherry-stones and cocoanut-shell (about 280 and 250 times the volume respectively); this absorption is increased nearly 20 per cent. by a preliminary treatment of the material with chlorine. With the exception of that from carob seed, the surface of which is not sufficiently porous, the absorptive power of charcoal from any material is nearly proportional to its density.

W. A. D.

Solutions of the Alkali Metals in Liquid Ammonia. OTTO RUFF and JULIAN ZEDNER (*Ber.*, 1908, 41, 1948—1960. Compare Ruff and Geisel, *Abstr.*, 1906, ii, 228; Joannis, *ibid.*, ii, 161; 1907, ii, 459; Kraus, *Abstr.*, 1907, ii, 935).—The boiling-point and the melting-point curves of solutions of lithium, sodium, and potassium in liquid ammonia at different concentrations have been plotted. The boiling-point curves at small concentrations are of the usual type, but

the b. p.'s of solutions containing more than 8 (atomic) % of the metal begin to rise rapidly, indicating possibly the existence of compounds.

In particular, the behaviour of sodium in ammonia has been examined at temperatures below the boiling points at atmospheric pressure. Above -46° , only one liquid phase exists at any concentration, but below this temperature, separation into two liquid phases or one solid and one liquid phase occurs. Evidence of the existence of compounds has not been obtained, except perhaps at the eutectic point, -111° , where the composition corresponds with the formula $\text{Na}(\text{NH}_3)_5$.

Saturated solutions of lithium, sodium, and potassium boil at temperatures which are practically the same as those at which Moissan first observed a reaction between the metal and liquid ammonia.
C. S.

Extraction of Potassium from Felspathic Rock. ALLERTON S. CUSHMAN and PREVOST HUBBARD (*J. Amer. Chem. Soc.*, 1908, 30, 779—797).—The object of the experiments was to obtain a remunerative process for extracting potassium from rocks for agricultural purposes. A certain amount of the potassium of feldspars is dissolved by water when the mineral is finely ground, and the amount dissolved is increased by addition of substances such as ammonium salts, lime, and gypsum. Complete solution of the potassium can be effected by means of an electrolytic method, both with and without addition of hydrofluoric acid; the method would, however, probably be too costly for practical purposes. Attacking the silicates by means of potassium hydroxide or carbonate, &c., or with hydrofluoric acid, are suggested as possible methods which should receive further study.

Diagrams are given showing the amounts of potassium dissolved by water and the action of acids in relation to fineness and to duration of action. As regards the action of water, it is shown that the amount of potassium dissolved does not increase in exact ratio to the increase of surface area, probably owing to increased coagulation as the particles decrease in size.
N. H. J. M.

Polyiodides of Potassium, Rubidium, and Cæsium. HARRY W. FOOTE and W. C. CHALKER (*Amer. Chem. J.*, 1908, 39, 561—567).—Abegg and Hamburger (*Abstr.*, 1906, i, 747) have made a study of the polyiodides of the alkali metals, and have concluded that the following salts exist as stable solids at 25° : KI_7 ; RbI_3 , RbI_7 , RbI_9 ; CsI_3 , CsI_5 or CsI_7 , and CsI_9 . Johnson (*Trans.*, 1877, 249) has described the compound KI_3 , whilst Wells and Penfield (*Abstr.*, 1892, 773) and Wells and Wheeler (*Abstr.*, 1893, ii, 67, 68) have prepared the salts RbI_3 , CsI_3 , and CsI_5 , but were unable to obtain higher iodides of potassium than KI_3 .

From experiments on the solubility relations of the cæsium periodides, Foote (*Abstr.*, 1903, ii, 367) concluded that CsI_3 and CsI_5 were the only compounds found at the temperatures investigated. A similar study has now been made of the solubility relations of the polyiodides of potassium, rubidium, and cæsium at 25° , and the composition of the residues has been determined. The results prove

the existence of the salts KI_3 , RbI_3 , CsI_3 , CsI_5 , and KI_7 , but do not give any indication of the formation of the compounds RbI_7 , RbI_9 , CsI_7 , and CsI_9 .
E. G.

Explosion Produced by an Ordinary Reagent. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1908, [iv], 3, 618—619).—On attempting to move a glass vessel containing an ammoniacal solution of silver oxide which had been left for twenty-four hours, a violent explosion occurred. This was found to be due to the formation of silver nitride, or products intermediate between this and the oxide, according to the equation $3AgOH + NH_3 = NAg_3 + 3H_2O$.

The mixture constitutes Berthollet's fulminating silver, and had dried on the surface of the glass. Such a solution should therefore be thrown away after use.
J. C. C.

Compounds Formed by Silver Selenide with the Selenides of Arsenic, Antimony, and Bismuth. HENRI PÉLABON (*Compt. rend.*, 1908, 146, 975—977).—The freezing-point curves of mixtures of silver selenide with the selenide of antimony or bismuth, obtained by plotting the number of mols. of the added selenide per 100 mols. of the silver selenide as abscissæ against the freezing point of the mixture as ordinates, are closely similar, and consist of four branches, showing two minima and one maximum; the latter corresponds with the freezing point of the compound, $3Ag_2Se, 4Sb_2Se_3$, f. p. 650° , or

$3Ag_2Se, 4Bi_2Se_3$,
f. p. 773° , respectively. The freezing-point curve of mixtures of silver and arsenic selenide shows a maximum corresponding with the freezing point of the compound $3Ag_2Se, 4As_2Se_3$.

Similar evidence was obtained of the existence of compounds of silver selenide with the lower selenides of antimony (Chrétien, *Abstr.*, 1906, ii, 550); these compounds are represented by the formulæ $SbSe, \frac{1}{2}Ag_2Se$, Sb_3Se_4, Ag_2Se , and $4Sb_4Se_5, 5Ag_2Se$ respectively.

M. A. W.

Chemical Properties of Calcium. HUGO ERDMANN and HEINRICH VAN DER SMISSEN (*Annalen*, 1908, 361, 32—68).—As calcium is now prepared technically on the large scale, it was thought of interest to undertake a systematic investigation of the chemical properties of the metal. The calcium employed in the experiments now described was chiefly filings from the electrolytic metal. For some experiments, crystalline calcium was prepared by reduction of calcium iodide by Moissan's method.

Whilst readily attacked by air or liquid nitrogen (Erdmann, *Abstr.*, 1906, ii, 349; Jordis and Rosenhaupt, this vol., ii, 172), calcium is highly stable towards dry oxygen. Calcium oxide and mercury are formed only on prolonged heating of 1% calcium amalgam in a current of oxygen at 400 — 500° ; mercuric oxide also is formed if the oxygen is ozonised. The formation of calcium peroxide could not be detected. On the other hand, calcium is oxidised so rapidly in presence of moisture that, whilst when cut under mercury the fresh surface of the metal is amalgamated instantaneously, a surface which has been

exposed to moist air for a quarter of a second is amalgamated only at 100—200°.

Contrary to statements in the literature, calcium hydride, whilst energetically attacked by water, is extremely stable towards anhydrous reagents. With certain precautions, calcium hydride is recommended as a source of pure hydrogen, as also for the preparation of hydrogen on the large scale.

Calcium nitride, Ca_3N_2 (Maquenne, Abstr., 1892, 776), is prepared by passing a current of nitrogen through fused calcium in an iron crucible, or by the action of liquid nitrogen on the metal. Contrary to Kaiser's statement (French Patent, 350966, 1905), ammonia is not formed when hydrogen is passed over calcium nitride or nitrogen over the hydride at 500—800° (compare Haber and Oordt, Abstr., 1905, ii, 159, 384, 814).

Moissan has shown (Abstr., 1899, i, 410; ii, 152, 153) that calcium reacts with ammonia at -78° to 20° , forming calcium ammonia, $\text{Ca}(\text{NH}_3)_4$, but at 500—1000°, forming calcium nitride and hydride, whilst an analogous derivative of methylamine cannot be obtained. It is now found that calcium reacts with ethylamine at 250—400°, yielding hydrogen, nitrogen, calcium nitride, calcium hydride, and carbon. On the other hand, calcium reacts with aromatic amines, forming compounds of the type $(\text{NHR})_2\text{Ca}$.

Calcium anilide, $(\text{NHPh})_2\text{Ca}$, prepared by heating calcium with aniline in an atmosphere of hydrogen at 200° , is obtained as a white, microcrystalline powder, D 1.17, which is insoluble in organic solvents, decomposes when exposed to moist air, explodes in dry oxygen, and yields aniline and calcium hydrate when treated with water, or aniline and calcium salts with acids. When treated with oxygen highly diluted with nitrogen at -20° , the anilide absorbs 1.3 atoms of oxygen for each atom of calcium, and forms a black, resinous mass of basic character. With ethyl iodide at the ordinary temperature, the anilide forms ethylaniline; with benzoyl chloride in ethereal solution, benzanilide; with gaseous carbonyl chloride, carbanilide; with carbon disulphide, thiocarbanilide; with sulphur dioxide, a yellow product, which evolves sulphur dioxide when heated; and with carbon dioxide, *calcium phenylcarbamate*, $(\text{NHPh}\cdot\text{CO}_2)_2\text{Ca}$. Heat is developed by the reactions with carbon disulphide, sulphur dioxide, and carbon dioxide. Calcium phenylcarbamate is formed also when calcium is heated with aniline at 250° in an atmosphere of carbon dioxide; when heated, it decomposes, forming calcium carbonate and carbanilide.

Calcium o-toluidide, $(\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{Ca}$, formed from calcium and *o*-toluidine at 240° , resembles the anilide. It absorbs carbon dioxide, forming *calcium o-tolylcarbamate*, $(\text{C}_8\text{H}_7\text{O}_2\text{N})_2\text{Ca}$, which is decomposed by acids, forming carbon dioxide, *o*-toluidine, and the calcium salts, and, when heated, yields calcium carbonate and *s*-di-*o*-tolylcarbamide.

Calcium p-toluidide, formed from calcium and *p*-toluidine at 260° , absorbs carbon dioxide, forming *calcium p-tolylcarbamate*.

Calcium diphenylamide, $(\text{C}_{12}\text{H}_{10}\text{N})_2\text{Ca}$, prepared from calcium and diphenylamine at 355° , is obtained as a white powder, which is attacked only slowly by dry oxygen, becomes green in presence of

dry air, decomposes, developing heat on exposure to moist air, and explodes in moist oxygen. It is attacked only slowly by water or dilute acids, but forms diphenylamine and calcium sulphate with concentrated sulphuric acid. It yields the following substances when treated with the reagents named.

With benzoyl chloride, diphenylbenzamide; with carbonyl chloride, tetraphenylcarbamide; with an excess of carbonyl chloride, diphenylcarbamyl chloride, and with carbon dioxide, *calcium diphenylcarbamate*, which is obtained as a white powder, and when heated yields tetraphenylcarbamide.

Calcium reacts with the naphthylamines at 280° , evolving hydrogen and small amounts of ammonia, and forming a yellow, brittle glass. At 240° , calcium and *p*-anisidine form a brown *product*, which becomes dark blue on exposure to air. Calcium reacts also with ethylaniline at 240° , forming a brown *product*, which is sensitive to light; with acetamide at 140° , forming a gelatinous *substance*, and with acetanilide at 200° , forming, amongst other products, acetaldehyde and anilide. Calcium and benzidine do not react at 420° .

Phenylhydrazine reacts with calcium slowly at 100° and rapidly at 140 — 160° , forming nitrogen, hydrogen, ammonia, benzene, aniline, and a white *powder*, $C_{18}H_{18}N_4Ca$ (?), which is attacked violently by dry oxygen, and absorbs carbon dioxide with development of heat.

Contrary to Moissan's statement (Abstr., 1900, ii, 76), calcium hydride does not react with sulphur dioxide or with acetylene (Abstr., 1899, ii, 153). When heated with calcium at 400° , fluorene evolves hydrogen and forms a black mass, but, under the same conditions, benzene, naphthalene, tetraphenylmethane, and acenaphthene remain unchanged. On the other hand, ethyl acetate reacts with calcium at 300° , or in presence of traces of alcohol at 156° .

Ethyl calcioacetoacetate, $(C_6H_5O_2)_2Ca$, formed from calcium and ethyl acetoacetate at 150° , is obtained as a white, crystalline powder, m. p. 215 — 220° (decomp.) if rapidly, or decomp. 180° if slowly, heated. Also, ethyl ethylacetoacetate reacts with calcium at 170° , evolving hydrogen. A pure product could not be obtained. Ethyl malonate and calcium evolve hydrogen at 160 — 180° , forming a yellow, flocculent *product*, which could not be purified.

G. Y.

A New Calcium Silicide. L. HACKSPILL (*Bull. Soc. chim.*, 1908, [iv], 3, 619—621).—A new *calcium silicide*, Si_2Ca_3 , is obtained by heating to 1000° a mixture of calcium filings and powdered silicon compressed in a hole, 4—5 mm. diameter, bored in a calcium cylinder fitting in an iron test-tube, which is placed in a porcelain tube. On cooling, excess of calcium is removed by sugar solution, and the remaining slender needles are washed with alcohol and ether. The silicide is readily powdered, and has D_4^{25} 1.64. It is attacked by halogens in the cold, and by oxygen at a red heat. With dilute mineral acids, it is decomposed with evolution of spontaneously inflammable silicon hydrides.

J. C. C.

Micrography of Cement. E. STERN (*Ber.*, 1908, 41, 1742—1745).—Hardened cements, or cements in the process of hardening, have

been examined micrographically in reflected light by the method employed for metals and alloys. The etched sections show the original cement particles, *A*, composed mainly of alite, and a portion, *B*, in which the process of hardening takes place; very little alteration in appearance occurs during the hardening process, although *B* slowly increases at the expense of *A*. The sections yield characteristic results when etched with alkalis, alcoholic hydrochloric acid, alcoholic iodine solution, or 25% hydrofluoric acid. Portland cement and iron-Portland cement can be distinguished by this micrographic process.

The action of salt solutions, sea-water, &c., has been examined, and also the effect of high temperature. J. J. S.

Cæsium Dicalcium Sulphate. JOH. D'ANS (*Ber.*, 1908, 41, 1776—1777).—In continuation of his study of double sulphates (*Abstr.*, 1906, ii, 751; 1907, ii, 168; this vol., ii, 104, 289), the author has prepared *caesium dicalcium sulphate*, $\text{Ca}_2\text{Cs}_2(\text{SO}_4)_3$, by adding gypsum to a solution of caesium sulphate. It forms crystals similar to those of ammonium and rubidium dicalcium sulphates, and is extremely stable, the stability increasing with the temperature. Attempts to prepare a salt analogous to syngenite, or a pentacalcium salt, have been unsuccessful. The temperature limit of stability of the calcium double sulphates falls as the mol. weight of the alkali sulphate increases. Whilst potassium syngenite is stable far above 100° , rubidium syngenite decomposes above about 40° ; on the other hand, whilst ammonium dicalcium sulphate exists only above 80° , caesium dicalcium sulphate is formed below 0° .

A thallium calcium sulphate could not be prepared.

G. Y.

Neutral Triple Sulphates of Calcium. JOH. D'ANS (*Ber.*, 1908, 41, 1777—1779).—Only two neutral triple sulphates of calcium, the naturally-occurring polyhalite, $\text{Ca}_2\text{MgK}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Basch, *Abstr.*, 1901, ii, 168), and krugite, $\text{Ca}_4\text{MgK}_2(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$ (Geiger, *Abstr.*, 1904, ii, 268), have been studied previously. The observation of the formation of a polyhalite, in which the magnesium is displaced by copper by the action of copper sulphate solution on potassium syngenite, has led the author to investigate the formation of such triple sulphates.

It is found that polyhalites, in which the magnesium is displaced by copper, cadmium, nickel, or zinc, and the potassium by ammonium, are formed when gypsum is boiled with suitably concentrated solutions of the other two sulphates. The synthetical salts crystallise more readily than the naturally-occurring triple sulphates; the *copper ammonium* and *copper potassium* salts are light blue. Analyses are quoted of the *dicalcium copper diammonium*, $\text{Ca}_2\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, and *dicalcium cadmium dipotassium*, $\text{Ca}_2\text{CdK}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, sulphates.

These results have led to the synthesis of polyhalite by boiling gypsum, or a mixture of this with syngenite, with a concentrated solution of magnesium sulphate containing about 4% of potassium sulphate.

G. Y.

Composition of Artificial Magnesite Stone. FELIX CORNU (*Centr. Min.*, 1908, 305—310).—The basic refractory bricks used for

lining iron furnaces, which are made by igniting the coarsely crystalline magnesite (or rather breunnerite, since it contains 3.2—3.5% iron) from Veitsch in Styria, were found to consist largely (94%) of a crystalline aggregate of grains of periclase together with some glassy material. Enclosed in the grains of periclase are skeletal growths of magnesioferrite.

L. J. S.

Amalgamated Zinc. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1908, 5, 356—359).—A theoretical paper, reviewing the theories advanced to explain the lack of activity displayed by amalgamated zinc towards dilute sulphuric acid.

A. J. W.

New Reaction of Thallous Salts. FRITZ EPHRAIM (*Zeitsch. anorg. Chem.*, 1908, 58, 353—355).—A clear aqueous solution of antimony chloride and potassium iodide gives with an acid or neutral solution of any thallous salt a characteristic voluminous, orange to cinnabar-red precipitate of the compound $3\text{TlI}, 2\text{SbI}_3$. Thallous salts in a dilution of 1 in 20,000 can be detected in this way, but the compound cannot be used for the quantitative determination of thallous salts, as it is decomposed by water.

G. S.

Effect of Glass and Traces of Organic Substances on Mercuric Chloride Solution. WILLEM VAN RYN (*Pharm. Weekblad*, 1908, 45, 636—637).—Dilute aqueous solutions of mercuric chloride (1:4000 to 5000), preserved in corked bottles, are completely reduced in a few days either to a mixture of mercuric oxychloride and mercurous chloride or to mercurous chloride only. The author attributes the reduction to the action of the glass, of the cork, and of traces of organic matter in the solution.

A. J. W.

Resolution of Ytterbium into its Elements. CARL AUER VON WELSBACH (*Monatsh.*, 1908, 29, 181—225).—It was stated in a previous communication (Abstr., 1907, ii, 26) that the fraction obtained during the separation of the elements of the ytterbium group, which should have contained pure ytterbium, gave a spark spectrum which differed considerably from the ytterbium spectrum; for instance, the four lines in the green, $\lambda = 5353.0, 5347.4, 5345.9$, and 5335.2 , so characteristic of ytterbium had almost disappeared. The conclusion was drawn therefore that the ytterbium had partly been resolved. At the same time, a fraction was obtained between the erbium and thulium fractions which gave a spectrum termed Ery. This fraction has been further investigated, and by repeated fractional precipitation of the oxalate by ammonium oxalate a fraction was finally obtained which gave a spark spectrum in which the lines which were missing or were very faint in the first-mentioned spectrum, for example, the four lines in the green, were exceedingly intense.

Large quantities of the fractions containing the two new substances were therefore carefully fractionated by repeated precipitation of the oxalates, and finally two fractions were obtained which could not be further resolved. It is proposed to name the two new elements so obtained *aldebaranium* (Ad) and *cassiopeium* (Cp). Their atomic weights, determined by conversion of the oxides into sulphates, were found to

be $\text{Ad} = 172.9$ and $\text{Cp} = 174.23$ ($\text{O} = 16$). The two elements cannot be distinguished one from the other by chemical means; they, of course, possess the chemical properties ascribed to ytterbium.

The principal lines of the spark spectrum of aldebaranium are $\lambda = 5353.0, 5347.4, 5345.9, 5335.2, 4786.8, 4726.0, 4181.0, 3988.2, 3694.3, 3289.5$, and 2750.6 ; of cassiopeium, $\lambda = 6222.0, 6160.2, 5984.0, 5476.9, 5135.2, 4994.3, 4785.5, 4684.0, 4181.4, 3694.3, 3554.6, 3507.6, 3472.7, 3397.2, 3289.5, 2911.5, 2900.4, 2895.0$, and 2615.5 . The two spectra combined practically give the spectrum of ytterbium, but there are nevertheless some lines present in the spectrum of the latter, for example, $\lambda = 5104.6, 5067.4$, and 5009.7 , which do not appear in the spectra of aldebaranium or cassiopeium. It is therefore evident that ytterbium also contains a third unknown element.

The original contains a complete list of the wave-lengths of the lines of the spark spectra of ytterbium, aldebaranium, and cassiopeium, also reproductions of the photographs of these spectra. W. H. G.

Silicon-Aluminium Alloys. WALTER FRAENKEL (*Zeitsch. anorg. Chem.*, 1908, 58, 154—158).—The aluminium used in the investigation contained nearly 99% of the pure metal; the specimen of silicon contained 96.6% of that element and about 1% of aluminium.

The elements are miscible in all proportions in the fused state, and do not enter into chemical combination. The freezing-point curve consists of two branches; the eutectic mixture contains about 10% of silicon, and solidifies at 576° . Whether mixed crystals are formed could not be satisfactorily determined; if they exist, those rich in aluminium do not contain more than 0.5% of silicon, and those rich in the latter element not more than 2% of aluminium. There is some evidence that silicon, like bismuth, expands on solidification. G. S.

Aluminium Silicates. FRITZ ULFFERS (*J. pr. Chem.*, 1908, [ii], 77, 549—552. Compare Abstr., 1907, ii, 776).—Polemical. A reply to Jordis (this vol., ii, 291). G. Y.

Manganese and its Alloys with Carbon. A. STADELER (*Metallurgie*, 1908, 5, 260—267, 281—288).—Manganese, prepared by the Goldschmidt method, contains 1.3% Si, 1.46% Al, and 1.05% Fe. The silicon may be removed by fusion with potassium permanganate, but the iron is less readily oxidised than the manganese, and, as the loss by volatilisation is considerable, dry refining of the manganese is impracticable.

In the investigation of the manganese-carbon alloys, the mixtures were fused in crucibles, lined with magnesite, in a current of nitrogen.

The maximum solubility of carbon in manganese at 2000° is 6.72%, corresponding with the carbide, Mn_3C . The mixtures solidify to form a continuous series of mixed crystals, having a maximum freezing point at 1271° and 3.32% C, and falling to the freezing point of the carbide at 1217° . The metallographic examination of quenched alloys confirms the existence of mixed crystals, visible as polyhedra in alloys containing less than 3.32% C, and as long needles in alloys richer in carbon. At a lower temperature, rising from 817° at 0.72% C to

855° at 3·60% C, these crystals break up into other mixed crystals, one series of which is nearly pure manganese, and the other rich in carbide. Alloys containing more than 3·60% C have the same structure whether slowly cooled or quenched.

Manganese does not take up carbon when heated in sugar charcoal for twelve hours at 1100°.

Manganese carbide, Mn_3C , has D 6·888, and is readily oxidised. Alloys containing more than 3% of carbon fall to pieces at once in water, and even disintegrate spontaneously in closed vessels after a few weeks, apparently owing to the evolution of retained gas.

C. H. D.

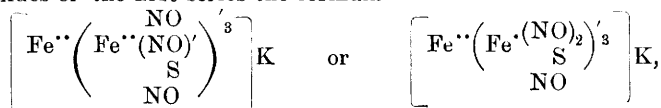
Preparation of Electrolytic Iron. RICHARD AMBERG (*Zeitsch. Elektrochem.*, 1908, 14, 326—328).—Electrolytic iron was prepared in quantities of 240 to 1000 grams by electrolysis of a solution of ferrous ammonium sulphate containing not less than 26 grams of iron per litre with a cathodic current density of 0·002 to 0·0065 ampere per sq. cm. With the highest current density, a stirrer was used. The anodes of wrought iron were enclosed in linen bags, and the surface of the bath protected from the air by a layer of solid paraffin. The iron, after removal of hydrogen, contained over 99·9% of iron, but difficulty was experienced with the anode mud.

T. E.

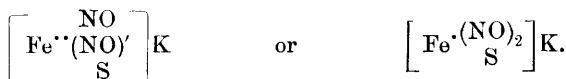
Optical Method for Determining the Relative Hardness of Contiguous Structural Elements of Alloys. M. K. CIGLER (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 584—591).—Soft iron nails were heated in boiling sulphur. Sections were prepared, and the hardness of the different parts determined by an optical method. The results show that the first product of the interaction of iron and sulphur at 448° is ferrous sulphide, which is afterwards converted into ferric sulphide by the further action of the sulphur.

T. H. P.

Probable Constitutional Formulæ of the Ferronitrosulphides. ITALO BELLUCCI and PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 545—552. Compare this vol., ii, 499).—The authors have studied (1) the conversion of ferronitrosulphides of the first series into those of the second series, which takes place according to the equation $2[Fe_4(NO)_7S_3]K + 4KHO = 6[Fe(NO)_2S]K + Fe_2O_3 + N_2O + 2H_2O$, and (2) the reverse change, which is expressed by the equation $4[Fe(NO)_2S]K + CO_2 + H_2O = [Fe_4(NO)_7S_3]K + H_2S + KNO + K_2CO_3$. Consideration of these results and of the products of decomposition of the anions $[Fe_4(NO)_7S_3]'$ and $[Fe(NO)_2S]'$ in alkaline and acid media (*loc. cit.*) leads the authors to propose for ferronitrosulphides of the first series the formula



and for those of the second series the formula



All the known reactions of the ferronitrosulphides are explained by either pair of these formulæ. T. H. P.

Alloys of Lead and Cobalt. F. DUCCELLIEZ (*Bull. Soc. chim.*, 1908, [iv], 3, 621—622).—Apparently homogeneous alloys of lead and cobalt can be obtained by subjecting mixtures of the two metals to hydraulic pressure, and then heating the masses so prepared at 1400° in magnesia crucibles in a current of hydrogen. Products made in this way and containing from 22.8% to 95.1% of cobalt behaved as mixtures of the two metals, and did not contain any definite compound. Vigouroux has already shown that, in like manner, nickel and lead form no definite compound (*Proc. verb. Soc. Sci. phys. nat., Bord.*, Nov. 21, 1907). T. A. H.

Reduction and Oxidation of Nickel Oxide under the Ordinary and High Pressures. WLADIMIR IPATIEFF (*J. pr. Chem.*, 1908, [ii], 77, 513—532. Compare Moissan, *Abstr.*, 1881, 74).—A study of the part played by nickel oxide in the mechanism of catalytic reductions (*Abstr.*, 1907, i, 828). The results of experiments on the action of hydrogen on nickelic and nickelous oxides at varying temperatures and under different pressures are tabulated. It is found that nickelic oxide is reduced to nickel by hydrogen under the ordinary pressure at 190 — 200° , whereas nickelous oxide, which appears to be present always in commercial nickelic oxide, is not reduced under the ordinary pressure below 200° ; but under high pressures it is reduced at 172° , unless first heated before the blowpipe, when reduction takes place only slowly at 250° .

If reduced below 270° and exposed to air at the temperature of the reduction, nickel inflames and is oxidised to nickelous oxide, but, if reduced at 270 — 280° , it is oxidised by dry air or oxygen only at 350° , or completely, forming nickelous oxide, at 400° , and can then be reduced by hydrogen under the ordinary pressure only at 300° . The temperature of oxidation of reduced nickel is lowered by the presence of moisture. Nickelous oxide is not oxidised by dry or moist air or oxygen under the ordinary or higher pressure within the temperature interval 220 — 480° .

Experiments on the reduction of the oxides of nickel by hydrogen under high pressures in presence of benzene show that, under these conditions, nickelic oxide is reduced to only a very slight extent at 250° , but the reduction of nickelous oxide takes place at the same temperature, 172° , as in the absence of benzene. If heated before the blowpipe, nickelous oxide reduces benzene catalytically only above 200° , and is itself only very slightly reduced.

These results are in agreement with the author's view that the catalyst in such reductions is nickelic oxide, and that the reduction is facilitated by the presence of moisture. G. Y.

Isomerism of Chromium Salts. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1908, 58, 317—324. Compare this vol., i, 506, 507, 508).—The paper contains a summary and bibliography of the 29 types of isomerism which have so far been observed for chromium salts. G. S.

Chromium Chlorosulphate. RUDOLF F. WEINLAND and TH. SCHUMANN (*Zeitsch. anorg. Chem.*, 1908, **58**, 176—182. Compare Abstr., 1906, ii, 233; 1907, ii, 623).—A green chlorosulphate of chromium, $[\text{CrCl}_5\text{H}_2\text{O}]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, in which the SO_4 group, but not the chlorine, is ionised, is already known (compare Recoura, Abstr., 1902, ii, 563; Weinland, *loc. cit.*). The authors have now prepared the isomeric compound $[\text{CrSO}_4 \cdot 5\text{H}_2\text{O}]\text{Cl}$, in which the chlorine, but not the SO_4 , is present as ion, as follows. Violet chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$, is heated at 80° until it loses $3\frac{1}{2}\text{H}_2\text{O}$ and is uniformly green, then dissolved in water, kept for three hours, cooled, and saturated with hydrogen chloride, when the salt in question separates as a green, crystalline powder.

When hydrogen chloride is led for a short time into a cooled saturated solution of the compound $[\text{CrCl}_5\text{H}_2\text{O}]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, a salt of the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ separates in slender, bluish-green needles. As rather more than two-thirds of the chlorine is precipitated by silver nitrate in nitric acid solution, the salt is probably a monochlorochromium dichloride (compare Bjerrum, Abstr., 1907, ii, 622).

G. S.

Complex Molybdates of the Rare Earths. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 540—545).—Conductivity and cryoscopic measurements of salts of the rare earths with strong acids (compare Muthmann, Abstr., 1898, ii, 586; Ley, Abstr., 1900, ii, 67; Meyer and Aufrecht, Abstr., 1904, ii, 175) show that, in aqueous solution, these salts are highly dissociated and hence only slightly hydrolysed. The rare earth metals have therefore a high electro-affinity, which is certainly greater than that of aluminium. The present paper describes the first of a series of investigations on the tendency of the rare earth metals to form complex ions, a tendency which is in inverse ratio to the electro-affinity.

Ammonium ceromolybdate, $(\text{NH}_4)_6\text{Ce}_2\text{Mo}_{14}\text{O}_{48} \cdot 24\text{H}_2\text{O}$, forms orange-red, monoclinic prisms, which give a solution of the same colour, whilst *ammonium lanthanomolybdate*, $(\text{NH}_4)_6\text{La}_2\text{Mo}_{14}\text{O}_{48} \cdot 24\text{H}_2\text{O}$, forms white, transparent crystals having a faint yellow tint.

T. H. P.

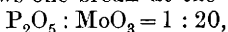
Silicides of Tungsten and of Molybdenum. EDOUARD DEFACQZ (*Bull. Soc. chim.*, 1908, [iv], **3**, 577—578).—A question of priority (compare Abstr., 1907, ii, 475, 676; Hönigschmid, *Chem. Zeit.*, 1907, **31**, 595; Abstr., 1907, ii, 877).

T. A. H.

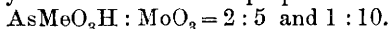
Complex Acids. I. ARTURIO MIOLATI and R. PIZZIGHELLI (*J. pr. Chem.*, 1908, [ii], **77**, 417—456).—A simple method for the study of the capacity of acids to form complex compounds with other acids has now been founded on the employment of the electrical conductivity as an indicator on the neutralisation of acids (Abstr., 1901, ii, 381). If an increasing amount of a substance is added to a solution of a second substance with which it reacts, some property of the solution, such as the specific electrical conductivity, must be a linear function of the proportion of the two substances in the solution. When the reaction is complete, a further addition of the substance must influence

the property measured to another extent, and hence a break must occur in the graph representing the rate of change. If two reactions take place successively, the graph must show two breaks, but, if the reactions are simultaneous, the property in question cannot be a linear function, and caution is required in interpreting the curve. In the light of these considerations, the authors have determined the electrical conductivities of solutions of molybdic acid containing varying amounts of other acids.

The graph for the electrical conductivity of solutions of molybdic and phosphoric acids shows one break at the proportion



whilst that for solutions of molybdic acid and disodium hydrogen phosphate has two breaks at the proportions $\text{P}_2\text{O}_5 : \text{MoO}_3 = 1 : 5$ and $1 : 16$. Breaks occur in the graph for solutions of molybdic and arsenic acids at $\text{As}_2\text{O}_5 : \text{MoO}_3 = 1 : 5$ and $1 : 20$, and in the graph for molybdic and methylarsonic acids at the proportions



Complex compounds of molybdic and methylarsonic acids have not been described. The graph for molybdic and cacodylic acids has one break at $\text{AsMe}_2\text{O}_2\text{H} : \text{MoO}_3 = 1 : 4$. The bearing of these observations on the existence of complex salts described by previous authors is discussed.

The basicity of phosphotungstic acid has been studied in the manner employed in the study of yellow phosphomolybdic acid (Abstr., 1904, ii, 263). Similar results are obtained, the electrical conductivity diminishing until 6 mols. of sodium hydroxide have been added, and then increasing steadily until the addition of 26 mols. of sodium hydroxide, the increase being still more rapid on further additions of alkali.

The paper closes with a long discussion of the constitution of the complex inorganic acids. Those containing 12MoO_3 or 12WO_3 may be conceived as derivatives of acids of the type $(\text{Mo}_6\text{H}_n)_x$, in which the whole of the co-ordinated oxygen atoms are displaced by the bivalent anion Mo_2O_7 or W_2O_7 . The basicity of the resulting acid is the difference between the sum of the basicities of the co-ordinated, negative acid groups and the positive valency of the central atom. Hence phosphomolybdic, $[\text{P}(\text{Mo}_2\text{O}_7)_6]\text{X}_7$, phosphotungstic, $[\text{P}(\text{W}_2\text{O}_7)_6]\text{X}_7$, and arsenomolybdic, $[\text{As}(\text{Mo}_2\text{O}_7)_6]\text{X}_7$, acids are heptabasic, whereas silicomolybdic, $[\text{Si}(\text{Mo}_2\text{O}_7)_6]\text{X}_8$, silicotungstic, $[\text{Si}(\text{W}_2\text{O}_7)_6]\text{X}_8$, and cobaltomolybdic, $[\text{Co}(\text{Mo}_2\text{O}_7)_6]\text{X}_8$, acids are octabasic. If the complex acid contains less than twelve MoO_3 groups, the number of these is related to the number of hydroxyls in the anion, each hydroxyl being capable of combining with two MoO_3 groups. Thus the conductivity graph for mixtures of molybdic and dichloroplatinic acids has breaks at the proportions $\text{H}_2\text{PtCl}_2(\text{OH})_4 : \text{MoO}_3 = 1 : 2$ and $1 : 8$. G. Y.

Electrolytic Formation of Peroxygenated Compounds of Tin. ANGELO COPPADORO (*Gazzetta*, 1908, 38, i, 489—508).—When concentrated alkali stannate solutions are electrolysed at low temperatures and with low current densities, perstannates are formed, owing to anodic oxidation. The proportion of perstannate formed is only

small, a condition of equilibrium being soon reached between the perstannate formed and decomposed. The addition of alkali fluoride to the electrolyte increases the rate of formation of the perstannate, but does not change the final equilibrium, so that the yield of perstannate remains unaltered. The presence of fluorine ions does not increase the anodic potential during electrolysis, and the conclusion is drawn that the fluorine enters into combination, forming either a stable perfluorine salt or an intermediate compound which favours the oxidation of the stannate. The fact that perstannates are formed even at low current densities shows that their formation is due to secondary oxidation of the stannate by the nascent oxygen rather than by the union of two stannic anions. The yield of perstannate diminishes rapidly as the temperature of electrolysis rises. In solution at the ordinary temperature, the perstannates undergo gradual decomposition, yielding stannates.

T. H. P.

Phosphides of Titanium and Zirconium. JULIUS GEWECKE (*Annalen*, 1908, **361**, 79—89. Compare Moissan, *Abstr.*, 1895, ii, 272; Chenevix, *Gmelin-Kraut*, II, 2, 15; Rose, *Ann. Phys. Chem.*, 1832, [ii], 24, 141; Wöhler, *Annalen*, 1853, **87**, 375).—When treated with hydrogen phosphide in the cold, titanium chloride forms a yellow, crystalline substance, which on being heated decomposes, yielding hydrogen phosphide, hydrogen chloride, and small amounts of titanium phosphide. A sketch is given of a convenient apparatus for carrying out these reactions. Titanium phosphide, TiP , forms a brittle mass with metallic lustre, D_4^{25} 3.95, burns when heated in air or when fused with potassium nitrate, is a conductor of electricity, is insoluble in dilute or concentrated acids or alkalis, and is oxidised to only a small extent when boiled with *aqua regia* or heated with fuming nitric acid at 250—300°. When heated in chlorine, the phosphide burns, forming white fumes of titanium chloride and phosphorus pentachloride, which condense as a yellow *sublimate*, $\text{TiCl}_4\text{,PCl}_5$.

Zirconium phosphide, ZrP_2 , forms a glistening, grey mass, D_4^{25} 4.77, and closely resembles the titanium phosphide in its physical and chemical properties. When sublimed in a current of hydrogen over heated potassium phosphide, zirconium tetrachloride formed a black mass containing potassium chloride, zirconium, phosphorus, and oxygen, which may have been derived from the presence of zirconium oxychloride.

Silicon tetrachloride reacts with hydrogen phosphide, forming a *silicon phosphide*, whereas thorium tetrachloride does not appear to react even at high temperatures.

G. Y.

Thorium Oxyfluoride and Fluoride. ED. CHAUVENET (*Compt. rend.*, 1908, **146**, 973—974).—When hydrated thorium fluoride (Chydenius, *Jahresb.*, 1863, 194) or silicofluoride is heated at 800° in a platinum tube in a current of dry hydrogen fluoride, it is converted into the *oxyfluoride*, ThOF_2 , a white, insoluble, amorphous powder yielding hydrogen fluoride on decomposition with sulphuric acid.

Thorium fluoride, ThF_4 (Moissan and Étard, *Abstr.*, 1896, ii, 422;

Duboin, this vol., ii, 297), is obtained as an amorphous powder, which cannot be decomposed by sulphuric acid when thorium bromide or chloride is heated at $350-400^{\circ}$ in a current of dry hydrogen fluoride.

M. A. W.

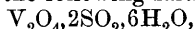
Mercuri-iodides of Thorium and Aluminium. ANDRÉ DUBOIN (*Compt. rend.*, 1908, **146**, 1027—1028).—When thorium iodide, prepared by the action of hydriodic acid on thorium carbonate, and mercuric iodide are alternately dissolved in water at a gentle heat to saturation, the liquid on cooling deposits, first, mercuric iodide and then a mass of extremely deliquescent crystals of *thorium mercuri-iodide*, $\text{ThI}_4 \cdot 5\text{HgI}_2 \cdot 18\text{H}_2\text{O}$, easily decomposed by water, and quickly changed by exposure to air, becoming red. The mother liquor is dark brown in colour, owing to the presence of free iodine, and the latter is removed by shaking with mercurous iodide, giving a yellow liquid, D¹⁸⁹ 3.512.

It has been shown previously that a saturated solution of mercuric iodide in aluminium iodide solution deposits an oxyiodide when left in dry air (Abstr., 1907, ii, 955). The mother liquor from this experiment, kept since then in the presence of anhydrous baryta, has deposited a very small quantity of elongated prisms of *aluminium mercuri-iodide*, $\text{AlI}_3 \cdot \text{HgI}_2 \cdot 8\text{H}_2\text{O}$, which is extraordinarily deliquescent, but dissolves in water without decomposition.

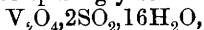
E. H.

Hypovanadic Acid and Some of its Compounds. GUSTAVE GAIN (*Ann. Chim. Phys.*, 1908, [viii], **14**, 224—228).—A résumé of work already published, with additional observations (compare Abstr., 1907, ii, 32, 97, 558, 627; 1908, ii, 284). The two isomeric hydrates of hypovanadic acid dissolve readily in dilute aqueous solutions of hydrogen chloride or hydrogen bromide, and by evaporation the corresponding halogen salts are obtained in well-defined crystals (compare Guyard, Abstr., this Journ., 1876, ii, 173; Crow, *ibid.*, 453). The chloride, $\text{VO}_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, is deep green when prepared from the green hydrate, but is blue when obtained from the rose hydrate, $\text{VO}_2\text{Br}_3 \cdot 5\text{H}_2\text{O}$, and forms large, rectangular tablets; an aqueous solution is intensely red, but becomes deep blue on the addition of hydrogen bromide in excess. The iodide was not obtained sufficiently pure for analysis; it forms a red aqueous solution turning blue on the addition of hydrogen iodide.

When the mixture of oxides (V_2O_3 and V_2O_4) resulting from the calcination of ammonium vanadate is treated in boiling aqueous solution with sulphur dioxide, a blue liquid is obtained, from which, under suitable conditions, the following salts can be isolated:



a blue, crystalline crust soluble in water; $\text{V}_2\text{O}_4 \cdot \text{SO}_2 \cdot 4.5\text{H}_2\text{O}$, a deep green, amorphous substance sparingly soluble in cold water;



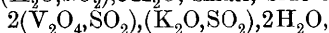
small, sky-blue crystals; $\text{V}_2\text{O}_4 \cdot 2\text{SO}_2 \cdot 8\text{H}_2\text{O}$, blue crystals. An aqueous solution of selenious acid dissolves the hydrate of hypovanadic acid, and, by allowing the solution to evaporate, pale blue, microscopic crystals of $\text{V}_2\text{O}_4 \cdot 2\text{SeO}_2 \cdot 4\text{H}_2\text{O}$ are obtained.

The author has also succeeded in obtaining a number of definite crystalline compounds by the union of hypovanadic acid with sulphuric acid. Some of these have already been described by Gerland and by Crow (*loc. cit.*), although only in the gummy or amorphous condition (compare Koppel, *Abstr.*, 1902, ii, 85; 1903, ii, 551). A description of the following salts is given: $V_2O_4 \cdot 2SO_3 \cdot 3H_2O$, elongated, deep blue prisms; $V_2O_4 \cdot 2SO_3 \cdot 5H_2O$, very bright blue, microscopic crystals; $V_2O_4 \cdot 4 \cdot 5SO_3 \cdot 11H_2O$ and $V_2O_4 \cdot 5SO_3 \cdot 12H_2O$ are very hygroscopic, blue, microcrystalline powders; $V_2O_4 \cdot 2 \cdot 5SO_3 \cdot 9H_2O$, azure-blue crystals; on ignition V_2O_5 is obtained; $V_2O_4 \cdot 3SO_3 \cdot 10H_2O$, turquoise-blue crystals; $V_2O_4 \cdot 3 \cdot 5SO_3 \cdot 10H_2O$, stable, bluish-green crystals. A new *selenate* has also been obtained in the form of a blue, microcrystalline powder having the composition $V_2O_4 \cdot 3 \cdot 5SeO_3 \cdot 7H_2O$.

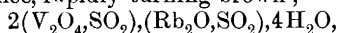
Hypovanadic acid dissolves in nitric acid, forming a blue solution, but, when allowed to evaporate, this deposits the red hydrate of vanadic acid. A nitrate could not be obtained. The following nitrites are obtained by dissolving $V_2O_4 \cdot 2H_2O$ in aqueous solutions of the alkali nitrites: $(V_2O_4 \cdot N_2O_3)(K_2O \cdot N_2O_3) \cdot 4H_2O$, colourless, regular hexagonal prisms; $[V_2O_4 \cdot N_2O_3][(NH_4)_2O \cdot N_2O_3] \cdot 6H_2O$, pale yellow prisms. The corresponding *sodium* salt is obtained as a colourless, very unstable powder.

Hypovanadic acid unites with many organic acids, forming stable salts. The formate, $V_2O_4(CHO_2)_2 \cdot 2H_2O$, is obtained as azure-blue crystals, which are less soluble in alcohol than in water. The *acetate*, $V_2O_4(C_2H_3O_2)_2 \cdot 5H_2O$, is a greenish-blue, crystalline mass. The *oxalate*, $V_2O_4(C_2O_4)_3 \cdot 7H_2O$, forms elongated, greenish-blue prisms. The *malonate* and *salicylate* are blue, whilst the *succinate* is green.

The following new double sulphites have been prepared by treating the alkali hydrogen sulphites with an aqueous solution of hypovanadic acid: $3(V_2O_4 \cdot SO_2) \cdot 2(K_2O \cdot SO_2) \cdot 5H_2O$, small, blue crystals;



large, deep blue crystals; $(V_2O_4 \cdot 2SO_2) \cdot 2[(NH_4)_2O \cdot SO_2] \cdot 2H_2O$, well-formed, greenish-blue crystals; $5(V_2O_4 \cdot SO_2) \cdot 2[(NH_4)_2O \cdot SO_2] \cdot 16H_2O$, a bluish-green substance, rapidly turning brown;



brilliant azure-blue crystals; $(V_2O_4 \cdot SO_2) \cdot 2(Tl_2O \cdot SO_2) \cdot 4H_2O$, emerald-green plates; $2(V_2O_4 \cdot SO_2) \cdot (Na_2O \cdot SO_2) \cdot 4H_2O$, bright green crystals, sparingly soluble in cold water.

The paper contains an account of the methods adopted for the analysis of the foregoing compounds. W. O. W.

Action of Potassium Iodide and Hydrochloric Acid on Antimonic Acid. A. KOLB and R. FORMHALS (*Zeitsch. anorg. Chem.*, 1908, 58, 189—201. Compare Youtz, *Abstr.*, 1904, ii, 150).—The oxidation of hydriodic acid by antimonic acid in the presence of hydrochloric acid according to the equation $Sb_2O_5 + 4HI \rightleftharpoons Sb_2O_3 + 2H_2O + 2I_2$ is a reversible reaction, and the same equilibrium point can be reached from both sides. The influence of varying concentrations of the reacting substances and of certain other compounds on the equilibrium point has been investigated systematically. When potassium iodide and especially hydrochloric acid are used in considerable excess,

the reaction is practically complete in the direction indicated by the upper arrow, which is of importance for the volumetric estimation of antimony compounds. Tartaric acid diminished the amount of iodine set free, and neutral salts increase it, as does rise of temperature. If cadmium iodide is used instead of potassium iodide, less iodine is set free.

The probable mechanism of the reaction is discussed.

G. S.

Hardness of Alloys. III. ALEXIS V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 665—673. Compare Abstr., 1907, ii, 869).—The hardness curve for alloys of antimony and bismuth exhibits a maximum at the composition $\text{Sb}_{4.05}\text{Bi}$, but does not indicate whether or not these two metals form a continuous series of solid solutions (compare Hüttner and Tammann, Abstr., 1905, ii, 327). The hardness curve for aluminium-tin alloys has also been constructed. The hardness falls rapidly as the percentage of tin present increases from 0 to 30, then rises to reach a maximum for 40% of tin, falls again, and attains another maximum very nearly at the composition AlSn .

T. H. P.

Atomic Weight of Bismuth. II. Synthesis of Bismuth Oxide. ALEXANDER GUTBIER and LOTHAR BIRCKENBACH (*J. pr. Chem.*, 1908, [ii], 77, 457—471. Compare Abstr., 1906, ii, 92).—Bismuth oxide has been formed by the action of nitric acid on three specimens of bismuth: (a) prepared by Schneider's process (Abstr., 1895, ii, 114); (b) prepared by a modification of Classen's method (Abstr., 1890, 706; 1891, 525; 1892, 20), and (c) a specimen supplied by Classen. Four experiments with (a) gave the mean value $\text{Bi} = 208.03$; four with (b) gave $\text{Bi} = 207.99$, whilst two with (c) gave $\text{Bi} = 208.00$. The extreme values obtained were $\text{Bi} = 207.88$ and $\text{Bi} = 208.20$. The value 208.0 ($\text{O} = 16$), which is now recommended as the atomic weight of bismuth, is in agreement with the joint results of the work of Schneider (*loc. cit.*) and Löwe (Abstr., 1884, 558).

G. Y.

Electrolysis of Bismuth Salt Solutions. ALEXANDER GUTBIER, LOTHAR BIRCKENBACH, and R. BÜNZ (*Chem. Zentr.*, 1908, i, 1256; from *Sitzungsber. Erlangen Physik-Med. Soc.*, 39, 172—175).—The previously observed bronze-coloured coating which covers the anode in a bismuth solution, and settles as small, lustrous plates to the bottom of the vessel, becomes redissolved on continuing the electrolysis. It is, however, formed in largest quantities from a solution of 20 grams of bismuth in 200 c.c. of nitric acid ($\text{D } 1.4$) diluted to 1500 c.c. with water containing 300 c.c. of concentrated ammonia solution in 2 litres, using $1.0\text{--}1.5^{-2}$ amp./qcm. When the electrolyte is slowly replaced by water, the metallic lustre of this substance suddenly disappears, and a light brown, amorphous powder remains, consisting of 97.93% Bi_2O_3 with about 2% active oxygen.

J. V. E.

Optical Properties of Colloidal Gold Solutions. WALTER STEUBING (*Ann. Physik.*, 1908, [iv], 26, 329—371).—When gold chloride solutions are reduced by means of hydrazine, red, blue, or violet

colloidal solutions of gold may be obtained. The solutions are very stable, and the colour depends on the temperature, the concentration, and the rapidity with which the reducing agent is mixed with the gold solution. The blue and red solutions both contain particles of uniform size, and both colours are given by solutions which contain particles of very different sizes. The colour of the colloidal gold does not therefore depend on the size of the particles, but there appear to be two distinct kinds of particles, the one giving rise to the red, and the other to the blue colour. The violet solutions contain both kinds of particles.

The author describes a method of measuring the light emitted laterally from the colloidal solutions when these are subjected to the influence of rays in a particular direction. This diffused light represents a very small fraction of the incident light, which is apparently absorbed. It is plane polarised to a large extent, and in the case of the light emitted at right angles to the direction of the incident beam, the proportion of plane polarised light has a maximum value of 90%.

When examined in the ultra-microscope by means of polarised light, the red and blue solutions exhibit considerable differences, and these are supposed to be due to differences in the geometrical form of the two kinds of particles. The laterally emitted light from the red solutions exhibits a maximum intensity in the region $560-570\ \mu\mu$; that from the blue solutions a feeble maximum at $570\ \mu\mu$ and a more strongly pronounced one in the red region. Violet solutions behave like a mixture of the red and blue solutions. A maximum of absorption is shown by red solutions at $525-530\ \mu\mu$, and a minimum by blue solutions at $490\ \mu\mu$; the absorption effects of the blue solutions are, however, not so sharply defined as those of the red.

Greyish-green colloidal solutions of gold have also been obtained by reduction with hydrazine in presence of a little potassium hydroxide. These solutions emit very little light laterally, and show fairly uniform absorption. It is supposed that the particles in these solutions are formed by condensation of the particles which give rise to the red and blue colours.

H. M. D.

Action of Silver Nitrate on Chloroauric Acid and the Preparation of Fulminating Gold. JULES JACOBSEN (*Compt. rend.*, 1908, 146, 1213—1214).—On adding silver nitrate to a solution of chloroauric acid, a brown precipitate is obtained according to the equation $\text{HAuCl}_4 + 4\text{AgNO}_3 + 3\text{H}_2\text{O} = \text{Au}(\text{OH})_3 + 4\text{AgCl} + 4\text{HNO}_3$.

By the action of ammonia, this is converted into fulminating gold, which has the formula $\text{Au}(\text{OH})_2 \cdot \text{NH}_3$ or $(\text{AuN}, 2\text{H}_2\text{O}), \text{H}_2\text{O}$. The substance, when washed with aqueous ammonia, followed by water, alcohol, and ether, and dried at a low temperature, explodes violently when touched with a knife. The explosion takes effect in a downward direction. On boiling fulminating gold with potassium hydroxide, a blackish-brown, flocculent product is obtained, which is still more explosive, and probably has the composition $\text{Au}(\text{OH})_2 \cdot \text{NH} \cdot \text{Au}(\text{OH})_2$.

J. C. C.

Passivity of Platinum. RUDOLF RUER (*Zeitsch. Elektrochem.*, 1908, 14, 309—314).—Previous experiments (Abstr., 1903, ii, 407)

led to the view that the insolubility of a platinum anode was due to a coating of a peroxide. The coatings observed by Marie (Abstr., 1907, ii, 698) may be the peroxide in question. Further experiments show that the coating is formed with pure platinum in sulphuric acid containing from $2\frac{1}{2}$ to 10% of the acid. In stronger acids, no visible coating is formed. The coating is yellow to brown in colour; it is insoluble in cold sulphuric acid alone, but dissolves in presence of a reducing agent. It is a good conductor of electricity. The potential of a coated electrode is the same as that of one saturated with oxygen; it falls gradually to the potential of platinum charged with atmospheric oxygen. The coating has therefore the properties of the hypothetical peroxide, but, since it is not formed in 50% sulphuric acid and, in fact, dissolves when a coated plate is used as anode in acid of this strength, it cannot explain the insolubility of platinum in the strong acid.

T. E.

Definite Compounds of Silicon and Palladium. PAUL LEBEAU and PIERRE JOLIBOIS (*Compt. rend.*, 1908, 146, 1028—1031).—Boussingault has shown (Abstr., 1876, 47; 1879, 286) that palladium combines with silicon to the extent of 3.9%. When an intimate mixture of palladium and crystallised silicon is introduced into a porcelain crucible heated by means of a blowpipe, a contraction first occurs, and then, at 500—600°, combination is produced, accompanied by a bright incandescence and sufficient elevation of the temperature to cause complete fusion. The fusion temperature of mixtures of silicon and palladium varies largely with the content of silicon. With an increasing proportion of silicon, the m. p. falls from 1587° for pure palladium to the minimum 670°, corresponding with 6% of silicon; it then rises rapidly to the maximum 1400° for 11.76% of silicon (corresponding with SiPd_2); the m. p. then again falls, reaching a second minimum of 750° for 16% of silicon, and afterwards rising to a second maximum of 990° for 21% of silicon (corresponding with SiPd). With 25% of silicon there occurs another minimum of 825°, corresponding with an eutectic, and then the m. p. rises gradually to that of pure silicon. Observation of the rate of cooling of the mixtures shows that, for all those containing less than 20% of silicon, a well-defined slackening takes place, followed by a recalescence, the rise in temperature being sufficient to raise the mass to a bright red heat. The increase in incandescence so observed starts at a point in the mass and spreads in a manner similar to the crystallisation of a super-saturated solution, and the similarity in the two phenomena is further shown by the fact that the recalescence is prevented by contact of the mixture at the commencement of solidification with a small fragment of a similar ingot previously prepared. The behaviour, on cooling, of mixtures containing more than 21% of silicon, indicates the presence of the eutectic ($\text{SiPd}-\text{Si}$).

Comparison of different ingots which have undergone recalescence with the same products, tempered before the appearance of this phenomenon, reveals an interesting difference in structure. In the latter case, two homogeneous constituents are always observed, and are very easily distinguished by oxidation. When, however, recal-

escence has occurred, the more oxidisable constituent is besprinkled with small crystals.

The ingots corresponding with the compositions SiPd_2 and SiPd are both homogeneous, but only the latter silicide has been isolated in a crystalline form. When ingots containing above 60% of silicon are treated with dilute potash, the free silicon dissolves, leaving small, very brilliant, bluish-grey fragments of *palladium silicide*, SiPd , D¹⁵ 7·31, which, when hot, is attacked by fluorine and chlorine, is superficially oxidised by oxygen at a dull red heat, is attacked by cold nitric acid and aqua regia, but not by hydrochloric or sulphuric acid, and is slowly attacked by alkali hydroxides.

E. H.

Mineralogical Chemistry.

Proustite and Argentite from Colorado. FRANK R. VAN HORN (*Amer. J. Sci.*, 1908, [iv], 25, 507—508).—A vein of argentiferous galena occurring in the California or Bell mine near Montezuma in Summit Co., Colorado, contains blende and chalybite together with some proustite (anal. I), and argentite (anal. II); the last two are massive and intimately intermixed with quartz:

	Ag.	As.	Sb.	S.	Insol.	Total.
I.	67·60	13·85	0·93	17·40	—	99·78
II.	83·57	—	—	12·66	3·62	99·85

L. J. S.

Composition of Certain Chilean Caliches. FRANZ W. DAFERT [with A. HALLA and R. WASCHATA] (*Monatsh.*, 1908, 29, 235—244).—The results of complete analyses of several samples of natural Chili saltpetre from Santa Clara are recorded. It is found that, although several caliches contain perchlorate, there are others which do not, whilst all contain more or less iodate. As a rule, the caliches rich in sodium nitrate also contain considerable quantities of potassium nitrate and small amounts of chromate.

The author discusses the bearing of his results on the various theories which have been put forward to explain the formation of saltpetre deposits.

W. H. G.

Paligorskite Group. A. FERSMANN (*Bull. Acad. Sci. St. Petersburg*, 1908, [vi], 637—666).—The author makes a critical comparison of all the analytical data published concerning the members of the paligorskite group, which he divides into the following classes: (1) Paramontmorillite, having the general composition $H_{12}Al_2Si_4O_{17}$; (2) α -paligorskite, $H_{32}Mg_2Al_4Si_{11}O_{46}$; (3) β -paligorskite, $H_{20}Mg_2Al_2Si_7O_{29}$; (4) α -pilolite, $H_{23}Mg_4Al_2Si_{10}O_{41}$; (5) β -pilolite, $H_{36}Mg_6Al_2Si_{13}O_{53}$; (6) parasepiolite, $H_8Mg_2Si_3O_{12}$; (7) ferruginous paligorskite. The

arrangement under this classification of the minerals known as mountain leather, mountain cork, lassalite, morencite, hydrous anthophyllite, &c., is explained.

The constitution of the basic series of the paligorskite group may be explained by the assumption of an orthosilicate (*A*) in the nucleus and an aluminosilicate or ferrisilicate (*B*) in the side-chain, the relations between these two silicates being expressed by simple whole numbers. In the extreme members of the series, there may be a deviation from these relations, owing to the presence of other silicates in varying proportions. The analytical numbers indicate that the group cannot consist of isomorphous mixtures of the two silicates, *A* and *B*, neither is the constitution in accord with an equivalent substitution of the magnesia of sepiolite by alumina. T. H. P.

A New Variety of Paragonite Mica. PHILIPPE BARBIER (*Compt. rend.*, 1908, 146, 1220—1221).—A specimen of silvery mica, resembling muscovite in appearance, from Mesvres, near Autun, was analysed with the following results: loss on ignition, 4.60 (fluorine is absent); the calcined material gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	K ₂ O.	Na ₂ O.	Li ₂ O.	Total.
49.18	36.56	2.19	3.12	7.63	1.26	99.94

The mineral is therefore a lithium-bearing variety of soda-mica, and for it the name *hallerite* is proposed. L. J. S.

Gedrite from Canada. N. NORTON EVANS and J. AUSTEN BANCROFT (*Amer. J. Sci.*, 1908, [iv], 25, 509—512).—Gedrite, the aluminous variety of anthophyllite, occurs abundantly as a constituent of amphibolite in the township of Harcourt, Haliburton Co., Ontario. The amphibolite is associated with limestone and granite of Laurentian age, and contains, in addition to anthophyllite, garnet and cordierite, with subordinate amounts of quartz, biotite, iron-ore, and rutile. The anthophyllite has the form of sheaves of long, narrow crystals of a delicate clove-brown colour and characteristic pleochroism; it is optically negative with straight extinction. Analysis of material separated from the powdered rock by means of an electromagnet and heavy liquids gave the following results, agreeing with Rammeisberg's formula $4\text{RSiO}_3 \cdot \text{Al}_2\text{O}_3$, where $\text{R} = \text{Mg}, \text{Fe}, \text{H}_2$:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	K ₂ O, Na ₂ O.	Total.
44.32	16.04	2.80	16.88	0.09	0.77	15.95	1.31	1.86	100.02

The mineral is thus very similar to the original gedrite from Gédres, in the Pyrenees. Neither anthophyllite nor cordierite have before been recorded from Canada. L. J. S.

Delorenzite, a New Mineral. FERRUCCIO ZAMBONINI (*Zeitsch. Kryst. Min.*, 1908, 45, 76—81*).—The mineral occurs associated with strüverite (this vol., ii, 398) in the pegmatite of Craveggia, Piedmont. The crystals are orthorhombic [$a:b:c = 0.3375:1:0.3412$], with prismatic habit closely resembling polycrase; they are black and opaque, but thin splinters are brown and isotropic. The fracture is conchoidal, with a brilliant pitchy to resinous lustre. Hardness

* and *Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 113—118.

$5\frac{1}{2}$ —6 ; D about 4·7 ; the mineral is strongly radioactive. Analysis by J. S. Štěrbá gave :

TiO ₂ .	SnO ₂ .	UO ₂ .	Y ₂ O ₃ .	FeO.	Total.
66·03	4·33	9·87	14·63	4·25	99·11

This corresponds with the formula $2\text{FeO}, \text{UO}_2, 2\text{Y}_2\text{O}_3, 24\text{TiO}_2$, or written as a metatitanate, $2\text{FeTiO}_3, \text{U}(\text{TiO}_3)_2, 2\text{Y}_2(\text{TiO}_3)_3, 7(\text{TiO})\text{TiO}_3$.

The new mineral is thus nearer to yttrocrasite (Abstr., 1907, ii, 103) than to polycrase in composition.

L. J. S.

Physiological Chemistry.

Influence of the Amount of Carbon Dioxide in the Respired Air on the Changes in Weight of Butterfly Pupæ. MARIA (GRÄFIN) VON LINDEN (*Bied. Zentr.*, 1908, 37, 427—429; from *Arch. Physiol.*, 1907, 162. Compare Abstr., 1906, ii, 95).—Experiments with two varieties of chrysalides show that carbon dioxide is absorbed, and that their existence as chrysalides is more prolonged in an atmosphere rich in carbon dioxide than in air. Carbon dioxide does not act as a narcotic, but acts rather as a stimulant, without, however, causing loss of weight, and the conclusion is drawn that carbon dioxide is a direct nutrient.
N. H. J. M.

The Influence of the Reaction of Blood-plasma on the Formation of Fibrin. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1908, [vi], 27, 518—522).—The addition of salts of calcium to an oxalated plasma produces no coagulum if the mixture is first made acid with acetic acid. The addition of alkalis produces the coagulum as soon as the reaction of the mixture is alkaline, provided that the mixture has not remained acid for very long. If, however, the mixture of oxalated plasma, calcium salt, and acetic acid has stood for a day, the addition of alkali fails to produce a coagulum. In this case, coagulation can be made to take place by the addition of normal serum. The fibrin ferment seems to have been destroyed by remaining for a long time in acid solution.
S. B. S.

Albumose in the Blood. EMIL ABDERHALDEN (*Biochem. Zeitsch.*, 1908, 10, 277—282).—Polemical mainly against Freund. The present author withdraws none of his previous statements regarding the absence of albumoses in blood, blood-serum, and blood-plasma.
W. D. H.

Origin of the Saccharifying Power of Human Saliva. W. MESTREZAT (*Bull. Soc. chim.*, 1908, [iv], 3, 711—713).—Preparations of saliva extracted under aseptic conditions from the parotid and submaxillary glands are shown to possess the property of saccharifying

starch mucilage, that from the parotid gland being the more active. A mixture of the two secretions has a saccharifying power approximately the mean of those due to the two acting separately, and similar to that of ordinary saliva. The hydrolysis of starch by the latter is therefore due to a diastase (ptyalin) of glandular origin, and not to the action of bacteria occurring in the mouth (compare Duclaux, *Traité de Microbiologie*, 1899, 2).
T. A. H.

The Diastase in Cat's Saliva. ANTON J. CARLSON and J. G. RYAN (*Amer. J. Physiol.*, 1908, 22, 1—15).—Diastase is present in the blood in greater concentration than in the saliva; an increase in salivary diastase occurs after intravenous injection of human ptyalin and pancreatic amylase. Concentration of organic solids and of salivary diastase vary together. There is more diastase in the submaxillary than in the parotid saliva. These results were obtained by experiments on the cat; a few experiments made on dogs confirm them.
W. D. H.

Milk Curdling in the Infant's Stomach. ALOIS KREIDL and ALFRED NEUMANN (*Zentr. Physiol.*, 1908, 22, 133—136).—In the stomach of the sucking child and animal, rennin is present, and causes curdling of various kinds of milk. Whether curdling of human milk takes place was not observed directly, but it probably does, for the juice contains both acid and rennin, and curdles human milk *in vitro*.
W. D. H.

Remarks on Aron and Sebauer's Work on the Nutritive Value of Calcium Salts. ARNOLD ORGLER (*Biochem. Zeitsch.*, 1908, 10, 236—239. Compare this vol., ii, 208).—A criticism of Aron and Sebauer's methods and results.
W. D. H.

Specific Dynamic Action of Proteins. NATHAN ZUNTZ (*Zentr. Physiol.*, 1908, 22, 67—68).—The views of Graham Lusk (this vol., ii, 574) on this question are criticised. The heat value of lactic acid in the body is greater, not less, than that of alanine if allowance is made for the unburnt nitrogenous residue it yields. The work of the alimentary canal during digestion, involving as it does muscular and glandular activity lasting for many hours, cannot be a negligible factor in metabolism.
W. D. H.

Metabolism of Injected Proteins, Immunity and Hypersensitiveness. ULRICH FRIEDEMANN and S. ISAAC (*Chem. Zentr.*, 1908, 1, 967; from *Zeitsch. expt. Path. Ther.*, 1907, 4, 830—866).—The authors, in continuation of their former work (*ibid.*, 1905, 1, 573), have sought an explanation of the fate of proteins injected into the organism of dogs and of larger herbivora (goats and sheep). They found that during starvation such proteins cause a general rise in protein decomposition, such as follows protein administration by the alimentary tract. The increased nitrogen excretion will follow the injection of sera, either of the same or of other animals, as well as egg-proteins. In the case of dogs in nitrogenous equilibrium, protein injection on carbohydrate-free diet

causes increased protein decomposition, which can be inhibited by the addition of carbohydrates to the diet. The fact that proteins of different origin exert the same influence on nitrogenous excretion stands in contrast with their behaviour when tested by biological methods (precipitin and complement reactions). The parallelism between the nutrition phenomena and these biological phenomena is entirely wanting, for precipitins can be detected in the blood long after the injected proteins are eliminated from the body. From the facts, the authors conclude that the precipitable substances circulating in the serum are not identical with the injected protein.

The authors also noticed a characteristic phenomenon of hypersensitiveness in the case of dogs, in that a second injection following a preliminary injection of the same quantity of substance often causes acute intoxication leading to a fatal result. They ascribe this to a sudden inundation of the organism with toxic metabolism products, and compare this phenomena with what happens in diabetic coma, uræmia, and the alimentary intoxication observed by Finkelstein in infants. S. B. S.

Proteid Minimum in the Food of Cows. (*Bied. Zentr.*, 1908, 37, 393—413; from 60th and 63rd *Ber. Dänisch. Versuchslab.*, 1906 and 1907).—Nine cows were fed with hay (2.5 kilos.), straw (3.7—4.88 kilos.), and with different amounts of roots (increasing from 30 kilos. in the first period to 45 kilos. in the seventh) and cotton cake (decreasing from 2.5 to 1.5 kilos.). The amount of water consumed diminished as the amount of roots increased, so that the percentage of water in the total food remained about the same (80.8—82.5%). The food contained in the first period 221 grams of protein and 31 grams of amide nitrogen; in the fourth period, 128 and 35 grams respectively. The effect of reducing the amount of nitrogen, is diminution of nitrogen in the fæces and especially in the urine; the amount of excrement remained the same. The percentage of nitrogen in the milk was not altered, but the amount of milk was reduced. The first result of reducing the supply of nitrogen is to diminish the nitrogen of the urine, then that of the fæces, and thirdly that of the milk. When the amount is further reduced, nitrogen from the body is utilised for milk production for a short time, after which the yield of milk rapidly falls. Provided the amount of food is sufficient, the composition is unimportant, and may vary from year to year according to the magnitude of the crops, deficient crops being supplemented with suitable amounts of cake, &c.

Protein nitrogen must be given in sufficient quantity to correspond with the amounts in milk and fæces. Otherwise, even in presence of an excess of amides, nitrogen will be withdrawn from the body; in absence of amides, a further amount of protein nitrogen would be necessary for the production of urine. The economising effect of amides is, it is suggested, to supply material for the kidneys, which can only work properly when producing urea.

The results would seem to indicate, further, that cows require no

nitrogen for maintenance. It is probable, however, that a small amount of nitrogen, a few grams per day, is necessary.

Notwithstanding the, sometimes considerable, amounts of nitrogen as nitrates supplied in the food, no trace of nitrates could ever be detected in the excrementitious matters. Experiments in which nitrates were added to the contents of the large intestine showed that in three days the whole of the nitrate was lost as free nitrogen and some of the original nitrogen as well. In the case of the small intestine, a considerable portion of nitrate was denitrified in a week.

N. H. J. M.

Temperature-coefficient of the Velocity of Nerve Conduction. CHARLES D. SNYDER (*Amer. J. Physiol.*, 1908, 22, 179—201).—The temperature-coefficient of the velocity of conduction in frog's sciatic nerves lies for the most part between 2 and 3.

Exceptions to this rule are assumed to be due to differences in the chemical time reaction of the conducting substances in the nerve. The meaning of the results is discussed at length, but the most important conclusion reached is that nerve conduction cannot be a purely physical phenomenon.

W. D. H.

The Partition of Lecithin in the Animal Organism. JOSEPH NERKING (*Biochem. Zeitsch.*, 1908, 10, 193—203).—The whole animal, or its organs, was passed through a sausage machine, extracted with hot alcohol, and then with chloroform or ether. The residue of the extract was incinerated, and, from the phosphoric acid in the ash, the amount of lecithin was calculated. In two rabbits, the total yield was 0.36% and 0.4% of the body-weight respectively. In a hedgehog, the percentage reached 0.8. In other cases, the individual organs were examined, and the results are given in tables. The large percentage of lecithin in the hedgehog was again noted, especially in bone marrow and suprarenals; this is possibly related to the comparative immunity against snake-bite this animal possesses.

W. D. H.

Influence of Salts and Non-electrolytes on the Heart. STANLEY R. BENEDICT (*Amer. J. Physiol.*, 1908, 22, 16—31).—Experiments on strips of the turtle's ventricle show that certain substances alter its irritability without inciting rhythmical contractions. The sodium chloride latent period represents the time necessary to reach a condition of tonus suited to rhythmic activity; it is not caused by lack of calcium ions or of oxygen. The sodium chloride arrest is attributed to loss of irritability and not to asphyxiation. Langendorff's hypothesis that the products of activity act as stimuli to rhythmic action is regarded as probable. Excess of oxygen and of diffusible calcium compounds do not increase favourable oxidation as Martin considers. The anion probably plays an active rôle in the action of salt solutions on heart tissue, but under certain conditions non-electrolytes (sugars) may induce a series of beats.

W. D. H.

The Extractives of Muscular Tissue. X. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1908, 55, 466—480).—The main result of these investigations is to show that the base discovered by Gulewitsch and Krimberg, and called by them carnitine, is identical with the base described by Kutscher under the name of novaine.

Meat-extract solution was treated with tannic acid, and the filtrate, after separation of tannic acid, &c., made alkaline with lead hydroxide and evaporated to a small bulk; crystals separated, and the mother liquor was then treated with silver nitrate and barium hydroxide. From the precipitate, a base was obtained, m. p. 239—240°, whereas, according to Gulewitsch, carnosine has m. p. 241—245°. This is apparently identical with Kutscher's ignotine.

From the filtrate from the silver nitrate and barium hydroxide precipitation, a mixture of bases was isolated by means of phosphotungstic acid and mercuric chloride precipitations. From this mixture, the oblitine was separated by taking advantage of the relatively small solubility of the platinichloride; the other bases were separated by fractional precipitation with gold chloride. The greater part consisted of a base agreeing in properties with carnitine and with the base described as novaine. In addition, small quantities of another base were obtained from the last fraction; the composition of this corresponded with the formula $C_6H_{14}O_2N_2$, but it was not identical with lysine.

S. B. S.

Formation of Lactic Acid and Carbon Dioxide in Muscle. P. W. LATHAM (*Bio Chem. J.*, 1908, 3, 193—206).—Theoretical views as to the way in which lactic acid and carbon dioxide may originate from the protein of muscle during the processes of contraction and rigor mortis.

W. D. H.

Chemical Investigations on the Teeth. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1908, 55, 455—465).—The inorganic constituents and loss on destruction of organic matter were estimated. The loss on ignition varied in the different kinds of teeth investigated between 18·33% and 25·99%; the calcium between 27·23% and 31·65%. The greater the former number the smaller the latter. No fluorine could be detected.

S. B. S.

The Cleavage Products of the Egg-shell of Scyllium stellare. FRITZ PREGL (*Zeitsch. physiol. Chem.*, 1908, 56, 1—10).—One hundred parts of the dry and ash-free organic substance of the egg-shell of this dogfish yield glycine, 2·6; alanine, 3·2; leucine and isoleucine, 5·8; proline, 4·4; phenylalanine, 3·3; aspartic acid, 2·3; glutamic acid, 7·2; tyrosine, 10·6; lysine, 3·7; arginine, 3·2; histidine, 1·7; tryptophan, present, and cystine, questionable. These numbers are compared in a table with the results obtained from the shells of *Testudo graeca*, the *membrana testacea* of the hen's egg, with keratin, and with koilin. The figures are very different in each case; the high percentage of tyrosine in the present analysis is striking.

W. D. H.

Elementary Analysis and Distribution of Nitrogen in Various Egg-shells. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1908, 56, 11—17).—The following table contrasts the elementary composition of the egg-shells or membranes examined in the following animals :

	<i>Scyllium stellare.</i>	<i>Pristiurus melanostomis.</i>	<i>Scyllium canicula.</i>	<i>Scyllium catulus.</i>	Membrana testacea of hen.	<i>Coluber natrix.</i>
C	53.92	51.45	53.64	51.50	48.78	54.68
H	7.33	6.61	6.49	6.51	6.64	7.24
N	15.08	14.33	14.23	15.34	16.43	16.37
S	1.44	1.52	1.33	0.88	4.20	0

The following table gives the distribution of nitrogen (Hausmann's method); the figures not in brackets give the percentage of nitrogen in the material; those in brackets, the percentage in relation to total nitrogen :

	Ammonia N.	Melanin N.	Mono-amino N.	Di-amino N.
<i>Scyllium stellare</i>	0.7 (5.09)	0.08 (0.56)	10.96 (79.66)	2.17 (15.8)
<i>Pristiurus mel.</i>	0.75 (5.13)	0.02 (0.14)	9.70 (66.45)	4.2 (28.8)
<i>Scyllium canic.</i>	0.64 (4.49)	0.04 (0.24)	9.21 (64.19)	4.4 (30.75)
Memb. testacea	0.89 (6.6)	0.03 (0.21)	9.81 (72.7)	2.77 (20.5)

W. D. H.

The Relations between Lipoid Liquefaction and Cytolysis. ERICH VON KNAFFL-LENZ (*Pflüger's Archiv*, 1908, 123, 279—293).—The experiments were carried out with sea-urchin eggs (*Strongylocentrotus purpuratus*). They were placed in sea-water to which had been added various substances, such as the ordinary organic solvents, fatty acids, chloral hydrate, bile salts, &c., and then re-immersed in ordinary sea-water and examined under the microscope to determine whether fertilisation, membrane formation, or cytolysis had taken place. The results obtained lead to the conclusion that the essential constituent of a cell-membrane is not a substance of a fatty nature; that the protoplasm is rich in lipoids, and is an emulsion of these substances with proteins; that physical and chemical treatment of the egg, which causes liquefaction of lipoids, causes also cytolysis; that the egg-protein can swell or be dissolved only after a change in the state of aggregation of the fats, and that cytolysis is brought about by the liquefaction of the lipid and subsequent imbibition of water by, or solution of, the protein. All reagents which can liquefy the lipoids and cause cytolysis of the egg can, by short action and suitable concentration, lead to the formation of membranes (fertilisation membranes). The results thus confirm Loeb's hypothesis that membrane formation is due to lipid liquefaction. S. B. S.

Excess of Chlorides in Lymph. ANTON J. CARLSON, J. R. GREER, and A. B. LUCKHARDT (*Amer. J. Physiol.*, 1908, 22, 91—103).—Lymph contains more chlorides than serum; the osmotic pressure of the neck lymph of the dog is higher than that of the serum, but anaesthesia produced by ether or by chloroform reverses this osmotic relation. The excess of chlorides is more than sufficient to account for the difference, and it renders filtration and transudation theories of lymph-formation untenable. The explanation of the excess is to be sought in the

relation of the lymph to the tissues rather than in the relation of the lymph to the blood. W. D. H.

Lymphagogue Action of Lymph. ANTON J. CARLSON, J. R. GREER, and F. C. BECHT (*Amer. J. Physiol.*, 1908, 22, 104—115).—Injection of lymph intravenously increases the flow of lymph from the thoracic duct. There is also an increase from the neck lymphatics, but the experimental evidence of this is not so clear. Among the views advanced to explain this, the hypothesis is put forward that a lymph-forming hormone is produced in the tissues. The formation of lymphatic lymph and tissue lymph do not always run parallel; thus activity of the salivary glands and pancreas do not always increase the lymph flow from those organs. W. D. H.

Comparative Investigations on the Elimination of Iodine after Administration of Potassium Iodide and Saiodin. EMIL ABDERHALDEN and KARL KAUTZSCH (*Chem. Zentr.*, 1908, i, 874; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 716—719. Compare Basch, this vol., ii, 521).—Saiodin [the calcium salt of iodobenenic acid, $(C_{23}H_{42}O_2I)_2Ca$] does not undergo scission after treatment either with steapsin, gastric juice, or pancreatic and gastric juices. After administration of the drug, alkali iodides were sought for in the fæces to determine whether such substances had been excreted by the intestine. They were not found, but the iodine, after full absorption of the saiodin, can be detected in the urine. The rate of excretion, however, is very much retarded when compared with that which follows the administration of potassium iodide. S. B. S.

Excretion of Bromides by the Kidney. WORTH HALE and CASRIEL FISHMAN (*Amer. J. Physiol.*, 1908, 22, 32—42).—After a single dose, the excretion of bromides is much delayed, but the delay is less after successive doses. Iodides are excreted more rapidly. The excretion of calcium bromide and sodium bromide occurs at the same rate. The amount of diuresis holds no absolute relation to the amount of bromide excreted. The observations were made on man. W. D. H.

The Elimination of Alanine by the Urine. THEODOR BRUGSCH and RAHEL HIRSCH (*Chem. Zentr.*, 1908, i, 874; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 947—948).—The authors maintain the correctness of their statement, despite Oppenheimer's adverse criticism (*Abstr.*, 1907, ii, 900), that the assimilation limits of *dl*-alanine during starvation are far below the normal. S. B. S.

The Elimination of Conjugated Glycuronic Acid in the Bile. MANFRED BIAL (*Chem. Zentr.*, 1908, i, 1076; from *Zentr. Physiol.*, 1908, 21, 751—756).—The separation of conjugated glycuronates by means of the bile constitutes a specific secretion, and, under certain conditions, considerable quantities of paired glycuronates are eliminated in this way instead of by the urine. S. B. S.

Origin of Uric Acid and its Relation to Digestion. THEODOR BRUGSCH and ALFRED SCHITTENHELM (*Chem. Zentr.*, 1908, i, 873; from *Zeitsch. exper. Path. Ther.*, 1907, 4, 761—768).—The authors

controvert Hirschstein's view (*Arch. expt. Path. Pharm.*, 1907, 57, 229), according to which at least 70% of the uric acid excreted is due to digestion processes, and therefore appears in the urine after a purine-free diet. They hold rather that the principal part of the uric acid and purine compounds is due to destruction in the organism resulting from the ordinary processes of life. S. B. S.

Glycogen in Mouse Tumours. M. HAALAND (*J. Path. Bact.*, 1908, 12, 439).—There was found to be no relation between the amount of glycogen and the rate of growth in mouse tumours as was stated to be the case by Brault. W. D. H.

Influence of Cold and Exercise on Sugar Excretion in Phloridzin Glycosuria. GRAHAM LUSK (*Amer. J. Physiol.*, 1908, 22, 163—173).—Lüthje states that in pancreatic diabetes, external cold raises the excretion of sugar; this conclusion is doubtful, and has been criticised previously by others. In phloridzin glycosuria, the dextrose: nitrogen ratio is unchanged by feeding on fat, by the application of cold, or by mechanical work. All this proves that sugar is derived from protein and not from fat. Misstatements regarding the magnitude of the dextrose: nitrogen ratio made by others are corrected. W. D. H.

Production of Sugar from Glutamic Acid Ingested in Phloridzin Glycosuria. GRAHAM LUSK (*Amer. J. Physiol.*, 1908, 22, 174—178).—Subcutaneous injection of glutamic acid in phloridzin glycosuria (in a dog) raises the output of sugar. The results, which are stated in the form of tables, support the author's previously expressed views on carbohydrate metabolism. W. D. H.

Effect of Potassium Iodide on Ptyalin. C. H. NEILSON and O. P. TERRY (*Amer. J. Physiol.*, 1908, 22, 43—47).—The addition of small quantities of potassium iodide to saliva increases the amount of maltose formed. When the drug is given by the mouth and the saliva collected, the secretion has its amylolytic power increased, except in a few patients in whom, for some reason, no potassium iodide appeared in the saliva. W. D. H.

Action of Lactic Acid on the Isolated and Surviving Heart of Mammals. E. LOUIS BACKMAN (*Chem. Zentr.*, 1908, i, 1076; from *Skand. Arch. Physiol.*, 1908, 20, 162—196).—The action was investigated by means of the method of Langendorff and Locke with Göthlin's solution (0.63% NaCl, 0.025% CaCl₂, 0.05% KCl, and 30% NaHCO₃) as perfusion medium. In addition to a general vasodilatation, two special actions were noticed, namely, a muscular paralysis with low concentration, and a stimulating action on the motor ganglia of the heart with more concentrated solutions (0.25—0.5% solutions); they confirm Ranke's hypothesis that lactic acid is a cause of peripheral fatigue. S. B. S.

Action of Digitalis and Strophanthus on the Circulation. CARL TIGERSTEDT (*Chem. Zentr.*, 1908, i, 1077; from *Skand. Arch. Physiol.*, 1908, 20, 115—167).—Measurements of blood pressure and

volume lead to the conclusion that the increased pressure produced by digitalis and strophanthus is mainly due to contraction of the vessels. No distinct difference could be detected between the behaviour of digitalis and strophanthus. S. B. S.

The Behaviour of Salicin in the Normal and Diabetic Organism. KAORU OMI (*Biochem. Zeitsch.*, 1908, 10, 258—263).—The alimentary canal contains no ferments which act on salicin, but the liver and kidney of herbivora (rabbit, sheep, ox, pig) contain an emulsin which can be demonstrated by the use of extracts of those organs. In carnivora and man, this action is either slight or absent. In dogs, however, after extirpation of the pancreas, the emulsin action occurs in liver extracts. W. D. H.

Excretion of Ethereal Sulphates after giving Salicin to Normal and Diabetic Dogs. CHASABURO KUSUMOTO (*Biochem. Zeitsch.*, 1908, 10, 264—274).—In herbivora (rabbits), the administration of salicin by the mouth or under the skin causes the excretion of salicylic acid and an increase in the ethereal sulphates of the urine. In normal dogs, this is more marked, especially when the drug is given by the mouth. At least 10% of the amount given is acted on by the emulsin of the tissues. In dogs deprived of the pancreas, this is usually increased. W. D. H.

Atoxyl and Aniline Poisoning. FERDINAND BLUMENTHAL and FRIEDRICH HERSCHMANN (*Biochem. Zeitsch.*, 1908, 10, 240—244).—The toxic effects of atoxyl have been attributed by some to arsenic and by others to aniline poisoning. The latter view is rendered unlikely by the discovery that neither aniline nor *p*-aminophenol-sulphonic acid can be detected in the urine after administration of atoxyl. The drug is apparently excreted in the form of a closely-allied derivative still containing both arsenic and the amino-group. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Reservoir for Storing Aseptic Liquids. LOUIS GAUCHER (*Ann. Chim. anal.*, 1908, 13, 212—214).—The reservoir (flask, or Woolf's bottle, with a syphon) is made entirely of glass without corks, and is so arranged that no air can enter without first having been filtered through a layer of cotton-wool. For details of construction, the illustrations in the original should be consulted. L. DE K.

Behaviour of Algæ to Salts at Certain Concentrations. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 623—629).—Solutions of potassium nitrate, chloride and sulphate, mono- and di-potassium

phosphate, the corresponding salts of sodium, and calcium chloride and nitrate were employed in equal molecular and equivalent concentrations, the standard solution being a 1/10 gram-mol. solution of potassium nitrate. Threads of *Spirogyra nitida* were kept in the solutions at 8—20°.

Potassium nitrate (1.01%) killed all the cells in eight days. In the corresponding calcium nitrate solution, the cells remained healthy much longer, and even in 2.46% solutions most cells seemed normal after two weeks.

Taken altogether, the results show that calcium salts, at moderate concentrations, are less injurious than equivalent amounts of sodium and potassium salts. The injurious action of magnesium salts can only be completely overcome by calcium and not by sodium or potassium salts.

N. H. J. M.

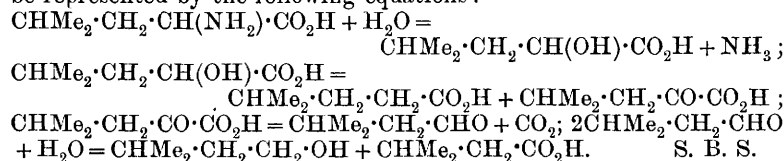
Galvanotropism in Bacteria. JAMES FRANCIS ABBOTT and ANDREW CREAMORE LIFE (*Amer. J. Physiol.*, 1908, 22, 202—206).—*Termo*, *subtilis*, and *typhus* bacilli in a neutral medium form definite gatherings at the cathode, an extremely weak current being used. If grown in acid media, this response is intensified. In alkaline media, they gather at the anode. Bacteria killed by heat show no response.

W. D. H.

The Decomposition of Amino-acids by *Bacillus proteus vulgaris*. PAUL NAWIASKY (*Arch. Hygiene*, 1908, 66, 209—243).—The decomposition products obtained by the action of *B. proteus vulgaris* on various amino-acids were investigated, and in certain cases determined quantitatively. Not all amino-acids are readily attacked by the bacillus. The following acids, which were investigated, are arranged in order according to the readiness with which they are attacked, the most easily decomposable being placed first; aspartic acid, leucine, aminovaleric acid, phenylalanine, tyrosine, arginine, creatine, glycine, alanine. In the cases of *l*-proline and glutamic acid, the decomposition is due entirely to respiration.

Asparagine is readily decomposed into succinic and acetic acids, ammonia, and carbon dioxide. This decomposition can also be brought about by dead bacteria, although slowly and incompletely; the rate of decomposition is proportional to the acting mass of the bacteria.

Aminovaleric acid yields as a decomposition product, butyric acid, and leucine yields amyl alcohol. The decomposition of the latter may be represented by the following equations:



S. B. S.

Nitrification in Black Soils. Influence of Different Factors on Nitrification and the Amounts of Nitrates in the Soil at Different Times of the Year. W. SASANOFF (*J. exper. Landw.*, 1907, 8, 35—38).—Whilst the black soils of Russia are greatly

benefited by superphosphate, sodium nitrate is only required in very small quantities. It is shown that in the Spring the soil may contain very small amounts of nitrates; in such cases, applications of 8 to 30 kilos. of sodium nitrate, not sown broadcast, but drill-sown below the seed, enable the plants to make a start. Later on, nitrification is sufficiently rapid for the requirements of the crop.

In order to promote the accumulation of nitrates in the soil, it is shown that suitable tillage, at the proper time, is of great importance. Farmyard manure was found to be of little, if any, use, whilst undecomposed organic matter, such as straw, hindered nitrification at first. Green manuring with leguminous and other crops has no appreciable effect on nitrification, and has the disadvantage that the growing crop disperses the moisture of the soil and takes up the nitrates.

N. H. J. M.

Inoculation Experiments with *Azotobacter*. JACOB C. LIPMAN and PERCY E. BROWN (28th Ann. Rep. New Jersey State Agric. Exper. Stat., 1906—1907, 141—170).—Successive gramineous crops (oats, maize, rye, maize, rye, and maize) were grown in sixty large cylinders containing sandy loam both without manure and with calcium carbonate, basic slag, farmyard manure, calcium carbonate + farmyard manure, and the same as the last with basic slag in addition. One series was without inoculation, and the others with *Azotobacter Vinelandii* and *A. Beijerincki* respectively. The soils were manured and inoculated the first time about a year before the first seeds were sown, and the inoculation was repeated later on. The rye crops (green) were dug in each time.

The results obtained with the first crop showed on the whole greater yields of dry matter and nitrogen without than with inoculation. An examination of the soil then showed that, whilst *Azotobacter Beijerincki* was abundant and vigorous in the pots manured with calcium carbonate and dung, most of the bacteria had either become feeble or failed altogether in the other pots. The soil conditions would seem to be more unfavourable for *A. Vinelandii*, which is much less abundant than *A. Beijerincki* in the soils of New Brunswick (N. J.), than for *A. Beijerincki*. The second crop (maize) gave somewhat similar results as the first, whilst the third crop (rye) gave greater yields in the inoculated than in the uninoculated pots. Taking the whole series, however, the final results showed no benefit from inoculation, whilst, as regards the soils themselves, there was sometimes a gain and sometimes a loss of nitrogen irrespective of inoculation.

Treatment with carbon disulphide before the fifth crop had no immediate uniform effect, but it seemed to benefit the sixth crop.

N. H. J. M.

Formation and Disappearance of Acetaldehyde under the Influence of Yeasts. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1908, 146, 996—999).—When baker's pressed yeast is vigorously stirred with dilute alcohol for several hours with free access of oxygen, acetaldehyde can be separated by distillation (1—2.5% of the alcohol employed). The action is primarily a vital one. At the

same time, acetaldehyde disappears fairly rapidly when added to yeast in dilute alcohol. G. B.

Effect of Temperature on the Respiration of Apples. FRED. W. MORSE (*J. Amer. Chem. Soc.*, 1908, 30, 876—881).—Apples undergo chemical changes twice or three times as fast with a rise of temperature of 10° between 0° and 20°. Respiration and, consequently, destruction of cell tissues goes on at low temperatures, and the keeping quality of apples is therefore limited even in cold storage.

N. H. J. M.

The Liberation of Carbon Dioxide by Dead Parts of Plants. A. J. NABOKICH (*Ber. deut. bot. Ges.*, 1908, 26a, 324—332).—In a high vacuum, seeds, seedlings, and various other plant objects gradually give off, after death, not inconsiderable quantities of carbon dioxide. This liberation of carbon dioxide is independent of ferments or bacteria, and also of the manner in which the plant has been killed (whether by freezing, heating, boiling acids, or superheated steam).

Aerobic cultures of fungi set free ammonia, which is retained by the carbon dioxide of respiration as ammonium carbonate, and is slowly set free in anaerobic life by the organic acids formed under such conditions; this slow liberation of carbon dioxide simulates intramolecular respiration. G. B.

Influence of Didymium [and Glucinum] on Plants. C. KANOMATA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 637—640).—Barley was grown in pots containing 10 kilograms of loamy soil, manured with minerals and potassium nitrate. Three pots received, in addition, 0.01, 0.1, and 0.5 gram of “didymium” nitrate (the unseparated salts of praseodymium and neodymium) previously neutralised with sodium hydroxide. The plants grown with 0.01 gram of “didymium” nitrate showed a considerable increase in total weight (17.5%), and in the weight (42.4%) and number of ears, as compared with the control pot, whilst the larger applications diminished the yield. A similar stimulating effect was observed when neutralised “didymium” nitrate was applied to mustard, *Raphanus sativus radícula*, and tobacco at the rate of 1 per million of soil.

The increase in the three last experiments amounted to 13.7% with mustard, 27.0% with *Raphanus*, and 32.1% with tobacco.

Glucinum nitrate neutralised with sodium hydroxide, when applied to oats at the rate of 10 per million of soil, had no decided effect (the yield of fresh substance was 4.5% higher than in the control pot), whilst larger amounts (100 and 500 per million) reduced the yield.

N. H. J. M.

Oxydases in India-rubber. DAVID SPENCE (*Bio.-Chem. J.*, 1908, 3, 165—181).—The observations recorded show that the darkening of raw rubber is due to an oxydase associated with the protein or so-called insoluble constituent of the rubber. Whether it is responsible for other changes which occur on keeping (decomposition, &c.), further

work will determine. The ferment is probably reversible in its action, and it is suggested that the function of caoutchouc in the latex is not merely protective to the plant, and that the latex does not merely serve as a reserve store for water; caoutchouc itself is probably a reserve food-stuff for the plant.

W. D. H.

Toxic Substance Excreted by the Roots of Plants. F. FLETCHER (*Mem. Dept. Agric. India; Bot. Ser.*, 1908, 2, No. 3).—Plot experiments were made in which sorghum, cajanus, cotton, and sesamum were grown next to each of the others and next to fallow. Taking the yield of the outside rows next to fallow as 100, the differences in the middle rows of each plot and of the outside rows next to the plots bearing the other crops are assumed to indicate depression of yield due to a toxic substance secreted by its own roots and by the roots of the other plants. A further experiment is described in which cotton and sorghum were grown in alternate rows two feet apart. The results show great regularity, and the conclusions are drawn (1) that all plants excrete a substance which is toxic to themselves and to other plants; (2) that different crops excrete varying amounts of the substance, and (3) that the sensitiveness of different crops to the same amount of the poison varies.

Water culture experiments were made with the above plants and with wheat and grain in addition, each plant being grown in water previously used for the same plant and for each of the others. Gram water was found to be the most toxic, then sesamum, wheat, cotton, cajanus, and sorghum water. The strength of the solution is, of course, arbitrary; the regularity of the results indicates, however, that the toxic substance is the same in all plants.

As regards the amount of toxic substance produced, the solution in which ten cotton plants (weighing 0.4 gram when air dry) were grown gave with potassium sulphate a precipitate weighing, when dry, 0.21 gram. The substance seems to be an alkaloid (the base itself, not a salt) which differs from the commoner alkaloids in being sparingly soluble. Its toxic effect is corrected by tannic acid, and it is usual to manure spice gardens and rice fields with leaves containing tannic acid.

N. H. J. M.

Composition of Rice Straw. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 619—621).—Analyses of two samples of straw (1) from a favourable harvest and (2) from a poor harvest give the following results:

Dry matter.	N.	Crude fat.	Crude fibre.	Dextrose.	Sucrose.	Starch, hemi-celluloses.	Pentosans.	Crude ash.	SiO ₂ .
1. 87.69	0.97	1.36	31.16	2.25	0.79	14.86	14.28	11.42	5.39
2. 90.15	1.48	1.65	28.72	3.28	0.96	18.75	16.55	12.35	6.13

N. H. J. M.

Continuous Growth of Peas on the Same Soil. SHIGEHIRO SUZUKI (*Bull. Coll. Agr. Tōkyō*, 1903, 7, 575—577).—Experiments with peas grown for four years in succession in the same humous loam

with mineral and nitrogenous manures failed to give any indications of pea-sickness. The yield tended rather to increase. Very few nodules were found on the roots of the plants.

Heating the soil in steam at 100° for four hours on three consecutive days had practically no effect on the yield.

The conclusion is drawn that pea- and clover-sickness may be sometimes due to deficiency of phosphoric acid in the soil, and sometimes to want of potash, as suggested by Gedroiz (*J. exper. Landw.*, 1908, 8, 61).
N. H. J. M.

Behaviour of Onions to Stimulants. I. NAMBA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 635—636).—Addition of 0.1 gram of manganese sulphate to 8 kilograms of soil, corresponding with 22 kilos. per hectare, increased the yield of onions (leaves, bulbs, and roots) 59.2%, whilst 0.2 gram gave an increase of 34.2%.

Sodium fluoride applied at the rate of 2.2 kilos. per hectare (0.01 gram in 8 kilos. of soil) increased the yield 80.2%. With 0.05 and 0.2 gram, the increase was reduced to 31.5 and 7.8% respectively.
N. H. J. M.

Cultivation of Sugar-Beet. Potassium Manuring of Beet Soils. E. SAILLARD (*Bied. Zentr.*, 1908, 37, 426—427; from *J. d'Agric. Prat.*, 1907, i, 454).—Determinations of sugar, potassium, and sodium in sugar-beet from all parts of France where they are grown showed that with diminished percentages of sugar there is a regular increase in the sodium expressed as percentage in the portion of the ash soluble in hydrochloric acid. The potassium was found to vary very slightly. Roots containing 16—17% of sugar contained 3.6% K_2O and 5% Na_2O in the ash (excluding insoluble portion), whilst roots with 8—11% of sugar contained 38% K_2O and 17.5% Na_2O in the ash. The paralysing action of sodium is shown by results obtained near the sea, where it is impossible to grow roots with high percentages of sugar. In manuring sugar-beet, sodium nitrate should be employed in moderation. The following manures are recommended: superphosphate, 300—500 kilos.; potassium (as sulphate, chloride, or kainite), 75—90 kilos.; nitrogen (as sodium nitrate), 25—40 kilos. per hectare, and the rest of the nitrogen in an organic form, as farmyard manure.
N. H. J. M.

Experiments with Different Varieties and on the Storage of Mangolds. BOUWE SJOLLEMA and C. K. VAN DAALEN (*Verslagen Landbouwkund. Onderzoek Rijkslandbouwproefstat.*, 1907, No 2, 31—49. Compare Miller, *Abstr.*, 1900, ii, 430; *J. Roy. Agric. Soc.*, 1902, 63, 135).—Experiments were made with fourteen varieties of mangolds, manured with superphosphate only and grown in rows 50 cm. apart, the distances in the rows being 40 and 50 cm. respectively. Determinations of total weight, dry matter, and sugar were made in October, when the crop was taken up, and also in the clamped roots in January and in April.

The weight of the roots was greatest, as well as the average yield of sugar, in the case of the roots grown 40 cm. apart.

In January the average loss in weight was 2%, and in the case of the varieties containing the lower percentages of sugar, about 1.5% of sucrose was converted into reducing sugar. Inversion was slower in the case of the roots containing high amounts of sugar.

In April there was a further loss of about 1% in the weight of the roots, and the amount of reducing sugar increased to 2—3%, although in some cases it remained below 1%.

The average loss of dry matter from October to April was 9.35%; the greatest loss was 20.6%, and in two cases there was a slight gain. The loss of sugar amounted in some cases to more than 10%.

N. H. J. M.

Manurial Experiments on Mangolds with Calcium Cyanamide and Sodium Nitrate. S. KLÖPPEL (*Bied. Zentr.*, 1908, 37, 386—391; from *Fühling's Landw. Zeit.*, 1907, 56, 535).—Field experiments with six varieties of mangolds resulted, in each case, in higher yields of dry matter and sugar when manured with calcium cyanamide than with sodium nitrate. The results are partly attributed to frequent rain and consequent washing of sodium nitrate into the subsoil.

N. H. J. M.

Occurrence of Cyanogenetic Glucosides in Feeding-stuffs. THOMAS A. HENRY and SAMUEL J. M. AULD (*J. Soc. Chem. Ind.*, 1908, 27, 428—433).—Since it has been found that many plants which are used as feeding-stuffs contain cyanogenetic glucosides (Dunstan and Henry, *Abstr.*, 1901, i, 39, 647; 1902, ii, 578; 1904, ii, 71; 1907, i, 1063; 1907, ii, 983; Dunstan, Henry, and Auld, *Abstr.*, 1906, ii, 794, 795; 1907, ii, 572), it has been considered desirable to record the amounts of hydrogen cyanide yielded under different conditions and to describe the methods employed in their estimation. In addition to giving this information, the present paper introduces certain new facts.

It has been found that when these plants are ground and macerated with water, the amount of hydrogen cyanide developed does not correspond with the quantity which would be produced by the total decomposition of the glucoside present. This is due to the inhibiting action exerted by the dextrose produced during the hydrolysis.

Two samples of linseed cake which were examined furnished 0.032 and 0.045% of hydrogen cyanide. It has been observed that some white varieties of the seeds of *Phaseolus lunatus* yield hydrogen cyanide. Traces were obtained from certain French haricots, from 0.026 to 0.068% from some Ceylon varieties, and 0.002% from "butter beans." In the case of the bitter cassava, the green branches did not yield any hydrogen cyanide, the stem furnished 0.007%, and the whole tubers, 0.013%. The stem of the sweet cassava gave 0.005%, the whole tubers, 0.014%, the rind of the tubers, 0.040%, and the inner portion, 0.007%.

E. G.

Effects of Feeding with Maize. Certain Properties of Zein. I. SILVESTRO BAGLIONI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 609—617).—The author discusses the work of Paladino-Blandini

(*Arch. farm. sper. ecc.*, 1907, 6, 57), Bezzola (*Zeitsch. Hygiene*, 1907, 56, 75), Scheunert and Grimmer (Abstr., 1906, ii, 239), and Szumowski (Abstr., 1902, ii, 674) on zein or maize as a food-stuff, and on its action in causing the disease termed pellagra.

Zein yields relatively large proportions of phenylalanine and tyrosine when decomposed, and free phenolic compounds can often be detected in maize which has been attacked by moulds or other micro-organisms. If zein, suspended in water, is treated with potassium hydroxide and copper sulphate solutions, the violet biuret coloration only appears after a few minutes; if, however, the zein is first treated for a short time with potassium hydroxide solution, it yields the coloration immediately the copper sulphate solution is added. The delay in the appearance of the reaction is occasioned by the insoluble zein requiring to be degraded into simpler proteoses by the action of the potassium hydroxide (compare Dennstedt and Hassler, Abstr., 1906, i, 916).

The digestion of zein by infusions of the pancreas or intestinal mucus of the dog or hog, or by commercial pepsin preparations, proceeds slowly and with difficulty. In no case did the zein undergo complete solution, possibly owing to the accumulation of the products of digestion, and to the weakening of enzymatic activity. Experiments on the digestion of zein by means of extracts of germinating maize corns have not, as yet, met with success.

Guinea-pigs fed on a paste of maize or wheat flour and water exhibit all the symptoms of general decline, and die in a period varying from a few days to a month. If part or all of the maize or wheat flour is replaced by zein, the animals exhibit symptoms of poisoning somewhat similar to those observed in cases of phenolic intoxication.

T. H. P.

New Apparatus for Showing the Ammonia-condensation Power of Soils. GEORG RÖSING (*Chem. Zentr.*, 1908, i, 1323; from *Zeitsch. landw. Vers-Wesen Oesterr.*, 1908, 11, 123—127).—A modification of the apparatus described by Wohltmann and Schneider (Abstr., 1905, ii, 649), whereby the volume of the gas before and after the adsorption may be arrived at, and thus the calculation of the amount by weight rendered possible.

J. V. E.

Physical and Chemical Processes in the Production of Soils. PAUL ROHLAND (*Bied. Zentr.*, 1908, 37, 289—291; from *Landw. Jahrb.*, 1907, 36, 473).—The diffusion of water and plant nutrients in soils is intimately connected with the presence of colloids, mainly silicic acid and aluminium hydroxide, produced by the interaction of felspar, water, and carbon dioxide. As regards chemical actions, the replacement of basic constituents in double silicates by bases dissolved in the soil water is of great importance, as, for instance, when sodium applied in a manure liberates potassium from insoluble compounds present in the soil.

The processes of adsorption depend on the different concentration of those portions of the soil water which are in contact with the surface of substances such as double silicates, clay, humus, and ferric

hydroxide, &c., the more complex substances, such as phosphates, being more readily adsorbed than simpler compounds like potassium chloride. Another factor of importance is the mutual action of salts on solubility. The solubility of calcium sulphate, for instance, is increased in presence of sodium, potassium, and ammonium salts, and more by sodium nitrate than by sodium chloride, so that the availability of superphosphate, in which the particles of phosphates are encased in calcium sulphate, is increased by the presence of the above-mentioned salts.

N. H. J. M.

Why are Poor Sandy Soils Often Easily Injured by Liming? H. YOKOYAMA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 615—617).—Experiments with oats grown in purified quartz sand manured with ammonium nitrate, potassium sulphate, sodium phosphate, and different amounts of limestone and magnesite showed that further addition of lime to sand poor in lime caused a greater depression in yield than in the case of sand rich in lime, and that the ratio $\text{CaO}:\text{MgO}=5:1$ is less favourable than the ratio $1.8:1$. The conclusion is drawn that injury to sandy soils by liming is not due to destruction of bacteria or to lessened assimilability of the phosphoric acid (except when bone-dust or phosphorite are present), but to an unsuitable lime-magnesia ratio. Dolomitic limestone should be employed.

N. H. J. M.

Changes of Availability of Nitrogen in Soils. OSCAR LOEW and KEIJIRO ASO (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 567—574).—A culture solution containing mineral nutrients and glycerol, inoculated with *Bacillus mycoides*, to which peptone and sodium carbonate were added subsequently, gradually developed films, which were distributed through the liquid by shaking. After six weeks, the contents of two flasks which no longer produced films were evaporated down in a vacuum. A gram of soil was added to one portion of the solution, whilst a second portion was boiled for a few minutes before addition of soil. The solution which had been boiled soon developed a luxuriant film of microbes, whilst the solution which had not been boiled remained unchanged for four weeks. The results show that soil bacteria can produce a bacteriolytic enzyme which renders new bacterial growth difficult, and furnishes some explanation why bacterial life does not increase infinitely in organically manured soils.

Gerlach and Vogel's observation that *Azotobacter* requires calcium was confirmed. In culture solutions containing mannitol and sodium malate respectively, growth failed until small amounts of calcium chloride were added (compare Christensen, this vol., ii, 67).

As regards the chemical process of nitrogen fixation, it is suggested that nitrogen combines with the elements of water, producing ammonium nitrite, the nitrous acid being at once reduced to ammonia. Nitrous acid has been detected in leguminous root nodules. The view that nitrous acid may be produced by oxidation is supported by results obtained by platinum black and alkali (compare Loew, *Abstr.*, 1890, 1051, and Wöhler, *Abstr.*, 1904, ii, 44).

N. H. J. M.

Ammonia-soluble Phosphoric Acid of the Soil. GEORGE S. FRAPS (*Amer. Chem. J.*, 1908, 39, 579—586).—In the course of an investigation on the phosphoric acid of the soil, a study has been made of the phosphoric acid which is extracted by ammonia from a soil which has been previously treated with hydrochloric acid. It has been found that the phosphoric acid so dissolved is partly in organic and partly in inorganic combination, and should therefore not be regarded as being entirely of the nature of "humus-phosphoric acid."

E. G.

Pot Culture Experiments, 1906-7. JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1907, 68, 264—266. Compare Abstr., 1905, ii, 754; 1906, ii, 888).—Lithium chloride or sulphate, in very small quantities (0.05 gram Li to 100 of soil) reduced the yield of wheat to 25%, the action being largely due to the stunting of root growth.

Iron sulphate, in similar amount, increased the produce materially, whilst manganese chloride and sulphate, not exceeding 1 cwt. per acre, are also beneficial.

The greater benefit observed in field experiments by the ploughing in of mustard as compared with vetches is shown by experiments in pots to be due to physical conditions of the soil, the vetches producing a light and open condition resulting in a much greater loss of water than is the case with mustard.

Experiments on the application of different amounts of lime and magnesia to soil growing wheat and barley showed that as the lime and magnesia ratio approaches 1 : 1, the wheat grain tends to show greater strength. When the relation of $MgO : CaO$ is increased, the roots become abnormally extensive and fibrous.

With regard to the acid condition produced in Stackyard Fields by the continued application of ammonium salts to a soil deficient in lime, it is shown that the failure of the crop is due to the presence of a poisonous substance soluble in water, or to the growth of some lower forms of vegetation.

N. H. J. M.

Manurial Experiments with Sodium Nitrate, Ammonium Salts, and Calcium Cyanamide. PAUL WAGNER, G. HAMANN, and A. MÜNZINGER (*Bied. Zentr.*, 1908, 37, 366—386; from *Arb. deut. landw.-Ges.*, 1907, No. 129. Compare *ibid.*, No. 80).—The results of experiments with cereals showed that manuring with ammonium salts produced 77% of the amount of grain obtained with corresponding amounts of sodium nitrate, and that 63% and 46% of the nitrogen applied as nitrate and as ammonium salts respectively was recovered. In the case of sugar-beet and mangolds, the amounts of nitrogen recovered were 63% and 43%.

The lower results obtained with ammonium salts as compared with nitrate are attributed to loss as ammonia, and to fixation, both chemical and physical, of some of the ammonia by zeolites. Clay soils retain appreciable amounts of ammonia even after distillation with magnesia. It is suggested that ammonia fixed in this manner escapes nitrification.

Calcium cyanamide has no injurious effect when applied immediately

before sowing the seed if employed in normal amounts and evenly distributed; its effect is, however, sometimes increased by applying a week or two before sowing. Soils very rich in humus or deficient in lime should be limed before using calcium cyanamide. Experiments with oats, winter rye, and barley showed that the amounts of nitrogen as cyanamide utilised were 83, 87, and 69 respectively compared with sodium nitrate = 100. In the case of mangolds, the result was less satisfactory, the amount of nitrogen recovered being 56% as compared with sodium nitrate.

N. H. J. M.

Manurial Experiments with Calcium Cyanamide. ALBERT STUTZER (*Bied. Zentr.*, 1908, 37, 422—423; from *Ill. landw. Zeit.*, 1907, 27, No. 78).—Field experiments, under very unfavourable climatic conditions, on a raw, sandy loam in which oats and barley were manured with ammonium salts, calcium cyanamide ("stickstoff-kalk"), and sodium nitrate respectively, in addition to soluble phosphoric acid (50 kilos.) and potash (100 kilos. per hectare). Sodium nitrate gave the highest results, whilst calcium cyanamide gave, on the average, 84.5% of the grain obtained with nitrate. The results obtained with ammonium salts were very variable.

N. H. J. M.

Efficacy of Calcium Cyanamide under Different Manuring Conditions. I. NAMBA and C. KANOMATA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 631—634).—In pot experiments with oats and onions, it was found that rather higher yields were obtained when calcium cyanamide was employed in conjunction with double superphosphate than with disodium phosphate. Similar results were obtained by Inamura (*Abstr.*, 1906, ii, 891) with *Brassica chinensis*.

Further experiments with *Brassica chinensis* and oats, in which bone-dust was used in conjunction with ammonium sulphate and calcium cyanamide respectively, showed that the latter had no depressing effect on the availability of the bone-dust.

N. H. J. M.

Action of "Kalkstickstoff," "Stickstoffkalk," and Calcium Nitrate. BOUWE SJOLLEMA and J. C. DE RUYTER DE WILDT (*Verslagen Landbouwkund. Onderzoek. Rijkslandbouwproefstat.*, 1907, No. 2).—Calcium cyanamide reacts with water, forming calcium hydroxide and the compound $\text{Ca}(\text{N}:\text{C}:\text{NH})_2$, the latter being gradually decomposed by calcium hydroxide and cyanamide into the basic salt, $\text{C}(\text{N}:\text{CaOH})_2$, which slowly polymerises to dicyanodiamide.

It is shown that the injurious action of calcium cyanamide on germination is not due to lime as stated by Immendorf and Thielebein (*Fühling's Landw. Zeit.*, 1905, 54, 792), or to the gases produced from calcium carbide and phosphide or to dicyanodiamide, but that it is due to the basic salt already mentioned. On the other hand, dicyanodiamide was found to cause injury to mustard and buckwheat plants, causing the edges of the leaves to become white, and in large amounts to destroy them altogether. Injury to germination by the basic salt and cyanamide would probably not as a rule occur under practical conditions.

The results of manurial experiments, in cylinders, in which oats were manured with sodium nitrate, ammonium sulphate, and calcium nitrate showed that the relative gain in total produce (grain and straw) was as 100:91.9:115.9. Experiments with calcium cyanamide gave conflicting results.

N. H. J. M.

Experiments with Basic Slag-ammonia. BACHMANN (*Bied. Zentr.*, 1908, 37, 423—424; from Fülling's *Landw. Zeit.*, 1906, 55, 808).—The manure contains: P_2O_5 (citrate soluble), 7.15; N as ammonia, 6.77, and CaO, 25.22%. When stored for three months there was a loss of 1.54% of nitrogen as ammonia. Experiments with rye, oats, and grass showed that lower results were obtained with the manure than with a mixture of equivalent amounts of basic slag and ammonium sulphate.

N. H. J. M.

Depression of Growth by Large Amounts of Calcium. C. KANOMATA (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 597—607).—In sand-culture experiments, the yield of oats was reduced 39% by altering the ratio CaO/MgO from 1/1 to 100/1, whilst in soil there was a decrease of 48% when the ratio was altered from 1/1 to 10/1.

Similar results were obtained with rice, barley, buckwheat, mustard, and onion.

An experiment with buckwheat in which powdered magnesite was added in such quantity to the soil injured containing an excess of calcium carbonate that the ratio CaO/MgO was changed from 100/1 to 100/100, showed a restoration of favourable conditions. It is therefore not the absolute amount of calcium carbonate which is injurious, but its relation to the amount of magnesium present.

N. H. J. M.

Gypsum as a Manure. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 583—597).—A large number of pot experiments are described in which peas, barley, oats, beans, rice, and spinach were manured with different forms of phosphoric acid and nitrogen without and with addition of gypsum. Experiments were also made on the effect of gypsum in presence of magnesia alba.

It is shown that calcium sulphate is very beneficial when sodium nitrate is employed, or more generally when any alkaline reaction is produced in the soil. In presence of superphosphate or ammonium sulphate, it tends to depress the yield.

Calcium sulphate is also beneficial in the case of soils containing an excess of magnesium, and may be employed with advantage in the case of spinach, for which calcium carbonate is unsuitable.

N. H. J. M.

Absorption of Varying Amounts of Lime and Magnesia by Plants. T. TAKEUCHI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 579—581).—Oats were grown in (1) soil in which by addition of calcium carbonate the ratio CaO:MgO was 10:1, and in (2) a control pot

containing soil having a ratio of about 1:1. The following results were obtained:

Leaves.				Roots.			
Fresh weight,* grams.	Crude ash, per cent.	Per cent. in ash.		Dry weight, grams.	Crude ash, per cent.	Per cent. in ash	
		CaO.	MgO.			CaO.	MgO
1. 106.3	11.97	18.82	4.85	4.4	8.17	32.31	8.69
2. 301.0	12.43	10.94	4.42	13.5	9.45	13.22	6.66

* Including the stems.

The greatest height of the plants of the two pots was (1) 92 and (2) 108 cm., and the number of shoots (1) 32 and (2) 42. N. H. J. M.

Agronomical Equivalent of Artificial Magnesium Carbonate. S. KANAMORI (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 609—612).—The availability of artificial magnesium carbonate is greater than that of the natural substance, owing to difference in composition and to its more finely-divided condition. The results of pot experiments with oats showed that 0.1—0.6 gram of magnesia alba is agronomically equivalent to 5 grams of magnesite, and that larger amounts (in 2.5 kilos. of sand) reduced the yield. Similar results were obtained with barley.

N. H. J. M.

Top-dressing with Magnesium Sulphate. J. N. ZIRKER (*Bull. Coll. Agr. Tōkyō*, 1908, 7, 613—614).—Application of magnesium sulphate, at the rate of 10 kilos. per hectare, to half of a plot which had received slaked lime at the rate of 10,000 kilos. per hectare increased the yield of barley 31%.

N. H. J. M.

Analytical Chemistry.

Apparatus for Testing Burettes and Pipettes ; also Mercury Measuring Tubes. O. VON SPINDLER (*Chem. Zentr.*, 1908, i, 1419—1420 ; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 145—148).
—A modification of the Ostwald pipette. The burette to be tested is placed on the long arm of a U-shaped tube, whilst on the shorter arm is placed a standard graduated pipette. Both arms are fitted with glass stopcocks ; a third stopcock at the bottom serves for the purpose of emptying the apparatus, and a fourth one regulates the supply of liquid contained in a reservoir, from which the apparatus is filled. By proper regulation of the stopcock, the burette to be tested is filled with water up to the top mark, whilst the calibrated pipette (moist inside) stands at zero. Any quantity of liquid running from the burette through the U-tube can be read off in the standard pipette. In the case of a mercury measuring tube, it may be arranged so that a given volume of mercury forces the same volume of water into the burette.

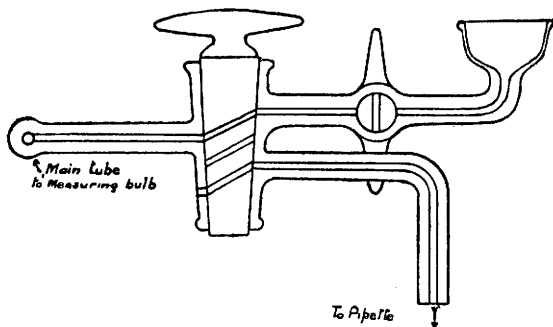
L. DE K.

Circulation Burette. GUSTAV MULLER (*Chem. Zeit.*, 1908, 44, 532).—An ordinary burette is surmounted by a closed stoppered reservoir which is fused on to a large double bored glass tap in such a manner that a liquid may pass through the smaller bore of the tap to the burette, while at the same time the displaced air passes through the second bore of the tap to the top of the closed reservoir. In this manner, the burette may be re-filled without opening to the atmosphere. To allow the burette to deliver the contained liquid, an additional small hole, communicating with the outside, is bored in the large tap.

J. V. E.

New Gas Analysis Apparatus. RAYMOND ROSS and JOHN P. LEATHER (*J. Soc. Chem. Ind.*, 1908, 27, 491).—The apparatus consists of a measuring bulb surrounded by a water jacket; it is provided with a three-way tap and connected by flexible tubing with a mercury reservoir and also with an 800 mm. graduated tube. The measuring bulb communicates with eight absorption pipettes by means of a capillary provided with specially designed taps. The construction of these is shown in the diagram.

By raising the mercury reservoir, the measuring bulb and the whole



of the connexions are filled with mercury, which is allowed to flow through each tap in turn until the small glass cups are about half filled. The reservoir is then lowered so that the mercury falls to the mark on the measuring bulb. The barometric pressure is now read off in millimetres, including the pressure of aqueous vapour, sufficient water for this purpose being introduced with the mercury. The barometer tube is shut off and the measuring bulb re-filled with mercury, the gas to be analysed being introduced and brought exactly to the mark at atmospheric pressure. To introduce the gas into the required absorption pipette, the mercury reservoir is raised, and the mercury in the capillary connecting tubes driven forward into the cups until the gas just reaches the three-way tap. The small tap is then closed, and the absorbent is driven up until it fills the bore of the tap. The tap is next turned so as to allow the gas to enter the pipette. When the absorption is complete, the process is reversed, the gas being swept through the capillary tube into the measuring bulb by means of the mercury in the cup. The mercury is again brought to the mark in

the measuring bulb, connexion with the millimetre tube having been re-established. The reading, multiplied by 100 and divided by the first ("barometric") reading, gives the percentage absorption.

W. P. S.

Metanil Yellow; its use as a Selective Indicator. ERNEST LINDER (*J. Soc. Chem. Ind.*, 1908, 27, 485—488).—Strips of filter paper which have been dipped in a 0.1 solution of metanil yellow (the sodium salt of diphenylamineazo *m*-benzenesulphonic acid) and then dried, are coloured violet when exposed to gases containing vapours of mineral acids, whilst they are unaffected by sulphur dioxide, chlorine, hydrogen sulphide, or acetic acid. The colour change takes place within two minutes in an atmosphere containing 0.016 grain of HCl per cubic foot; with a longer exposure, the limit would probably be extended, as the effect appears to be cumulative. Moisture inhibits the formation of the violet colour, but solutions may be tested for the presence of mineral acid by placing a drop of the solution on a strip of the paper and re-drying the latter at a temperature of 40°. Free mineral acid in vinegar may be detected in this way.

W. P. S.

Estimation of Water of Hydration in Cellulose Materials. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1908, 21, 1321—1323).—Distillation with toluene or petroleum and measuring the layer of water in the distillate gives unsatisfactory results. The water of hydration may, however, be determined indirectly by hydrolysing the cellulose material and estimating the dextrose formed, for only hydrated cellulose is inverted comparatively rapidly. Three grams of the material are boiled with 250 c.c. of 5% sulphuric acid for fifteen minutes in a reflux apparatus, the requisite amount of alkali is added, and the solution is titrated with Fehling's solution.

L. DE K.

Volumetric Process for the Estimation of Chlorates. EDMUND KNECHT (*J. Soc. Chem. Ind.*, 1908, 27, 434—437).—In the method described, titanous chloride solution is employed as a reducing agent. The reaction proceeds according to the equation $6\text{TiCl}_3 + \text{KClO}_3 + 6\text{HCl} = 6\text{TiCl}_4 + \text{KCl} + 3\text{H}_2\text{O}$, and the estimation is carried out as follows: 50 c.c. of standardised titanous chloride solution are run into 5 c.c. of concentrated hydrochloric acid contained in a conical flask through which a current of carbon dioxide is passed. Ten c.c. of the chlorate solution under examination are then added, and, after the lapse of three minutes, potassium cyanate is added, and the excess of titanous chloride is titrated with standardised iron alum solution. All the values being based on an iron standard, the calculation is simple, for six atoms of iron are equivalent to one molecule of chlorate.

W. P. S.

Detection of Potassium Perchlorate in Potassium Chlorate. EDUARD A. KLOBBIE and H. L. VISSER (*Pharm. Weekblad*, 1908, 45, 718—720).—The presence of potassium perchlorate in potassium chlorate can be detected by slowly evaporating an aqueous solution of the mixture with a trace of potassium permanganate on a microscopic slide, the appearance of the mixed crystals being very characteristic.

A. J. W.

Apparatus for the Estimation of Sulphur in Iron and Steel. EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1908, 22, 181—183).—A combination of von Reis's generating flask (round-bottomed flask with side tube, and fitted with separating funnel) and Heinz-Nowicki's absorbing apparatus (cylinder and worm tube).

The absorption tube has now been fitted with a tube carrying a bulb, which also serves the purpose of a funnel through which the solution of bromine in hydrochloric acid is introduced. There is also a small horizontal outlet tube, which is afterwards connected to a long tube destined to carry off the obnoxious bromine fumes.

The gases given off on dissolving the sample in dilute hydrochloric acid are first passed through an empty bulb and then through the absorber. The last traces of hydrogen sulphide are removed by a current of carbon dioxide. The sulphuric acid formed is then estimated as usual.

L. DE K.

Sodium Peroxide in Certain Quantitative Processes. SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1908, 30, 764—770).—*Sulphur (and Arsenic) in Pyritic Ores of Iron and Copper.*—A mixture is made of 10 grams of sodium peroxide, 0.5 gram of potassium chlorate, and 0.5 gram of benzoic acid (by careful shaking). 0.25 Gram of the ore is then carefully mixed with the reagent in an improved Parr bomb, where it is ignited by means of a red-hot nickel wire. The fused mass contains the sulphur as sulphate. *Sulphur in Coal, Coke, Ashes.*—The same process is applied, but in the case of coal and coke, 0.5 gram should be taken for analysis, and the benzoic acid be omitted from the mixture. *Sulphur in Indiarubber.*—0.1 Gram of the sample is burnt with the mixture containing 0.3 gram of benzoic acid. *Halogens, Sulphur, &c., in Organic Compounds.*—Instead of the above mixture the following one is used: 10 grams of sodium peroxide and 1—2 grams of "boro-magnesium" mixture (five parts of boric acid, four parts of potassium nitrate, one part of magnesium, all in fine powder), and 0.3—0.5 gram of the organic compound is taken for analysis. The fused mass contains the halogen and the sulphur. The same mixture also serves for the estimation of carbon in *carborundum*. The fused mass contains the carbon as carbonate.

L. DE K.

The Estimation of the Total Sulphur in Urine. ARTUR KONSCHEGG (*Pflüger's Archiv*, 1908, 123, 274—278).—When the organic matter in urine is oxidised with nitric acid alone, and the sulphur is precipitated as sulphate by barium chloride, the results obtained are too low. This is probably due to loss of sulphuric acid by volatilisation. Better results are obtained if potassium nitrate is added to the mixture of urine and fuming nitric acid.

S. B. S.

Use of Phenolphthalein as Indicator in the Titration of Acids in the presence of Sulphurous Acid. M. EMMANUEL POZZI-ESCOFF (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 25, 941—944).—It is shown that, employing phenolphthalein as indicator, the titre of a sulphuric acid solution remains the same after the addition of normal

sodium sulphite as it was before the addition, and consequently this indicator may be used in the presence of sulphurous acid in spite of statements by other observers to the contrary. W. P. S.

Estimation of Nitrogen by Dumas' Method. H. LEEMANN (*Chem. Zeit.*, 1908, 32, 496).—The carbon dioxide used to expel the air from the combustion tube is generated in a separate tube by heating sodium hydrogen carbonate. Between this and the combustion tube is interposed a tube fitted in the middle with a three-way cock. When the supply of carbon dioxide must be temporarily stopped, the stopcock is turned through 90°, and the carbon dioxide still being evolved escapes through a mercury valve.

When the combustion is over, the sodium hydrogen carbonate is heated again, and the stopcock turned into its original position. L. DE K.

Estimation of Phosphorus in Phosphorised Oils. EMIL WÖRNER (*Pharm. Zeit.*, 1908, 53, 398).—Five grams of the oil are treated in a 500 c.c. Jena flask, drop by drop, with 5 c.c. of fuming nitric acid, and, when the first violent action is over, a gentle heat is applied. Ten c.c. of a mixture of equal volumes of sulphuric acid and nitric acid are then slowly added, and the heating continued until the charring action of the sulphuric acid becomes visible. Nitric acid is now added until the violent evolution of brown fumes diminishes. If charring occurs again on heating, more nitric acid should be added. Finally, the whole is heated until sulphuric fumes appear, a few more drops of nitric acid being added if necessary.

The residue, when cold, is boiled with 20 c.c. of water, and the phosphoric acid formed estimated by Neumann's process (precipitating with ammonium molybdate and ammonium nitrate, dissolving the yellow precipitate in excess of $N/2$ sodium hydroxide, boiling off the ammonia, and titrating the excess of alkali with $N/2$ acid, with phenolphthalein as indicator; 1 c.c. of alkali = 0.5536 mg. of phosphorus).

L. DE K.

Estimation of Phosphorus in Phosphor-tin. WILLIAM GEMMELL and SYDNEY L. ARCHBUTT (*J. Soc. Chem. Ind.*, 1908, 27, 427—428).—The following process, in which the phosphorus is evolved as hydride and the latter absorbed and converted into phosphoric acid, is stated to give trustworthy results in the estimation of phosphorus in phosphor-tin. From 2 to 5 grams of the sample are placed in a 500 c.c. flask provided with a two-way tapped funnel and a delivery tube. The gas is absorbed in a set of three Drechsel bottles, the first two containing a depth of about 0.25 inch of bromine, covered by bromine water, and the third, bromine water only. The air is first removed by passing a current of carbon dioxide through the apparatus for five minutes. Concentrated hydrochloric acid is then introduced, the contents of the flask are heated gently until the action has practically ceased, and finally boiled. Carbon dioxide is next passed through the apparatus for a further five minutes to drive any remaining traces of evolved gases into the Drechsel bottles. The contents of the latter are then transferred to a beaker, boiled to

remove the bromine, and the phosphoric acid is precipitated as ammonium magnesium phosphate. If arsenic be present in the sample, it is estimated with the phosphorus and separated subsequently.

W. P. S.

Qualitative Analysis of Phosphates and Other Salts Soluble in Acids. H. CARON and D. RAQUET (*Bull. Soc. chim.*, 1908, [iv], 3, 622—626).—A critical résumé is given of some of the methods at present in use for the analysis of the group III precipitate when this contains phosphates or other salts soluble in dilute acids, and a new method depending on the use of sodium dioxide is described.

The precipitate is suspended in 10% sodium carbonate solution, a little sodium dioxide added, and the solution boiled for a few seconds. After this treatment, the solution will contain any aluminium, chromium, zinc, or uranium that may be present in combination with sodium, as also the acids (oxalic, phosphoric, boric, &c.), whilst in the precipitate will be found manganese (as the hydrated dioxide), iron (as phosphate), and any alkaline-earth compounds, the latter being soluble in acetic acid, by means of which they can be separated from the manganese and iron. Nickel and cobalt should not occur in the group III precipitate in presence of excess of ammonia, but if they do, the cobalt will, after this treatment, occur as the brown oxide and be insoluble in acetic acid, whereas the nickel will be in a form soluble in this acid. A table showing the scheme of separation is given in the original.

T. A. H.

The Reactions of Urine. L. DE JAEGER (*Zeitsch. physiol. Chem.*, 1908, 55, 481—504).—To determine the acidity of the urine, the latter was titrated with sodium hydroxide solution (1) in presence of phenolphthalein alone, and (2) in the presence of phenolphthalein after addition of calcium chloride. The phosphoric acid was also estimated. The phosphates are present in the form of diacid salts. If A represents the acidity, x the phosphates present as Na_2HPO_4 or K_2HPO_4 , y , phosphates present as calcium phosphate, and z those present as magnesium phosphate, and a represents the acidity due to other substances, then Ac_1 (acidity due to direct titration) $= a + x + 1\frac{1}{3}y + 1\frac{1}{3}z$. The acidity determined after addition of calcium chloride, $Ac_2 = a + 2x + 2y + 2z$. Now $2x + 2y + 2z = \text{mg P}_2\text{O}_5/71$ and $Ac = Ac_2 - \text{P}_2\text{O}_5/71$. By three sets of determinations, therefore, the acidity due to the diacid phosphates and the other acidity can be determined. For the theory of the method by means of which the results are arrived at, reference must be made to the original paper.

S. B. S.

Estimation of Carbon in Steel, Ferro-alloys, and Plumbago by means of an Electric Furnace. CHARLES M. JOHNSON (*J. Amer. Chem. Soc.*, 1908, 30, 773—779).—The sample contained in a clay boat is heated inside a steel combustion tube in a current of oxygen, the source of heat being a quartz tube wound with Hoskins' resistance wires. Some alloys, such as ferro-chrome, ferro-boron, &c., require an addition of red lead to facilitate the oxidation. For details, the illus-

tration in the original paper should be consulted (also compare Abstr., 1906, ii, 630, as to weighing apparatus and purifying train).

L. DE K.

A New Catalyst in Organic Combustion according to the Carrasco-Plancher Method. ORESTE CARRASCO and E. BELLONI (*J. Pharm. Chim.*, 1908, [vi], 27, 469—473. Compare Abstr., 1906, ii, 200, 201).—Instead of mixing the substance to be burnt in a current of oxygen with copper oxide or lead chromate, use is made of platinised, powdered, unglazed porcelain ("biscuit platiné"). This is prepared as follows:

Unglazed porcelain is broken up into powder and passed through a sieve having eighty meshes per cm., and then through another having 400 meshes per cm. The mass remaining on the latter is washed, heated with *aqua regia*, again washed, and then calcined. Fifty grams of the "biscuit" are heated on the water-bath with a solution of 1 gram of platinum tetrachloride in 20 c.c. of water, and, when perfectly dry, an excess of solution of ammonium chloride is added. After six hours, the clear liquid is decanted, and the mass dried and ignited in a platinum crucible. The platinising process is then once more repeated. It is advantageous also to platinise the interior tube of the combustion apparatus, which also is constructed of unglazed porcelain.

L. DE K.

Detection of Small Quantities of Carbon Monoxide in Air. JULES OGIER and ÉMILE KOHN-ABREST (*Ann. Chim. anal.*, 1908, 13, 169—173).—The air is introduced into a graduated tube connected at its lower end with a mercury reservoir. The upper part of the tube is surrounded by a water-jacket, and contains a platinum spiral which can be heated by means of an electric current. After the air has been introduced and its volume measured, the platinum spiral is brought to a red heat, then allowed to cool, again heated, and so on until no further contraction in the volume of the air takes place. The pressure and temperature are adjusted before taking the final reading, and the contraction observed corresponds with half the volume of carbon monoxide present. The ignited air is then treated with potassium hydroxide in order to absorb the carbon dioxide formed; the contraction observed is equal to the volume of the carbon monoxide. This second manipulation is necessary in case hydrogen is present in the air under examination. Should the air contain hydrocarbon gases, these must be removed previously in the usual way.

Carbon monoxide and dioxide may be estimated in one portion of air by passing a large measured volume of the latter through a series of vessels containing concentrated sulphuric acid, and pumice and sulphuric acid, then through weighed potash bulbs, and finally through a tube containing iodic acid and surrounded by a steam jacket. The carbon dioxide is absorbed in the potash bulbs, whilst the iodine liberated by the action of the carbon monoxide on the iodic acid is collected in potassium iodide solution and titrated. A current of pure air is employed to drive the sample of air through the apparatus.

W. P. S.

Detection of Small Quantities of Carbon Monoxide in Air. JULES OGIER and E. KOHN-ABREST (*Ann. Chim. anal.*, 1908, 13, 218—224).—The detection is based on the well-known action of carbon monoxide on diluted defibrinated blood and subsequent spectroscopic examination after treating with ammonium sulphide. The volume of air passed before a reaction is obtained gives an idea as to the quantity of carbon monoxide present.

The improvement made by the authors consists in the fact that the air is first deprived of oxygen by means of a solution of sodium hyposulphite.

L. DE K.

Universal Volumetric Method for the Estimation of Magnesium. FERNAND REPITON (*Chem. Zentr.*, 1908, i, 1329; from *Mon. Sci.*, 1908, [iv], 22, i, 33—35).—The solution is evaporated with excess of nitric acid, the residue is taken up with nitric acid, and should phosphoric acid be present, excess of ammonium molybdate is added and the precipitate washed with ammonium nitrate. The filtrate is treated with nitric acid, neutralised with ammonia, and evaporated to dryness. The residue is dissolved in dilute nitric acid and introduced into a measuring flask. A known volume of standardised triammonium phosphate, 2% of citric acid, and ammonia are added, and, after twenty-four hours, the flask is filled up to the mark with ammonia and well shaken. An aliquot part of the filtrate is then titrated with uranium solution for phosphoric acid. The difference in phosphoric acid added and found represents the magnesia.

In the absence of phosphoric acid, the treatment with molybdate is, of course, superfluous.

L. DE K.

Separation of Magnesium from the Alkalis by Alcoholic Ammonium Carbonate. FRANK A. GOOCH and ERNEST A. EDDY (*Amer. J. Sci.*, 1908, [iv], 25, 444—448*).—A modification of Schaffgotsch's process (*Annalen*, 1857, 104, 482). The solution containing about 0.25 gram of the mixed salts is diluted to 50 c.c. and 50 c.c. of absolute alcohol are added. The magnesium is now precipitated by adding 50 c.c. of saturated normal ammonium carbonate solution containing 50% of alcohol, and the whole is left for twenty minutes, stirring every five minutes. The precipitate is collected, washed with the ammonium carbonate solution, dried, ignited, and weighed as magnesium oxide.

If the amount of alkali salts is very large, it is advisable to redissolve the precipitate, after decanting the clear liquid, in the smallest possible amount of hydrochloric acid, and to throw down once more with the precipitant.

L. DE K.

Volumetric Estimation of Zinc. GEORGE C. STONE (*J. Amer. Chem. Soc.*, 1908, 30, 904—905).—A criticism of the paper by Keen on this subject (this vol., ii, 431). The method given for standardising is complicated and untrustworthy. The best way to prepare a zinc solution of known strength is to dissolve some zinc in dilute hydrochloric acid, leaving some of it undissolved, and then dilute with

* and *Zeitsch. anorg. Chem.*, 1908, 58, 427—432.

water so as to have about 5 grams of the metal per litre. The zinc is then estimated in a definite portion of the liquid as pyrophosphate.
L. DE K.

Accuracy of the Colorimetric Estimation of Lead. H. W. WOODSTRA (*Zeitsch. anorg. Chem.*, 1908, 58, 168—175. Compare Kühn-Abstr., 1906, ii, 493).—The colorimetric method for the estimation of small quantities of lead by comparison of the colour of the sulphide in colloidal solution with that of a corresponding solution of known strength, used by several previous investigators, has been tested with fairly satisfactory results, but the presence of iron is a source of inaccuracy. It is important that the amount of electrolyte in the tubes should be the same. To avoid the lengthy evaporation after the first precipitation of the sulphide, Kühn's method of getting the sulphide into a form suitable for filtration by shaking with finely-divided asbestos was found satisfactory, but barium chloride is preferable to sodium nitrate for coagulating the precipitate. After filtration, the sulphide is dissolved in hydrochloric acid, evaporated to dryness, the sulphide reprecipitated, and the process repeated. Finally, the chloride is dissolved in water, 10 c.c. of potassium hydroxide and of a saturated solution of hydrogen sulphide added, and the comparison made.

This method gives more accurate results with small quantities (0.05 mg.) of lead than the volumetric method given by Kühn (*loc. cit.*).
G. S.

Estimation of Lead in Lead-Tin Alloys. SIEGMUND HOLZMANN (*Pharm. Zentr.-h.*, 1908, 49, 417—422).—About 0.5 gram of the alloy is repeatedly oxidised with strong nitric acid in a 200 c.c. platinum crucible with the usual precautions and evaporated to dryness. The residue is treated with 150 c.c. of 10 (vol.) % nitric acid and, without removing the tin oxide, submitted to electrolysis, a platinum dish of about half the size, the outer surface of which has been exposed to a sand blast, serving as electrode. The current should be a weak one, so as to avoid evolution of gas as much as possible. The lead separates as peroxide, and is weighed as such, the last traces of moisture being removed by gently heating the inner side of the dish.
L. DE K.

Detection of Copper and Iron. MARCEL DELEPINE (*Bull. Soc. chim.*, 1908, [iv], 3, 652—654).—The method depends on the production of an intense coloration when a solution of a dialkyldithiocarbamate is added to a solution of a salt of either of these metals in water. The coloured substance produced is extracted with benzene, and the residue left on distilling off the solvent is dissolved in two drops of nitric acid and then ignited. To this residue one drop of nitric acid is added, which dissolves the copper oxide, but leaves the ferric oxide. A few drops of water are added, and the solution decanted into a small vessel, carefully evaporated to dryness, and a drop of a solution of an alkali dialkyldithiocarbamate added, when, if copper is present, an intense yellowish-brown coloration is produced. The residue of ferric oxide is fused with a minute portion of potassium

hydrogen sulphate, and to the fused mass, when cold, two drops of a solution of an alkali dialkyldithiocarbamate are added and then ether; on shaking, the ether develops a pink tint if iron is present. In dealing with solid matter, the latter is incinerated, the ash, dissolved in nitric acid, is re-ignited, and the residue so obtained is treated as described above. The most convenient reagent to employ is a solution of a dialkylamine dialkyldithiocarbamate, which can be made by simply mixing the appropriate dialkylamine with carbon disulphide, and diluting to at least one per cent. strength with alcohol or water. Such a reagent will detect 1 part of copper in 1,000,000 of solution. Colorations are also produced with nickel and cobalt. T. A. H.

Volumetric Estimation of Copper. GEORGE S. JAMIESON, L. H. LEVY, and HENRY L. WELLS (*J. Amer. Chem. Soc.*, 1908, 30, 760—764).—The sulphate solution obtained from the ore in the usual manner is nearly neutralised with ammonia, sulphurous acid is added, and, after heating to boiling, the copper is precipitated with ammonium thiocyanate. The filter containing the washed precipitate is placed in a bottle containing 5 c.c. of chloroform, 20 c.c. of water, and 30 c.c. of hydrochloric acid. The liquid is now titrated, with constant shaking, with standard solution of potassium iodate (11.784 grams per litre; 1 c.c. = 0.002 gram of copper) until the violet colour of the chloroform noticed at first suddenly disappears. L. DE K.

Rapid Method for the Estimation of Mercuric Salts in Aqueous Solution. SAMUEL G. LIVERSEDGE (*Analyst*, 1908, 33, 217—218).—The method depends on the solubility of mercuric iodide in ether, and is particularly applicable to the estimation of small quantities of mercury, as, for instance, in the “liquor hydrargyri perchloridi” of the Pharmacopœia. Twenty-five c.c. of the mercury solution are placed in a separating funnel, and 5% potassium iodide solution is added, drop by drop, until no further precipitate is produced; a large excess must be avoided. A few drops of phosphoric acid solution are next added in order to reduce the solvent action of the excess of potassium iodide on the mercuric iodide, and the mixture is then extracted three times with ether, using about 50 c.c. each time. The ethereal extracts are washed with water, evaporated in a weighed flask, and the residue of mercuric iodide, after being dried at 100°, is weighed. W. P. S.

Acidimetric Estimation of both Mercury Components in Mercury Oxycyanide. ERWIN RUPP (*Pharm. Zeit.*, 1908, 58, 435—436).—0.3 Gram of the sample is dissolved in 50 c.c. of hot water containing 0.5 gram of sodium chloride, and, when cold, titrated with *N*/10 hydrochloric acid, using 1 to 2 drops of 0.2% methyl-orange as indicator. This gives the mercuric oxide only; 1 c.c. of acid = 0.0108 gram of HgO.

1.5 to 2 Grams of potassium iodide and 100 to 125 c.c. of water are now added, by which neutrality is restored, and the titration is repeated. The result represents the mercuric cyanide; 1 c.c. of acid = 0.0126 gram of HgC_2N_2 . L. DE K.

Detection of Manganese and Chromium in the presence of each other. WILLIAM J. KARSLAKE (*J. Amer. Chem. Soc.*, 1908, 30, 905).—To the cold dilute nitric or sulphuric acid solution of the mixture are added 1 to 2 c.c. of silver nitrate reagent and then 2 to 5 grams of potassium persulphate, and the whole is heated until practically no more oxygen is evolved. The manganese and chromium are thus converted into their respective acids, the permanganate colour showing itself first. In order to detect the chromium, the colour of which is obscured by the permanganate, the liquid is cooled and shaken with ether or acetic ether and excess of hydrogen peroxide; the permanganate is decomposed, and the perchromic acid formed dissolves in the ether with a blue colour.

L. DE K.

Oxidising Power of Sodium Peroxide; its use in Qualitative Analysis. DANIEL F. CALHANE (*J. Amer. Chem. Soc.*, 1908, 30, 770—773).—Sodium peroxide in alkaline medium is recommended for the detection of chromium in presence of iron and aluminium. The oxidation, however, goes as far as the perchromate stage, and therefore the usual confirmatory test with lead acetate is not obtained until the liquid has been heated so as to reduce the perchromic acid.

L. DE K.

Simultaneous Qualitative Test for Nickel and Cobalt. HERMANN GROSSMANN and WALTER HEILBORN (*Ber.*, 1908, 41, 1878—1880. Compare Grossmann and Schück, *Abstr.*, 1906, ii, 903; 1907, ii, 582).—The presence of both nickel and cobalt may be detected with certainty by the following test: the solution to be examined is concentrated, freed from a large excess of acid, treated with an excess of ammonia, and then with 10—20 c.c. of a 10% sucrose solution; a sufficient quantity of a solution of dicyanodiamidine sulphate is added, and finally sodium hydroxide. The nickel present separates as a yellow, crystalline precipitate of nickel dicyanodiamidine, leaving, in the presence of cobalt, an intense red or reddish-violet solution.

W. H. G.

Estimation of Nickel. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 186*).—A reply to the criticism of Grossman and Schück (this vol., ii, 230). The author points out that he has laid stress on the fact that the separation from cobalt is accompanied by the formation of the double molybdate, and that he has already indicated the means to be taken to prevent the precipitation of blue cobalt molybdate. He has never claimed that the molybdate process is capable of estimating mere traces of nickel in the presence of cobalt.

W. P. S.

Rapid Estimation of Nickel in the presence of all Elements of Groups 4, 5, and 6. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 215—216).—The solution is concentrated to a small bulk, and, after neutralising the excess of acid, a large excess of a solution of ammonium molybdate is added, also a little ammonium chloride. The whole is heated to 60—70° and well shaken for a few

* and *Bull. Soc. chim.*, 1908, [iv], 3, 775.

minutes, when it is suddenly cooled. The precipitate, which contains all the nickel, is washed with saturated ammonium chloride solution, and then boiled with water and excess of ammonia for a few minutes. All the nickel is dissolved, and thus separated from any iron, chromium, manganese, and aluminium. If it is feared that the precipitate still retains nickel, it may be redissolved in hydrochloric acid and again treated with ammonia in excess.

The united ammoniacal filtrates are boiled with potassium hydroxide to expel the ammonia, and a little bromine is added to peroxidise the nickel, which is then washed, redissolved in hydrochloric acid, and finally deposited by electrolysis. L. DE K.

Stannometric Estimation of Alkali Vanadates. T. WARYNSKI and B. MDIVANI (*Bull. Soc. chim.*, 1908, [iv], 3, 626—628; *Ann. Chim. anal.*, 1908, 13, 209).—The method depends on the reduction of vanadic acid by stannous chloride in presence of acids. The best results are obtained with a solution containing approximately 2% of stannous chloride and standardised against a solution of iodine of known strength. As indicator, ammonium molybdate, which gives a blue coloration with mere traces of stannous chloride, is used, drops of the indicator being placed on white porcelain. The results are equally good in presence of hydrochloric or sulphuric acid and in either hot or cold solution. T. A. H.

Electrolytic Estimation of Antimony. O. SCHEEN (*Zeitsch. Elektrochem.*, 1908, 14, 257—263).—The electrolytic deposition of antimony from a solution containing sodium sulphide and potassium cyanide has been said to yield too high results. Sodium sulphide (80 c.c.; D 1.14) and potassium cyanide (30 c.c.; 30%) are mixed with the neutralised antimony solution, the mixture diluted to 140—150 c.c., and electrolysed in a platinum basin with 1.2 to 1.3 amperes at 60—70°. The voltage must not exceed 1.7 volts. The results obtained are too high with a thickly platinised basin, with wire gauze cathodes, and with rotating electrodes; on the other hand, perfectly correct results are obtained with a polished basin (using not more than 0.1 gram of antimony) and with a very slightly etched or platinised basin, using up to 0.2 gram of antimony. A large excess of sodium hydroxide or too high current density also leads to incorrect results. On a rough surface, the deposit is formed most quickly on the highest points, and so the depressions are bridged over and enclosures of solution are formed which cannot be removed by washing. T. E.

Electrolytic Estimation of Antimony. ERNST COHEN (*Zeitsch. Elektrochem.*, 1908, 14, 301).—The error in the electrolytic estimation of antimony has been shown by Dormaar (*Abstr.*, 1907, ii, 200) and by Foerster and Wolf (*ibid.*, ii, 508) to be due to oxidation of the antimony, and only to a very small extent to enclosures of mother liquor, as Scheen supposes (preceding abstract). T. E.

Volumetric Estimation of Antimony. A. KOLB and R. FORMHALS (*Zeitsch. anorg. Chem.*, 1908, 58, 202—208).—In the light of the

results described by the authors (this vol., ii, 599), it is pointed out that antimony, in the form of antimonious acid, can be titrated accurately by the iodine-thiosulphate method when the hydrochloric acid and potassium iodide are used in sufficient concentration; 20—25 c.c. of acid, D 1.125, and 0.5—1.0 grams of the iodide give good results when the total volume is 100 c.c. It is further of advantage to use air-free reagents.

When metallic antimony is dissolved in aqua regia and the excess of nitric acid removed by evaporation, this volumetric method gives results which are about 1% too low, owing probably to incomplete oxidation of the antimony. Accurate results are obtained by the following somewhat complicated method. The metal or a compound is dissolved in aqua regia or in bromine and hydrochloric acid, the nitric acid or bromine removed by evaporation, the solution diluted, the antimony precipitated as sulphide, the latter dissolved in dilute potassium hydroxide, and the mixture oxidised by hydrogen peroxide, first in dilute and then in strong alkali; the solution is then made strongly acid with hydrochloric acid, potassium iodide added, and the titration completed in the usual way. G. S.

The "Hydrogen Number" as a means for determining Unsaturated Organic Compounds in a manner similar to the Iodine Numbers of Hübl and Wys. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 700—709).—The author defines the "hydrogen number" of an organic compound as the number of c.c. of hydrogen at 0° and 760 mm. pressure absorbed by one gram of the compound. For carrying out the test, the author has devised an apparatus consisting of a distillation flask (50—150 c.c.) having a small beaker fused inside on the bottom and connected by means of the side-tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed 0.1—0.02 gram of molecular platinum moistened with 0.25—0.5 c.c. of water, and in the flask, the substance to be examined and 20—30 c.c. of alcohol free from dissolved oxygen. The flask is shaken by a shaking machine.

The following are the hydrogen numbers obtained by the author, the values in brackets being either the hydrogen numbers corresponding with Wys' iodine number, or, where indicated, the theoretical hydrogen numbers. Elaidic acid, 78.6—81.4 (78.8); oleic acid, 86.6—87.2 (86.2); fatty acids from sunflower oil, 119.6—120.8 (122.9); fatty acids from linseed oil, 164.9—166.3 (166.0); castor oil, 73.7 (75.5); croton oil, 260.9 (theoretical 258.4); undecic acid, 115.6 (114.1); erucic acid, 39.4 (65.6); maleic acid, 190.6—191.6 (theoretical 191); aconitic acid, 131.0 (theoretical 127.7); citraconic acid, 175.2 (theoretical 171.1); cinnamic acid, 215.0 (150.1). Colophony, naphthalene, benzoic acid, resorcinol, quinol, catechol, pyrogallol, and cymene give zero hydrogen numbers. T. H. P.

Indirect Estimation of Alcohol by Refraction. ADOLPH FRANK (*Chem. Zeit.*, 1908, 32, 569—570).—The indirect estimation of alcohol in worts, beers, wines, cordials, &c., by observing the refraction before and after expelling the alcohol has been shown by the author to be quite untrustworthy. L. DE K.

Detection of Methoxyl- and Methylimino-groups. JOSEF HERZIG (*Monatsh.*, 1908, 29, 295—297. Compare Kirpal, this vol., ii, 436).—Goldschmiedt (Abstr., 1905, i, 900) and Herzig and Polak (this vol., i, 546) have shown that tetramethylellagic acid and similar compounds must be heated several hours with hydriodic acid before all the methoxyl groups are completely hydrolysed. In estimating methoxyl groups by Zeisel's method, it is therefore advisable to heat several times with fresh additions of strong hydriodic acid, and to use fresh solutions of silver nitrate, until the latter ceases to become turbid on dilution. Further, the presence of a methoxyl- and not a methylimino-group is only indicated with certainty when the theoretical quantity of methyl iodide is liberated in the time normally required for the estimation of methoxyl by Zeisel's method (compare Herzig and Meyer, Abstr., 1895, ii, 296; 1898, i, 53).
W. H. G.

Bang's Method of Estimating Sugar. H. JESSEN-HANSEN (*Biochem. Zeitsch.*, 1908, 10, 249—257. Compare Abstr., 1906, ii, 136).—This method was tested, and is highly commended.

W. D. H.

The Reduction of Cuprous Oxide in the Estimation of Reducing Sugars. VLADIMÍR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1908, 32, 497—499).—The cuprous oxide obtained by the action of a reducing sugar on Fehling's solution is collected on a layer of asbestos in a Gooch porcelain or copper crucible and washed in the usual way. The crucible is then gently heated over a spirit-flame, and immediately suspended in a beaker containing a small quantity of 70% methyl alcohol, the beaker being heated with a small flame, so that it is filled with vapours of methyl alcohol. The latter reduce the cuprous oxide to metallic copper, and the crucible and its contents are then dried at a temperature of 100° and weighed. Before use, the crucible containing a layer of asbestos is submitted to similar treatment.

W. P. S.

Colour and Spectral Reactions of Sugars with Naphtharesorcinol and Hydrochloric Acid. BERNHARD TOLLENS and F. RORIVE (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 629, 521—526; *Ber.*, 1908, 41, 1783—1787).—The authors have examined the colour reactions of a number of sugars and allied substances with naphtharesorcinol and hydrochloric acid. A few grains of the sugar and about the same quantity of naphtharesorcinol are mixed in a test-tube with 10 c.c. of a mixture of equal volumes of hydrochloric acid, D 1.19, and water, and the liquid heated slowly to gentle boiling, which is maintained for one to three minutes. After three to five minutes, the tube is cooled, the solution filtered, and the residue on the filter washed three or four times with water until the wash-water becomes colourless. Alcohol, 95° Tr, is then poured on to the filter, and the alcoholic solution of the residue passing through is examined spectroscopically.

When gently warmed with naphtharesorcinol and hydrochloric acid, lævulose and sorbose give a fine red coloration, which is somewhat more violet than that given by lævulose with resorcinol. Dextrose

and mannose, as well as substances which yield these sugars when hydrolysed, give, when treated as above, faintly fluorescent alcoholic solutions, which exhibit a band in the green portion of the spectrum. In absence of lævulose, galactose and galactosides yield alcoholic solutions showing a band on the *D*-line and one in the green; if lævulose is present, it may be destroyed beforehand by heating with the diluted hydrochloric acid. With pentoses, and more especially with methylpentoses, the green fluorescence of the alcoholic solutions obtained is very marked; the methylpentoses yield violet-blue alcoholic solutions, which exhibit a band on the *D*-line and another in the green. Glycuronic acid gives a fine blue alcoholic solution showing a band on the *D*-line.

T. H. P.

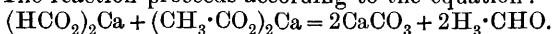
Simple Method of Detecting Glycuronic Acid and its Derivatives in Presence of Pentoses and in Urine. BERNHARD TOLLENS (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 629, 526—528; *Ber.*, 1908, 41, 1788—1790. Compare preceding Abstract).—Glycuronic acid may be readily detected as follows. A piece of the substance to be examined as large as a pea is heated in a wide test-tube with 5—6 c.c. of water, 0.5—1 c.c. of a 1% alcoholic naphtharesorcinol solution, and 6—7 c.c. of hydrochloric acid, *D* 1.19, the liquid being kept gently boiling for a minute. After standing for four minutes, the liquid is cooled, mixed with an equal volume of ether, and well shaken. When the liquid has settled, the upper ethereal solution has a blue or red colour, exhibits blue fluorescence, and has a band slightly to the right of the *D*-line if glycuronic acid is present; 0.1%, or even less, of glycuronic acid can be detected by this reaction, which is also given by compound glycuronic acids and by various plants, for instance, *Fucus* and *Laminaria*.

T. H. P.

The Quantity of Formic Acid in Honey. K. FARNSTEINER (*Zeitsch. Nahr. Genussm.*, 1908, 15, 598—604).—It is shown that only very small quantities of free formic acid (from 0.0011 to 0.0024%) occur in honey, the greater part of the acidity of the latter being due to some other acid, possibly malic acid. About 0.02% of formic acid is present in a combined state, probably as an ester.

W. P. S.

Detection of Formic Acid in Foods. ALPHEUS G. WOODMAN and A. L. BURWELL (*Tech. Quarterly*, 1908, 21, 1—3).—In the method proposed, the formic acid is converted into its calcium salt, and the latter is subjected to dry distillation in the presence of calcium acetate. The reaction proceeds according to the equation:



The acetaldehyde formed is then detected by means of magenta-sulphurous acid reagent. The details of the method are: 50 grams of the sample are acidified with 20 c.c. of 20% phosphoric acid and steam distilled until about 200 c.c. of distillate have been collected. To the distillate are added 2 c.c. of 30% acetic acid and 20 c.c., or more, of milk of lime, and the solution is evaporated to dryness. The dry residue is then transferred to a test-tube provided with a bent delivery tube, and is there subjected to dry distillation. The distillate is

collected in a little water, and the solution is treated with the magenta-sulphurous acid reagent. A slight coloration nearly always develops, even in the absence of formic acid, and the latter must not be considered to have been present in the sample unless the coloration obtained exceeds that of a solution prepared by diluting 8 c.c. of cupric chloride solution (12 grams of the crystallised salt per litre) and 12.5 c.c. of cobaltous chloride solution (24 grams of the crystallised salt and 100 c.c. of hydrochloric acid per litre) with water to 100 c.c. If the food contained 0.05 per cent. of formic acid, the coloration obtained will be about six times as dark as that of the comparison solution.

W. P. S.

Detection of Citric Acid in Wine, &c. G. FAVREL (*Ann. Chim. anal.*, 1908, 13, 177—179).—When citric acid is heated with sulphuric acid, formic and acetonedicarboxylic acids are formed; the latter acid may then be separated and identified. In testing wine, 100 c.c. are evaporated to dryness on the water-bath, the residue is dissolved in 7 c.c. of boiling water, and to the solution are added 35 c.c. of 95% alcohol. At the end of thirty minutes, the mixture is passed through a filter, and the filtrate is treated with 0.4 gram of calcium acetate dissolved in 5 c.c. of water. The calcium citrate which is precipitated (if citric acid is present in the wine) is collected on a filter and, when dry, transferred to a test-tube, 3 c.c. of concentrated sulphuric acid, heated previously to 100°, are added, and the solution is kept at a temperature of 80° to 90° for two minutes. It is then cooled, diluted with three times its volume of water, again cooled, and shaken with alcohol-free ether. On evaporating the ethereal solution, acetonedicarboxylic acid crystallises out; when dissolved in water, this acid gives a characteristic violet-red coloration with ferric chloride. The test is not affected by the presence of formic, acetic, butyric, tartaric, malic, lactic, or oxalic acids in the wine or other liquid under examination, but salicylic acid must be removed previously by extraction with ether after acidifying with hydrochloric acid. The method will detect 0.005% of citric acid in wine.

W. P. S.

Citric Acid and Natural Wines. H. ASTRUC (*Ann. Chim. anal.*, 1908, 13, 224—226).—The author states that natural wines may contain citric acid. The presence of this acid is detected with safety by Denigès' reagent (ministerial decision, Jan. 18, 1907).

L. DE K.

The Normal Citric Acid of Wines. GEORGES DENIGÈS (*Ann. Chim. anal.*, 1908, 13, 226—227).—The author states that he had noticed ten years ago that new wines contain 3—6 centigrams of citric acid per litre as a natural constituent.

Probably owing to bacterial influences, the acid cannot be detected in some old samples.

L. DE K.

Phenolsulphonic Acid and its Salts. GERHARD HÜBENER (*Chem. Zeit.*, 1908, 32, 485—486).—The phenol group is but im-

perfectly precipitated by bromine, and cannot therefore be titrated by the usual volumetric bromine and iodine methods. On boiling, however, with a saturated solution of bromine in hydrochloric acid, the phenol is completely eliminated, whilst the sulphonyl group is converted into sulphuric acid, which may then be estimated in the filtrate as usual. From this should be deducted any free sulphuric acid the compound may contain, which is estimated by simply adding barium chloride and a few drops of hydrochloric acid.

L. DE K.

The Freezing Point of Milk. A Method of Detecting Adulteration. W. R. GELSTON ATKINS (*Chem. News*, 1908, 97, 241—242).—The results of a considerable number of determinations are given, showing that the freezing point of milk is practically a constant, namely, -0.55° ; the variations from this rarely exceed 0.03° above or below the mean. Determinations of the freezing point and specific gravity of a sample of milk are sufficient to show whether water has been added or fat removed. The freezing point of milk is not affected by the presence or absence of fats.

W. P. S.

Flask for Fat Estimation. WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1908, 30, 797—798).—The flask recommended by Wheeler and Hartwell (*Abstr.*, 1901, ii, 586) and modified by Robison has been replaced by one of the Erlenmeyer type. The flask is fitted to the condensing apparatus by means of a seal consisting of a maple cup made to fit over an ordinary rubber stopper through which passes the neck of the flask. The seal is made by mercury in a manner similar to the device used by Wheeler and Hartwell.

L. DE K.

New Method for the Estimation of Fat in Cocoa. ADOLF KREUTZ (*Zeitsch. Nahr. Genussm.*, 1908, 15, 680—683).—A weighed portion of about 1.5 grams of the cocoa is placed in a small flask, 3 grams of solid chloral alcoholate are added, and the mixture is heated on a water-bath until melted to a homogeneous mass. About 15 c.c. of ether are next added, and the contents of the flask are shaken; a further quantity of 35 c.c. of ether are then added, and the mixture is poured on a filter, the ethereal filtrate being received in a weighed flask. The residue on the filter is washed twice with ether, the washings being also collected in the flask, from which the ether is then evaporated, and the residue of fat dried at a temperature of $105-110^{\circ}$ and weighed. The chloral alcoholate is expelled completely from the fat at this temperature.

W. P. S.

The Ethyl Ester Value of Fats. A New Constant for the Detection of Coconut Oil. JOSEF HANUŠ and LAD. ŠTEKL (*Zeitsch. Nahr. Genussm.*, 1908, 15, 577—587).—The process is based mainly on the different amounts of lauric acid occurring in coconut oil and other fats. The glycerides are converted into ethyl esters and the volatile portion of these is distilled and estimated. Five grams of the filtered fat to be tested for coconut oil are placed in a 200 c.c. Erlenmeyer flask and heated for fifteen minutes to a temperature

of 50°. Thirty c.c. of *N*/10 alcoholic potassium hydroxide solution are then added, the contents of the flask are shaken until a clear solution is obtained, and again heated for ten minutes at 50°. Two c.c. of sulphuric acid (which quantity must be capable of exactly neutralising the 30 c.c. of alkali added) are then added, the whole is diluted with water to a volume of 145 c.c., and distilled, a little pumice-stone being added. The first 30 c.c. of alcoholic distillate are rejected, whilst the next 100 c.c. are collected and transferred to a flask. Alcohol is added until the turbid solution becomes clear, and the free acid is titrated, using phenolphthalein as indicator; 40 c.c. of *N*/2 alcoholic potassium hydroxide solution are added, the solution is boiled for forty-five minutes under a reflux apparatus, and the excess of alkali is then titrated. The quantity of alkali required for the saponification, expressed in c.c. of *N*/10 solution, is termed the ethyl ester value of the fat. This value for various fats is: cocoanut oil, over 40; palmit oil, about 25; butter, from 7 to 14; lard, cacao butter, sesame oil, cotton oil, olive oil, &c., less than 3. The value is particularly useful for detecting the presence of cocoanut oil in lard, cacao butter, and margarine, but it will not indicate, with certainty, a less quantity than 15% of this oil in butter.

W. P. S.

Abrastol. DIOSCORIDE VITALI (*Boll. chim. farm.*, 1908, 47, 291—301).—Abrastol, or calcium β -naphthol- α -sulphonate, is used as an internal antiseptic and as a precipitant for tartrates in wine, instead of other calcium salts. A number of colour reactions are described, one of the best being that obtained by evaporating with a solution of mercurous nitrate (reddish-violet colour). From wine, the acid may be extracted by amyl alcohol or ethyl acetate, or it may be isolated as potassium salt on evaporating the wine, after making it alkaline, and extracting the residue with alcohol; the acid can then be further purified by lead acetate and hydrogen sulphide. G. B.

Gall-Iron Inks. ERICH KEDESZ (*Chem. Zentr.*, 1908, i, 991; from *Mitt. K. Materialprüfs.-Amt.*, 25, 268—269).—*Detection of Tannin and Gallic Acid with Molybdate Solution.*—Tannin and gallic acid give with acid ammonium molybdate solution a sherry or even dark brown coloration. The residue obtained from the extraction with ethyl acetate (see this vol., ii, 544) is dissolved in 100 c.c. of water, 1—2 c.c. are diluted to 25 c.c., and mixed with 5 c.c. of Finkener's molybdate solution.

An approximate estimation may be made by comparing the depth of colour with a standard solution. This may be made by extracting an ink of known composition with ethyl acetate and proceeding as already directed. L. DE K.

A Colour Reaction of Histidine. FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1908, ii, 356).—On adding bromine water to an aqueous solution of histidine or a histidine salt, decolorisation at first takes place. On further addition of the reagent, the mixture assumes a permanent yellow colour; on warming, it again becomes at first

colourless, but after a time a pink colour appears, which afterwards deepens to a deep wine-red. Later, black, amorphous particles separate from the solution. Too large an excess of bromine destroys the reaction. A number of iminoazole derivatives nearly allied to histidine fail to give the reaction. The reaction is sensitive with solution of 1 in 1000. S. B. S.

Alkaloid Reactions (Tropacocaine). C. REICHARD (*Pharm. Zentr.-h.*, 1908, 49, 337—342).—A series of tests is given of which the following are examples. When examined with a magnifying glass, tropacocaine hydrochloride shows a strong double refraction, and exhibits all the colours of the rainbow. When moistened with water, it gives no aromatic odour, thus distinguishing it from cocaine. Warmed with potassium ethyl sulphate and sulphuric acid, it gives the odour of ethyl benzoate, whilst cocaine gives a strong odour of peppermint.

Sulphuric acid gives no characteristic colour. The reactions with sodium nitroprusside and with copper sulphate are very much like those obtained with cocaine. A more characteristic reaction is obtained with nitric acid. On evaporating with nitric acid to dryness, an opaque, white residue is obtained; cocaine yields a transparent, varnish-like substance. The behaviour with cobalt nitrate is also important. If to a small drop of cobalt nitrate is added a slight excess of tropacocaine hydrochloride, the mixture turns yellow; on warming, the colour changes to blue, but on cooling the yellow colour is restored. Cocaine when treated similarly yields a permanent blue spot. L. DE K.

Estimation of Albumin in Urine by Esbach's Method. J. C. VAN DER HARST (*Pharm. Weekblad*, 1908, 45, 489—492).—A criticism of the popular Esbach albumimeter, the indiscriminate use of which has already been condemned by various authorities. It now appears that some urines contain a colloidal substance which prevents the formation of the albumin picrate; this may, however, be eliminated by boiling the urine with strong acetic acid, but in such a case a different apparatus would have to be constructed.

L. DE K.

Reaction between Hæmoglobin and the Leuco-base of Malachite-green. GEORGE A. BUCKMASTER (*Proc. physiol. Soc.*, 1908, xi—xiv.; *J. Physiol.*, 37).—This base (tetramethyldiaminotriphenylmethane), first used by Adler for the detection of blood, is recommended for that purpose. Like the guaiacum reaction, the bluish-green colour developed is not due to the chlorides of blood (as Senter suggested) or to any ferment, but to the iron in hæmoglobin and its derivatives. It is termed a pseudo-peroxydase reaction.

W. D. H.

Sensitive Reaction for Carboxy-hæmoglobin. ANGELO DE DOMINICIS (*Boll. chim. farm.*, 1908, 47, 258—260).—The author finds that the tannic acid test for carboxy-hæmoglobin can be controlled by

examining the mixture of blood and tannic acid solution spectroscopically by means of reflected light. He uses Schulz's modification of this test, according to which 2 c.c. of blood, diluted to 10 c.c. with water, are shaken with 10 c.c. of 3% aqueous tannic acid solution; with normal blood, a brick-red colour is formed, which changes to brownish-grey, whilst blood containing carbon monoxide yields a persistent rose-red coloration. The spectroscopic examination is made twenty-four hours after the tannic acid has been added to the blood. The normal blood then exhibits a band in the red, whilst the bands due to the hæmoglobin are scarcely visible; when carbon monoxide is present, either no band or only a light one appears in the red, whilst the hæmoglobin bands are much more intense.

T. H. P.

Composition of Meat Extract. KARL MICKO (*Zeitsch. Nahr. Genussm.*, 1908, 15, 449—462).—The main part of the paper is devoted to the behaviour on hydrolysis of those constituents of meat extract which remain in solution after saturating the liquid with zinc sulphate. They are recovered from the filtrate by evaporating in a vacuum and extracting the dry residue with ammonia and alcohol (1 : 3).

When, after the purification with lead hydroxide, &c., the syrupy mass is boiled with hydrochloric acid, most of the matter is precipitated by phosphotungstic acid (diamino-acids). From the filtrate may then be recovered: taurine, glyoxime, alanine, leucine, aspartic acid, and glutamic acid; for working details, the original article should be consulted.

L. DE K.

The Mechanism of the Guaiacum Reaction. C. E. CARLSON (*Zeitsch. physiol. Chem.*, 1908, 55, 260—294).—The theory is advanced that the blue coloration of guaiacum tincture takes place in those reactions in which the atoms of water are in a "labile" condition and readily combine, as in the reaction $\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O}$. It is to the formation of water in such reactions that the blue coloration is due. There are certain exceptions, such as the reaction of sulphuric acid on zinc hydroxide, but a theory is advanced to explain why water is not formed in such reactions, but a stable hydrate. A theory is also advanced to explain the hydrolysis by means of enzymes, and to show why the latter give the guaiacum reaction.

S. B. S.

Criticism of Joulie's Process for Estimating the Acidity of Urine. FERNAND REPITON (*Ann. Chim. anal.*, 1908, 13, 147—148. Compare Abstr., 1907, ii, 409).—A controversy with Joulie on the subject of acidity in urines (compare Joulie, *Clinique et laboratoire*, Aug., 1907).

L. DE K.

General and Physical Chemistry.

The Ultimate Rays of the Metalloids, Tellurium, Phosphorus, Arsenic, Antimony, Carbon, Silicon, and Boron. ANTOINE DE GRAMONT (*Compt. rend.*, 1908, 146, 1260—1263. Compare Abstr., 1907, ii, 517).—Alloys of lead or tin with 10% to 0.001% of the metalloids mentioned in the title have been examined spectroscopically, and the ultimate rays of great persistence found to coincide with those previously observed in minerals containing the same metalloids. The lines are common to the arc and spark spectra, with or without condensation, and are not masked by the presence of other substances. They are all situated in the ultra-violet, and can only be photographed when prisms of quartz or calc spar are employed. W. O. W.

The Red Portion of the Calcium Chloride Arc Spectrum. C. F. O. MEISENBACH (*Zeitsch. wiss. Photographie, Photophysik. Photochem.*, 1908, 6, 258—270).—The red end of the calcium arc spectrum has been studied photographically by means of red-sensitive plates, a large Rowland grating being used. The number of bands observed is very large, and only a few of them can be resolved. Since the bands are sometimes degraded towards the red and sometimes towards the violet, it appears that bands of different origin, due probably to the chloride, the oxide, and the metal, occur together. Detailed measurements of the bands and of the line spectrum are given. Four groups of bands are found to obey Deslandres' law. C. H. D.

The Separation and Quantitative Spectra of Cerium, Lanthanum, and Didymium. JAMES H. POLLOK and A. G. G. LEONARD (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 257—269).—The separation of cerium from mixed cerite earths by the action of chlorine in alkaline solution is recommended, fusion of the nitrates being employed to separate lanthanum, didymium, and yttrium. Neodymium and praseodymium were not separated. The residual lines on sparking dilute solutions between gold electrodes have been recorded and photographed in the manner already described (Abstr., 1907, ii, 918). C. H. D.

The Quantitative Spectra of Molybdenum, Tungsten, Thorium, and Zirconium. A. G. G. LEONARD (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 270—279. Compare preceding abstract).—The lines observed on sparking solutions containing 1, 0.1, 0.01, and 0.001% of the element between gold electrodes have been measured and photographed. The most persistent lines occur in the more refrangible part of the spectrum. The vibrations of small wave-length are therefore the most easily excited. This explains the greater tendency of ultra-violet rays to induce chemical action. C. H. D.

A New Arrangement of the König Spectrophotometer and its Application to the Determination of Chemical Equilibria. JOEL HILDEBRAND (*Zeitsch. Elektrochem.*, 1908, 14, 349—353).—Two small tungsten filament lamps are connected in series so that variations of current affect them equally. The light from one lamp passes through the solution. The two beams are then polarised at right angles to each other, pass a direct vision prism, and are received by a telescope with a Nicol prism in the eye-piece. The telescope can be adjusted to receive light of any desired wave-length; by rotating the Nicol, the two beams can be made of the same intensity.

The dissociation of phenolphthalein is measured by means of the instrument. Phenolphthalein is dissolved in solutions of ammonia and ammonium chloride in which the concentration of the hydrogen ions is known. The amount of phenolphthalein dissociated is obtained by comparing the absorption with that observed in a completely dissociated solution. The dissociation constant, $[H^+][R^-]/[HR]$, where $[R^-]$ is the concentration of the phenolphthalein ion, is found to be 1.7×10^{-10} for solutions in which from 5 to 65% of the phenolphthalein is dissociated; for smaller degrees of dissociation smaller values are observed. T. E.

Optical Investigation of the Condition of Chromate and Permanganate Solutions. ARTHUR HANTZSCH and ROBERT H. CLARK (*Zeitsch. physikal. Chem.*, 1908, 63, 367—381).—By a study of absorption spectra and determination of molecular extinction coefficients, the authors have reached results for chromates, dichromates, and permanganates similar to those already reached for platinichlorides (see this vol., ii, 447).

Solutions of chromium trioxide in pure water and in aqueous sulphuric acid are at all concentrations optically identical with each other and with feebly acid solutions of potassium dichromate. Solutions of the latter in pure water deviate very slightly in the direction of monochromate solutions. Solutions of monochromates in pure water, in alkalis, and in methyl alcohol are at all concentrations quite different from dichromate and chromic acid solutions in their optical characteristics, but are identical among themselves except for a slight deviation of the pure aqueous solutions in the direction of the dichromate solution. The optical characteristics are independent, not only of the concentration and the solvent, but also of the temperature.

The chromophoric group in all acid solutions is the completely saturated complex Cr_2O_7 ; in all alkaline solutions the corresponding complex CrO_4 . From the optical point of view, it is immaterial whether these complexes are combined with hydrogen or alkali metal, dissociated or undissociated; the colour of the ions must be the same as that of the undissociated molecule.

Similarly, the absorption of permanganic acid and its salts is not appreciably influenced by the solvent, the temperature, or the degree of dissociation.

Emphasis is laid on the value of this optical method in studying constitutive changes due to the chemical influence of the solvent.

J. C. P.

Attempt to Produce Dichroism by Pressure in Silver Haloids. FELIX CORNU (*Centr. Min.*, 1908, 393—395).—A. von Lasaulx, in 1879, made the observation that dichroism is developed by pressure in crystals of chlorargyrite from Schneeberg, but the present author has been unable to confirm this observation by his experiments on chlorargyrite, embolite, and bromyrite from various other localities.

L. J. S.

Apparatus for Producing Flame Colorations and Other Changes of a Non-luminous Flame. F. SCRIBA (*Chem. Zentr.*, 1908, i, 1753; from *Zeitsch. physik-chem. Unterr.*, 1908, 21, 110—111).—A modified form of Bunsen burner made of glass and having a glass tube bent downward as air inlet. By this means a flame coloration is obtained by introducing the air inlet tube into a vessel containing the vapour or dust of the flame colouring substances.

J. V. E.

Polarimetric Measurements with Small Quantities of Liquid. JULIUS DONAU (*Monatsh.*, 1908, 29, 333—336).—In the experiments in question, a capillary tube of 0.4—0.5 mm. internal diameter and 5—10 cm. long, made of black glass, was fixed by means of rubber tubing into a wider tube; the liquid to be examined was then introduced, the ends closed with small glass covers, the tube pushed inside an ordinary polarimeter tube, and the measurements made in the usual way. Sodium light or, for the longer tubes, electric light is used, and the results are scarcely less accurate than those obtained in the ordinary method (compare Fischer, this vol., i, 544).

G. S.

Dispersion of Magnetic Rotatory Power in the Neighbourhood of Bands of Absorption in the Case of Rare Earths. JEAN BECQUEREL (*Phil. Mag.*, 1908, [vi], 16, 153—161. Compare Abstr., 1906, ii, 317, 421; 1907, ii, 147; this vol., ii, 78, 338).—In reference to recent communications of Wood (this vol., ii, 244) and Elias (this vol., ii, 549), the author discusses the results of his work on the influence of a magnetic field on the absorption bands of xenotime and tysonite, details of which have already been published.

It is maintained that the experimental observations are in agreement with the theory of magnetic rotatory polarisation, which is based on the Hall effect. The phenomenon in the case of crystalline substances is of the same nature as that found by Zeeman for vapours.

Differences are found in that the order of magnitude of the displacements for many of the bands of crystals is much greater than for the bands of vapours, and that when the optic axis of a uniaxial crystal is parallel to the lines of force of the field and the direction of propagation of the light, the bands corresponding with the absorption of the circular components of given sense are not all displaced in the same direction.

H. M. D

Photographic Capacity and Supposed Radioactivity of Hydrogen Peroxide. OCTAVE DONY-HÉNAULT and ALICE DONY-HÉNAULT (*Bull. Soc. chim. Belg.*, 1908, 22, 224—245. Compare Abstr., 1906, ii, 645).—The results of this work show that Russell's

view, that the latent images produced by various organic materials when placed on sensitised plates in the dark are due to the action of vapour of hydrogen peroxide directly evolved by these materials, is accurate, and that the action is not due to radiation, as suggested by Graetz (*Physikal. Zeit.*, 1904, 5, 698).

The vapour tensions of solutions of hydrogen peroxide have been ascertained by determining the amount of the peroxide carried away in a certain time by a known current of gas from a solution of the peroxide of known strength kept at a definite temperature. The peroxide was absorbed in a solution of titanous anhydride in sulphuric acid, and finally estimated by a standard solution of permanganate. At constant temperature, the vapour tension of hydrogen peroxide solution increases with the concentration, but for equal concentrations the partial vapour pressure may diminish with rise of temperature; thus a solution may give more water vapour and less hydrogen peroxide vapour at 40° than at 19° (compare Precht and Otsuki, *Abstr.*, 1905, ii, 296, 495). The vapour tensions observed are tabulated in detail in the original. The minimum quantity of hydrogen peroxide necessary to produce an image on a photographic plate is 1.2×10^{-8} gram. The vapour tension and photographic activity of hydrogen peroxide solution may be either increased or diminished by the addition of sulphuric acid, and, generally, parallel observations are concordant, but influences sometimes disturbing this concordance are (1) the slow interaction of the acid and peroxide, causing the vapour tension to vary with the duration of the experiment, and (2) the effect of increased humidity in intensifying the image on the plate.

From these observations, the conclusion is drawn that the photographic activity of solution of hydrogen peroxide is due to the actual transport of peroxide vapour to the sensitised layer of the plate. Incidentally, it is pointed out that the photographic method may be applied to the determination of the molecular structure of the unstable compounds of titanous anhydride and other oxides with hydrogen peroxide by noting the concentration of peroxide at which the solutions of the anhydride and peroxide in sulphuric acid begin to affect photographic plates, this being the point at which the anhydride has been saturated with peroxide. Results of such experiments indicate that the compounds TiO_2 , H_2O_2 and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}_2$ exist, which are stable in sulphuric acid solution.

T. A. H.

Radioactivity of Ordinary Metals and the Penetrating Radiation from the Earth. J. C. McLENNAN (*Physikal. Zeitsch.*, 1908, 9, 440—443).—The electrical conductivity of the air enclosed in cylinders of lead, aluminium, and zinc has been measured at a number of places in the neighbourhood of Toronto. The collected data lead the author to draw the conclusion that if the metals could be entirely freed from radioactive impurities, and if observations could be made under conditions such that penetrating radiations from external sources could be excluded, the conductivity of the enclosed air would have an extremely small value, and might disappear completely.

H. M. D.

Helium and Radioactivity in Rare and Common Minerals.

ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1908, 80, A, 572—594).—A large number of minerals, including sulphides, native elements and oxides, rare earth minerals, and igneous rocks, have been tested for the inert gases, more particularly helium. The general method of procedure was to heat the finely-powdered mineral to redness, absorb the ordinary gases given off, and examine the spectrum of the inert residue.

Practically all the minerals contain helium, and in the majority of cases in the proportion to be expected from the traces of uranium and radium which the minerals contain. Thus for samarskite, hæmatite, and quartz, which contain 1,500,000, 700, and 2 c.mm. of helium per kilogram respectively, the ratio of helium to uranium oxide varies only from 9:1 to 14:1. In a few cases in which the ratio is higher, the mineral contains thorium, apparently in sufficient amount to account for the greater helium content. The only exception to the above statements is beryl, which yields a proportion of helium much greater than corresponds with the amount of radioactive substance present.

The only minerals which contain appreciable amounts of argon are igneous rocks, and there does not appear to be any connexion between the radioactivity and the proportion of argon present. The results, therefore, afford no evidence that argon is one of the products of radioactive change.

G. S.

Radioactivity of Mineral Springs in the Tyrol.

MAX BAMBERGER (*Monatsh.*, 1908, 29, 317—332).—The measurements were made by Engler's method (*Abstr.*, 1907, ii, 218). The temperature and the radioactivity (in electrostatic units) of the water from a large number of wells are given in tabular form, as well as some geological notes on the localities. The radioactivity of sediments from four of the wells has also been determined.

G. S.

Radium Content of Deep-Sea Sediments.

JOHN JOLY (*Phil. Mag.*, 1908, [vi], 16, 190—197).—The author has examined the radioactivity of deep-sea sediments obtained from the "Challenger" and "Albatross" collections, and, further, of a specimen of Globigerina Ooze, and one of the mud thrown up by the volcanic disturbance of 1906 in the Bay of Bengal. These sediments are very much richer in radium than average terrestrial rocks. The richest sediments are those from the most central parts of the Pacific Ocean. Comparing the amounts of radium and calcium carbonate in the deposits, it is found that as the former increases, the latter decreases. This indicates that the amount of radium increases with the antiquity of the sediment. The largest amount of radium found was in the red clay from the Challenger Station, 276; per gram of air-dried material it contains 52.6×10^{-12} gram radium. Uranium has been found to be present in this red clay; a colorimetric determination of the amount present in the 8.42 grams examined gave 0.0006 to 0.0007 gram, whereas the amount calculated from the radium content is 0.0012 gram.

H. M. D.

Influence of Temperature on "Radioactive Changes. WILHELM ENGLER (*Ann. Physik.*, 1908, [iv], 26, 483—520. Compare Curie and Danne, Abstr., 1904, ii, 306; Bronson, Abstr., 1905, ii, 567; Makower, Abstr., 1906, ii, 259; Makower and Russ, Abstr., 1907, ii, 421; this vol., ii, 449; Schmidt, this vol., ii, 141).—A further attempt to settle the question whether the rate of decay of radioactive substances is independent of the temperature. The measurements were made on radium *B* and *C* and on radium emanation, the experiments being so arranged that the rate of decay could be measured during the period of heating and also immediately afterwards.

The observations with radium *B* and *C* indicate definitely that the rate of decay at 1100° to 1400° is greater than at the ordinary temperature, whilst, after cooling, the rate of decay is for some time less than the normal value. The influence of temperature on the rate of decay increases with the temperature.

In a similar way, when radium emanation is heated to temperatures above 1100°, an increase in the activity amounting to several units per cent. is observed. Even after heating for several hours, the activity is considerably greater than at the ordinary temperature. On cooling, the activity falls, and the normal value is attained at the end of about an hour. This decrease in the activity on cooling was not observed in all the experiments, and the suggestion is made that the samples of emanation which show the phenomenon contain another substance which is very sensitive to rise of temperature. This substance is apparently formed very slowly, for the emanation collected after a period of rest of eighteen weeks showed no decrease in activity on being cooled after exposure to a higher temperature.

H. M. D.

Secondary β -Rays. JOHN A. MCCLELLAND (*Proc. Roy. Soc.*, 1908, 80, 4, 501—515. Compare Abstr., 1907, ii, 420).—When radiation from radium, consisting of 96% of β -rays and 4% of γ -rays, is allowed to impinge on plates of various metals, the secondary radiation from the metal consists entirely of β -rays.

Although secondary β -rays are emitted in all directions, a very large proportion follows the ordinary law of reflection. The intensity of the reflected beam of β -rays does not vary much when one metal is substituted for another, but the intensity of the true secondary β -radiation, free from reflected rays, depends on the atomic weight of the metal in an even more striking manner than was shown in the previous work. If the amounts of true secondary radiation are plotted against atomic weights, the elements fall into divisions corresponding with the chemical periods. The higher the atomic weight the greater is the amount of β -radiation emitted, and the less the relative importance of the reflected portion.

Experiments were made in which the angle of incidence of the primary radium rays on the plate was 0°, 30°, 45°, 60°, and 75°, whilst the intensity of the emitted radiation was measured at all angles in the plane of incidence up to 75° on each side of the normal to the surface. When the incidence is normal to the surface, the secondary

radiation in any direction is proportional to the cosine of the angle between that direction and the normal. This might be expected from the fact that radiation from an element of volume deep in the plate traverses a thickness of material which is inversely proportional to the cosine of the angle between its direction and the normal.

Secondary radiation is much less from a thin sheet of aluminium than from a thick one, but the reflected portion increases less rapidly than the total radiation when the thickness of the plate is increased. Reflection is not merely a surface action, but goes on at successive layers beneath the surface.

There is good ground for dividing the total secondary radiation into two distinct parts, since true secondary β -rays appear to be more readily absorbed by tinfoil than either reflected or primary β -rays.

In addition to secondary radiation in the plane of incidence, the total radiation from an exposed plate has been measured by placing the plate at the base of an ionisation vessel consisting of three concentric tinfoil hemispheres. The ionisation current from the outer and inner to the middle hemisphere was approximately proportional to the total radiation, however distributed.

Measurements were made with lead, tin, copper, and aluminium, the angles of incidence varying from 10° to 80° to the normal. Given equal amounts of primary radiation falling on the plate, the total secondary radiation appears to vary somewhat with the angle of incidence. The higher the atomic weight the greater the total secondary radiation. With low atomic weights, reflected rays are an important factor, and the author supposes that these are not confined to the plane of incidence.

Reflected β -rays are supposed to actually consist of some of the incident β -particles, whilst true secondary radiation more probably consists of particles expelled from atoms perturbed by the entry of primary rays. The expelled particles may be original constituents of the atom or incident particles previously absorbed by the atom.

R. J. C.

Decay of Radium Emanation when Dissolved in Water.

RICHARD B. MOORE (*Proc. Roy. Soc.*, 1908, 80, A, 597—598).—The half-time period for the decay of radium emanation dissolved in water is 3·8 days, practically identical with that observed under ordinary conditions in air.

G. S.

Condensation of Radioactive Emanations. E. HENRIOT (*Chem. Zentr.*, 1908, 1, 1515—1516; from *Le Radium*, 1908, 5, 41—46).—With the object of ascertaining whether there is any relationship between the condensation of radium and thorium emanations by cooling and their adsorption by solids when heated, the adsorption of radium emanations by cocoanut charcoal has been studied. This substance was first treated in the cold with emanation, then heated in a closed vessel to a definite temperature, and the vessel connected with a larger evacuated chamber. The quantity of emanation thereby given up was measured and found to be a regular function of the

temperature; at 18° it is practically zero, and at 350° complete. When actinium emanation was connected by a U-tube to a zinc sulphide screen and the whole apparatus evacuated, no scintillations were produced when the temperature of the U-tube was below -145° , but with an increase of temperature an increased luminosity was observed. In a similar manner, it was found that radium emanation produced luminosity above -150° to -160° . An actinium salt was itself cooled, and the emanation conducted to a condenser by a current of air and measured; it was found that above -140° the quantity of emanation produced increased with the temperature. J. V. E.

Condensation of the Actinium and Thorium Emanations. S. KINOSHITA (*Phil. Mag.*, 1908, [vi], 16, 121—131).—A comparison of the condensation phenomena of the emanations of thorium and actinium has been made by a method similar to that used by Rutherford and Soddy for radium and thorium emanations (compare *ibid.*, 1903, [vi], 5, 361). Actinium emanation begins to condense at -120° , but until the temperature falls to -150° the condensation is incomplete. The temperature at which condensation begins, or at which a given proportion of the emanation remains uncondensed, depends largely on the pressure; it is the same whether the emanation is conveyed by air or by hydrogen.

Experiments on thorium emanation made with the same apparatus show that it condenses at temperatures from $2-3^{\circ}$ higher than the actinium emanation. The influence of pressure on the condensation phenomena is very nearly the same for both. H. M. D.

Emission of Electrons by Heated Metallic Oxides. FELIX JENTZSCH (*Ber. deut. phys. Ges.*, 1908, 6, 398—400. Compare Deininger, this vol., ii, 83).—The author has measured the number of electrons emitted by twenty different metallic oxides at high temperatures.

Platinum wires, coated with the oxides, were heated electrically and suspended axially in a brass cylinder between which and the oxide-coated wire a difference of potential was established, and the saturation current was measured. In all cases, the formula deduced by Richardson (*Phil. Trans.*, 1903, A, 201, 516) is satisfied by the experimental data.

Values representing (1) the number of electrons contained in unit volume of the emitting substance, and (2) the work done by an electron in passing through the surface of the active substance, are tabulated for the various oxides examined. The work done by an electron on emission is greater for the oxides of the electropositive metals than for those of the electronegative metals. On the other hand, the number of free electrons in the electropositive metals exceeds that in the electronegative. H. M. D.

Changes of Pressure which Accompany Point Discharge through Hydrogen containing Oxygen and Nitrogen. A. P. CHATTOCK and A. M. TYNDALL (*Phil. Mag.*, 1908, [vi], 16, 24—47).—Experiments have been made to ascertain the molecular complexity of

the ions in point discharge through hydrogen. By discharging from a platinum point against a platinum or palladium plate, the ions appear to be absorbed by the plate, resulting in a diminution of pressure, from which the number of molecules removed from the gas per ion can be calculated when the quantity of electricity passing through the gas during the discharge is known. (The expression "per ion" is to be interpreted as "per hydrogen atom set free in a voltameter placed in series with the discharge vessel.") The pressure changes were measured by means of a sensitive tilting pressure gauge capable of indicating differences of the order of $1 \cdot 10^{-8}$ atmosphere.

In pure hydrogen, the pressure change corresponds with the removal of one molecule per ion. In hydrogen containing 2 to 14% by volume of oxygen, positive point discharge brings about the combination of about 16 molecules of oxygen per ion, whilst negative discharge causes about 25 molecules of oxygen to combine per ion. When the percentage of the oxygen is less than 0.2, the number of molecules which combine in the positive discharge is approximately constant, and equal to about 10 per ion. For negative discharge, the combination increases rapidly when the percentage of oxygen falls below 2, and in hydrogen containing less than 0.01% of oxygen it attains the high value of 110 molecules per ion.

The presence of one part of oxygen in ten million parts of hydrogen can be detected by means of the pressure changes which accompany the point discharge.

When nitrogen is present with oxygen in hydrogen, even in large excess, the combination which takes place is chiefly, and perhaps entirely, between the oxygen and the hydrogen. H. M. D.

Does the Law of the Action of Mass Hold for the Silent Electrical Discharge? MAX LE BLANC and JOHN H. DAVIES (*Zeitsch. Elektrochem.*, 1908, 14, 361—366).—When dry ammonia gas is exposed to the silent discharge at constant temperature and constant current, the rate of decomposition is nearly proportional to the pressure. Temperature has a comparatively small influence on the rate of decomposition; a rise of 100° nearly doubles it. An increase of the current of one-third nearly doubles the rate of decomposition. The presence of excess of hydrogen diminishes the rate of decomposition, whereas nitrogen increases it. The luminosity of the discharge is much increased by nitrogen, but not by hydrogen. The final condition of equilibrium attained is found to be very little affected by the strength of current used. The ratio $[N_2][H_2]^3/[NH_3]^2$ for different mixtures of hydrogen and nitrogen is not even roughly constant. The law of mass action therefore does not hold. Apparently, it is only true when the temperature is so high that the reactions occur under the influence of heat alone. T. E.

Volatilisation of Cathodes in Attenuated Gases. FRANZ FISCHER and OTTO HÄHNEL (*Zeitsch. Elektrochem.*, 1908, 14, 366—367).—The authors have compared the volatilisation of different cathodes with the same current by using two discharge tubes in series. With the same metal and gas, the volatilisation is approximately inversely

proportional to the gas pressure and directly proportional to the square of the current density. The volatilisation in argon and hydrogen is the same; it is less in air than in hydrogen. The order of volatility of the metals is aluminium, iron, nickel, copper, platinum, silver. If the tubes are in parallel, the current passes more readily through argon than hydrogen, and the volatilisation in the argon tube is greater. Kohlschütter and Goldschmidt (this vol., ii, 457) find that different gases favour volatilisation in the order of their atomic weights. This is not in agreement with the present experiments, and is also contradicted by Kohlschütter and Goldschmidt's results when these are calculated for equal quantities of electricity. T. E.

Electrocapillary Measurements by the Method of Large Drops. LÉON G. GOUY (*Compt. rend.*, 1908, 146, 1374—1376).—The present paper deals with absolute measurements by means of a modified capillary electrometer. In order to obtain a rigorously hemispherical drop, the mercury is contained in a glass vessel, optically worked, and of 40 mm. radius. Results are given for solutions of hydrogen sulphate, sodium sulphate, hydrogen chloride, potassium bromide, and potassium iodide. W. O. W.

Determination of the Dielectric Constant of Helium. ERNST HOCHHEIM (*Ber. deut. phys. Ges.*, 1908, 3, 446—448).—The author has measured the dielectric constant of helium by the electrostatic null-method of Hopkinson-Lebedeff. The mean value reduced to 0° and 760 mm. pressure is $D = 1.000074 \pm 0.000004$. If the mean value n of the refractive index of helium is taken from the measurements of Scheel and Schmidt, Ramsay and Travers, and of Rayleigh, the relationship of Maxwell, $D = n^2$, is found to be satisfied. H. M. D.

Electrical Conductivity of Solid Cuprous Iodide. KARL BÄDEKER and E. PAULI (*Physikal. Zeitsch.*, 1908, 9, 431).—The electrical conductivity of cuprous iodide, which is abnormally high for a transparent substance, is found to diminish with time. By subjecting a very thin film of copper to the action of iodine vapour in a suitable apparatus, an initial maximum specific resistance equal to 0.01 ohm. was obtained for the iodide. In an atmosphere saturated with iodine vapour, the conductivity remains unchanged, but falls immediately when the iodine vapour is removed by a current of hydrogen or air. On saturating again with iodine vapour, the original high value of the conductivity is attained, and the transformation can be repeated with the same specimen of cuprous iodide as often as desired. H. M. D.

A Peculiar Type of Electrical Conductivity. KARL BÄDEKER (*Physikal. Zeitsch.*, 1908, 9, 431—433. Compare preceding abstract).—The rise of the electrical conductivity of cuprous iodide which is observed when the substance is brought into contact with saturated iodine vapour or a saturated iodine solution takes place asymptotically; approximately four-fifths of the total increase is observed in the first minute. The increase in the conductivity is accompanied by a slight darkening of the colour and by an increase in weight. The maximum

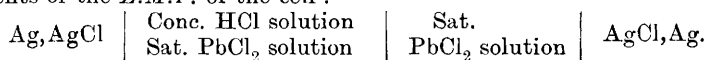
increase in weight of the substance when in an atmosphere of iodine corresponds with the addition of 0.00333 gram of iodine per gram of cuprous iodide. The proportion of absorbed iodine depends on the temperature and also on the pressure of the iodine vapour, or on the concentration of the iodine in the solution with which the cuprous iodide is in contact. Extremely small iodine vapour pressures or concentrations are, however, very active. The conclusion is drawn that the conductivity induced by the absorption of iodine is metallic in nature; the resistance is the same whether measured by direct or alternating currents, and prolonged passage of a direct current produces no change in the conductivity. The increase in conductivity observed when cuprous iodide is acted on by light is attributed to the separation of traces of iodine.

H. M. D.

Binary Electrodes and Electrochemical Adsorption. LEONOR MICHAELIS (*Zeitsch. Elektrochem.*, 1908, 14, 353—355).—By a binary electrode the author means a substance which sends out positive and negative ions when it dissolves. An acid of small solubility and high molecular weight sends out hydrogen ions and also anions; it may possibly continue to send these out after the solution is saturated; the ions will re-combine, and the undissociated molecules produced will separate out in the solid form. Owing to the different rates of diffusion of the hydrogen ions and the anions, the former will tend to escape from the surface of the solid, leaving it negatively charged. It therefore behaves like a hydrogen electrode, and the difference of potential between it and the solution depends on the concentration of the hydrogen ions in the solution. The addition of an acid diminishes the potential difference, and therefore increases the surface tension of the solid particles. The precipitation of a suspension of mastic by acids is explained in this way. The precipitation by a basic colouring matter, such as methyl-violet, is explained by the formation of a salt on the surface of the mastic particles. This diminishes the tendency to send out hydrogen ions, and so diminishes the potential difference and increases the surface tension. This theory is the opposite of that which explains adsorption as a pure surface effect due to the tendency of all substances to take on the form with the smallest surface tension.

T. E.

Thermodynamics of Liquid Cells. P. HENDERSON (*Zeitsch. physikal. Chem.*, 1908, 63, 325—345. Compare Abstr., 1907, ii, 426).—The formula deduced in the earlier paper (*loc. cit.*) has been tested by measurements of the *P.D.* between equally concentrated solutions containing bivalent ions, such as SO_4^{2-} , Ba, Cd, &c. The agreement between the observed and calculated values is fair. In respect to ease of manipulation, the author's formula is superior to Planck's, and the results which it gives are quite as satisfactory. An extension of the formula to concentrated solutions is deduced, and tested by measurements of the *E.M.F.* of the cell:



J. C. P.

Change of Free Energy Accompanying the Formation of Some Fused Salts of the Heavy Metals. RICHARD LORENZ and M. G. FOX (*Zeitsch. physikal. Chem.*, 1908, 63, 109—120).—The authors describe a form of chlorine or bromine electrode suitable for use at high temperatures, consisting of a hollow carbon tube kept charged with the halogen, and show that this electrode is reversible. The variation of *E.M.F.* with temperature has been determined for a number of cells containing fused salts, and the results are represented by the following formulæ: in these e_{AB} means the *E.M.F.* of the cell $A | AB | B$, AB being the fused salt formed from the elements A and B .

$e_{\text{PbCl}_2} = 1.263 - 0.000679 (t - 498^\circ)$ for the temperature-interval $498-660^\circ$; $e_{\text{CdCl}_2} = 1.258 - 0.000750 (t - 560^\circ)$, valid between 560° and 740° ; $e_{\text{PbBr}_2} = 1.0945 - 0.000714 (t - 367^\circ)$, valid between 367° and 640° ; $e_{\text{CdBr}_2} = 1.045 - 0.000742 (t - 580^\circ)$, valid between 580° and 720° .
J. C. P.

Thermodynamics of Cells with Fused Electrolytes. RICHARD LORENZ and M. G. FOX (*Zeitsch. physikal. Chem.*, 1908, 63, 121—125. Compare preceding abstract).—The Gibbs-Helmholtz formula is applied to the cells referred to in the preceding abstract, and the heats of formation of lead chloride and bromide and cadmium chloride and bromide are calculated. The values so found for the four salts are respectively 82.4, 71.5, 86.8, and 77.3 Cal. These figures represent the heats of formation at constant pressure in the temperature-intervals recorded in the previous abstract. So far as comparison is possible, the agreement with the values deduced thermochemically is fair.
J. C. P.

Differences of Potential at the Contact of Two Electrolytes. Nernst's Theory. J. GUYOT (*J. Chim. Phys.*, 1908, 6, 424—491).—Although the general formulæ for the potential difference at the contact of two electrolytes have not yet been obtained, it is shown theoretically that the calculation is not only possible for binary electrolytes with univalent ions (Nernst, Planck), but also for any two electrolytes of the same type (for example, BaCl_2 , CaCl_2), as well as for electrolytes with a common ion when the total ionic concentration is the same for the two solutions. Direct experimental verification of the formulæ is not possible, owing to the fact that no single potential difference is known with accuracy; in particular, it is pointed out that the Helmholtz-Ostwald method for determining single potential differences, depending on electrocapillary phenomena, is not trustworthy.

Measurements have therefore been made with "liquid chains," in which two solutions are in contact with each other and with mercury electrodes, forming cells of the type $M|S_1|S_2|M$. The total *E.M.F.* of such a cell is the algebraic sum of the potential differences at the two junctions metal|solutions, and that at the junction of the two solutions $S_1|S_2$. As the former can be calculated for electrodes of the same metal by the usual formula $E = RT/nF \log_e p_1/p_2$, the *E.M.F.* $S_1|S_2$ is readily obtained. For solutions of salts of the same type, measurements were made with alkali sulphates against sulphuric acid

and against each other, and for solutions of salts of different types such couples as $\text{HCl}|\text{BaCl}_2$, $\text{H}_2\text{SO}_4|\text{CuSO}_4$, and $\text{Na}_2\text{SO}_4|\text{ZnSO}_4$ were used. A few measurements were also made with liquid chains with identical extremities, for example,

$0.1N\text{K}_2\text{SO}_4|0.2N\text{Li}_2\text{SO}_4$ and $0.02N\text{H}_2\text{SO}_4|0.1N\text{K}_2\text{SO}_4$,
the *E.M.F.*'s at the junction metal|solution being thus eliminated. In all cases, the observed and calculated values were in satisfactory agreement. G. S.

A Method for the Calculation of Ionic Concentrations from Measurements of Potential in Concentration Cells. WARREN KENDALL LEWIS (*Zeitsch. physikal. Chem.*, 1908, 63, 171—176).—A method is given for calculating the dissociation of an electrolyte from potential measurements in concentration cells. Applied to the experimental determinations of Cumming with silver nitrate (this vol., ii, 253), very close agreement is obtained. New determinations with lead nitrate and chlorate are also given, the value for the normal lead electrode obtained being 0.402. The advantage of the method in the case of multivalent ions is that it is unnecessary to make any assumption as to dissociation in successive stages. C. H. D.

Electrochemical Equivalent of Silver, Especially in Reference to the So-Called Anode Liquid. FRIEDRICH KOHLRAUSCH (*Ann. Physik*, 1908, [iv], 26, 580—596).—The author has made experiments to ascertain whether the value obtained for the electrochemical equivalent of silver by F. and W. Kohlrausch in 1881, and 1883, requires correction in the light of recent researches on the properties of the anode-liquid. According to these, oxidation products are formed in the solution at the anode, and this leads to inaccurate values for the equivalent. Using the original pieces of apparatus and duplicates of these, the new experiments show that the arrangement of the electrodes is such that the abnormal properties of the anode-liquid do not exert any influence on the result obtained. The correction which might be applied to the value 0.01183 given by the older experiments is at any rate less than 0.002%. H. M. D.

A Lecture Voltameter. R. PITONI (*Nuovo Cim.*, 1908, [v], 15, 426—428).—The voltameter is of the Hofmann pattern, but the three tubes are of equal diameter and in the same plane. Each is fitted with an electrode, and the centre tube also has an outlet tube and tap at the lower end. In the electrolysis of water, the central electrode may be made the anode, and the two outer ones cathodes; the volume of gas collected in each tube is then equal. The application of the voltameter to polarisation experiments is also described. C. H. D.

Relation between the Ionising Power and the Dielectric Constants of Solvents. HERBERT N. MCCOY (*J. Amer. Chem. Soc.*, 1908, 30, 1074—1077).—Walden has shown (*Abstr.*, 1906, ii, 149) that when solutions of an electrolyte in various solvents have the same degree of dissociation, the product of the dielectric constant and the

cube root of the dilution for such solutions is a constant, or $\epsilon \sqrt[3]{V} = \text{const.}$ Kohlrausch's equation $\Lambda = \Lambda_{\infty} - k \sqrt[3]{C}$, where Λ is the equivalent conductivity at concentration C , Λ_{∞} the conductivity at infinite dilution, and k is a constant, may be written $\Lambda/\Lambda_{\infty} = 1 - k/\Lambda_{\infty} \sqrt[3]{C}$ or $\alpha = 1 - K \sqrt[3]{C}$ (1), where the degree of ionisation $\alpha = \Lambda/\Lambda_{\infty}$ and $k/\Lambda_{\infty} = K$, a constant. From equation (1) the expression $K = (1 - \alpha) \sqrt[3]{V}$ (2) is obtained. The data for sodium chloride are tabulated, in which the values of α are calculated by equation (1). Similar calculations have been made for about thirty other salts. The differences between the observed and calculated values of α do not exceed the probable experimental error. It is shown that equation (1) applies fairly accurately to many solutions in inorganic solvents, and the values of $K = (1 - \alpha) \sqrt[3]{V}$, ϵ , and $K\epsilon$ for tetraethylammonium iodide in various solvents are calculated from Walden's data. The results are also given for potassium iodide in water, ethyl alcohol, and acetonitrile, and for lithium nitrate in water, methyl alcohol, and 50% methyl alcohol. In the case of potassium iodide, the value of $K\epsilon$ is nearly the same for ethyl alcohol as for water, but is abnormally large in acetonitrile. For lithium nitrate, $K\epsilon$ has the same value for water and for methyl alcohol.

E. G.

Electrolytic Rectification of Alternating Currents. GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1908, 14, 333—347).—The author's experiments with direct current (*Ann. Physik*, 1906, 21, 929; 1907, 22, 543; 23, 226; 24, 43; 1908, 25, 775) have shown that the active electrode in an electrolytic rectifier is covered with a porous, non-conducting skin. The pores next to the metal are filled with gas, and the remainder are full of the electrolyte. When the electrode is cathode, negative corpuscles pass from it through the gas layer to the electrolyte without much resistance; when the electrode is anode, however, the carriers of the current in the electrolyte are anions which cannot pass through the gas layer. In the anode direction, the gas layer has a resistance of the order of 500 ohms per sq. decimetre; it also has a capacity of the order of 5 microfarads per sq. decimetre, and with alternating current of 50 periods per second, this allows the same current to pass as a resistance of 640 ohms. The resistance of the electrolyte is negligible compared with this, so that the current in the anode direction is conditioned by the resistance and capacity of the gas layer. In the cathode direction, the resistance of the gas layer and of the electrolyte are each of the order of 10 ohms per sq. decimetre; the capacity of the gas layer is therefore negligible. The theoretical shape of the current and *E.M.F.* curves are deduced from these considerations. A large number of curves are taken by means of an oscillograph, using electrodes of all the active metals known. The curves agree well with the theoretical forms. As a criterion of the relative values of the cells, the ratio of their apparent resistances in the cathode and anode directions is used. With aluminium in solutions of salts of potassium or sodium, the ratio is small, but the active layer soon breaks down. The danger of breakdown is smaller with ammonium salts, but the ratio is larger. Breakdown is never observed with

tantalum, but the ratio is much too large; its ability to resist *E.M.F.*'s of 1000 volts is of no use in practice, because of the very dilute solutions required. Magnesium has a very small ratio of resistances, but the active layer is very sensitive to rise of temperature. Since the liability to breakdown and a small ratio of resistances appear to be both due to the same cause (solubility of the solid skin in the electrolyte), it is improbable that a satisfactory electrolytic rectifier will be discovered.

T. E.

Theory of Dulong and Petit's Law. II. FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1908, 59, 146—160. Compare this vol., ii, 562).—A theoretical discussion of the causes which lead to deviations from Dulong and Petit's law. The author's theory, which requires that the product of the atomic weight and the specific heat at constant volume should be equal to 6.012, cannot be tested directly by ordinary experimental data. That elements of small atomic weight and small atomic volume represent exceptions is anticipated by the author's theory. In accordance with this, it is also found that of two allotropic modifications, the one with the smaller atomic volume has the smaller specific heat.

H. M. D.

Equation of Condition for Metals. MAX THIESEN (*Ber. deut. phys. Ges.*, 1908, 6, 410—415, 415—417. Compare Grüneisen, this vol., ii, 563).—A discussion of conclusions regarding the equation of condition, which may be drawn from the relationship pointed out by Grüneisen, that for a number of metals the quotient of the coefficient of expansion by the specific heat is almost independent of the temperature. The significance of this relationship depends on whether the equation of condition for a solid, crystalline substance is different from the equation for the same substance in the liquid condition or in another crystalline form, or whether the same equation of condition holds for all forms of the substance. In the first case, the relationship may be strictly true for certain crystalline forms, but in the second case the relationship can only be regarded as approximately valid for a finite portion of the curve of condition.

H. M. D.

Specific Heat and Molecular Magnetic Field of Ferromagnetic Substances. PIERRE WEISS and PAUL N. BECK (*Arch. Sci. phys. nat.*, 1908, iv, 25, 529—548).—The energy transfer when ferromagnetic substances are magnetised or demagnetised by alterations in temperature is of the same order as the energy required to effect the temperature change itself.

The authors endeavour to show that the anomalies exhibited by the specific heats of magnetic metals (Pionchon, *Abstr.*, 1887, 201) can be quantitatively explained as due to variations in the magnetic energy content.

Assuming each molecule to be a magnet producing lines of force, the energy of complete demagnetisation of iron is calculated to be 16.8 cal. per gram at 20°, becoming less as the temperature rises, and finally disappearing at 753°, at which temperature the iron loses its magnetic properties. The energy of demagnetisation of nickel varies

from 4.3 cal. at 22.9° to zero at 376°, whilst the corresponding values for magnetite are 14.4 cal. at 15.2° and zero at 588°.

At the ordinary temperature the magnetic phenomena should account for one-twentieth of the specific heat of iron, whilst in the neighbourhood of 753° the proportion would be as much as 43%. Thus the specific heat of iron undergoes an abrupt diminution at 753°.

Calorimetric measurements of the specific heat of iron, nickel, and magnetite over a wide range of temperatures show striking agreement with the results calculated from the magnetic properties. The specific heat of iron alters by 0.112 at 758°, whereas the figures calculated from the magnetic properties are 0.136 at 753°. Values for nickel and magnetite are in still better agreement with the theory.

R. J. C.

The Solid State. W. A. KURBATOFF (*J. Chim. Phys.*, 1908, 6, 337—354).—The melting points and equal fractions of the absolute melting points are to be regarded as corresponding temperatures for solids. It is shown by an examination of the available experimental data that at such temperatures the electrical conductivities, divided by the conductivities at the melting points, are equal for different metals, and that both electrical and thermal conductivity are periodic functions of the atomic weight. At corresponding temperatures, the law of Dulong and Petit holds rigorously, even for boron, carbon, and silicon. The evidence indicates that the molecules of solid metals are monatomic, those of solid non-metals being more complex. The molecules of sulphides, oxides, and other compounds with metallic lustre are non-associated.

C. H. D.

The Heat-contents of Binary Systems. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1908, 63, 129—140).—The thermal equilibrium of binary mixtures may be represented advantageously by means of a three-dimensional model. The ordinary temperature-concentration diagram is used as the base of the model, and perpendiculars are then erected, the heights of which are proportional to the heat-content of unit mass, the upper surfaces then being constructed by means of these perpendiculars. Sections perpendicular to the concentration axis give the variation of heat-content with temperature for a given composition. Photographs of a number of such models, with the corresponding temperature-concentration diagrams, are given for each of the cases discussed by Roozeboom.

In order to construct the model, cooling curves of the mixtures must be taken under similar cooling conditions, and the duration of each arrest determined, as in Tammann's method of thermal analysis (*Abstr.*, 1904, 113).

C. H. D.

Correction of the Ideal Melting-point Curves of Binary Alloys. DOMENICO MAZZOTTO (*Nuovo Cim.*, 1908, [v], 15, 401—422).—The author applies two corrections to the ideal melting-point curve, one depending on the heat of mixture, and the other on the association of the dissolved metal. The data for the former correction are obtained from the author's determinations (*Rend. R. Ist. Lombardo*,

1888, [iia], 18, 165), and those for the latter from the atomic depressions measured by Heycock and Neville (Trans., 1889, 55, 666; 1890, 57, 376, 656, 1892, 61, 888; 1894, 65, 31; 1897, 71, 383; Abstr., 1897, ii, 245). The application of these corrections to the melting points of alloys of bismuth and tin, lead and tin, and lead and bismuth, gives curves approximating very closely to the ideal curves. The method fails when the two components form a solid solution, as in the case of tin dissolved in zinc, or when chemical combination takes place, as in lead amalgams. The following coefficients of polymerisation were determined: Bi in Sn, 1.25; Bi in Pb, 2.2; Sn in Pb, 3.8; Zn in Sn, 1.15.

C. H. D.

A Cryoscope. M. C. DEKHUYZEN (*Biochem. Zeitsch.*, 1908, 11, 345—381).—The true freezing point of a solution can be expressed by the equation $t_w = t_s + k_a/K_E(t_s - t_c)$, where t_w is the true freezing point, t_s the apparent (actually read) freezing point, and t_c the "convergence temperature," that is, the temperature which the solution will attain when congelation does not take place. k_a is a constant depending on the rate at which the equilibrium of temperature between the freezing vessel and cooling bath is attained. K_E is a number, by means of which the rate can be calculated at which the ice in the supercooled liquid is formed or dissolved. The above formula is due to Nernst and Abegg. The constant k_a can be directly determined, the equation $-dt/dz = k_a(t - t_c)$, where z represents time, denoting the rate of temperature change of the liquid. From this equation,

$$k_a = 1/(z_2 - z_1) \cdot \log. \text{nat.} (t_1 - t_c)/(t_2 - t_c),$$

where t_c represents the temperature of the cooling mixture. To determine K_E , the following formula was evolved:

$$dt/dz = K_E(t_w - t_s) - k_a(t_s - t_c).$$

A practically constant cooling bath can be obtained by applying the principles that ice and salt solution attain temperature equilibrium with very small velocity if the surface of the ice and the stirring of the liquid be reduced to the lowest possible limits.

The apparatus employed consists of an inner cooling vessel with ground flange, fitted into a somewhat large cooling vessel, also with ground flange; the two ground surfaces are clamped together. This is covered with an ebonite plate, into which fit two tubes, one of which contains mercury, for quick cooling, and the other tube is a Dewar vessel, formed from two concentric test-tubes with an evacuated space between. A special arrangement made for transferring the vessel containing the liquid under investigation (with the Beckmann thermometer) from the quick-cooling to the Dewar tube is described, and also the methods for determining the values of k_a and K_E .

S. B. S.

Boiling and Freezing Points of Concentrated Aqueous Solutions and the Question of the Hydration of the Solute. SAMUEL M. JOHNSTON (*Trans. Roy. Soc. Edin.*, 1908, 45, Part 4, 855—884. Compare Abstr., 1906, ii, 9).—Boiling point, freezing point, and electrical conductivity data are recorded for concentrated

aqueous solutions of a number of electrolytes. The conductivity measurements were made at 0° and 99.4° .

In general, the rise of the boiling point produced by one gram equivalent has a minimum value at a concentration of 0.5 to 1.0 gram equivalent per litre. For higher concentrations than that corresponding with this minimum, the rate of increase of the equivalent boiling-point elevation gradually diminishes, and in certain cases a maximum can be observed.

From a comparison of curves which represent the variation of μ_v/μ_{∞} with the concentration of the dissolved electrolyte, the conclusion is drawn that the degree of ionisation is greater at 0° than at 100° in the case of dilute solutions, whereas concentrated solutions are more dissociated at the higher temperature.

Assuming that the ionisation can be obtained from conductivity data, and that the elevation of the boiling point (or depression of the freezing point) produced by a gram molecule or gram ion is independent of the concentration of the solution, the experimental data are used to calculate the degree of hydration of the dissolved electrolyte on the assumptions (1) that molecules and ions are hydrated; (2) that the ions only are hydrated, and (3) that the undissociated molecules only are hydrated. The fact that the values obtained on the first assumption are in some cases constant for a series of concentrations is regarded as evidence of hydration of both the undissociated molecules and the ions. For other electrolytes, hydration of the molecules or of the ions alone is assumed.

H. M. D.

Theoretical Determination of the Vapour Pressure of Solid and Liquid Carbon Dioxide. E. FALCK (*Physikal. Zeitsch.*, 1908, 9, 433—437).—The validity of Nernst's thermodynamic formula for the variation of vapour pressure with temperature has been examined for liquid carbon dioxide between -10° and -60° and for the solid between -60° and -154° . The agreement between the calculated and experimental values is very good, except in the neighbourhood of -100° to -130° . A similar deviation for an intermediate range of temperature was found by Naumann in the case of iodine.

The molecular heats of liquid and solid carbon dioxide are given by the formulæ $C_l = 3.8 + 0.077T$ and $C_s = 3.8 + 0.032T$ respectively. At all temperatures above absolute zero, liquid carbon dioxide has therefore the greater specific heat.

The free energy and the heat change for the passage of solid carbon dioxide into the liquid form at various temperatures are calculated. The curves representing these values are symmetrical and tangential to a straight line parallel to the axis of temperature.

H. M. D.

Mutual Action of Dissolved Substances as Deduced from their Vapour Pressures. ADAM WROCZYNSKI (*J. Chim. Phys.*, 1908, 6, 500—504).—Remarks on Konowaloff's recent papers (*Abstr.*, 1907, ii, 334, 602). It is shown that several of Konowaloff's formulæ can be deduced from the general Duhem-Margules formula for the vapour pressures of binary mixtures with the help of Raoult's law. It follows that, contrary to Konowaloff's view, there is no proof of

chemical combination under the conditions of experiment in many of the binary mixtures studied by that author. G. S.

Vaporisation I. HANNES VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1908, 63, 355—366. Compare Abstr., 1906, ii, 522; 1907, ii, 742).—The values of f calculated by the empirical equation $f=f_0-a\theta+b/(1-\theta)$ (see *loc. cit.*) are in the neighbourhood of the critical temperature greater than those derived directly from observation. The author now shows that when the third term on the right hand side of the foregoing formula is multiplied by the factor $1-\theta/[e(1-\theta)+1]$, where e is a constant, a better agreement is secured, as shown by figures for fluorobenzene, carbon dioxide, and ammonia.

By combining this modified equation with the Clapeyron-Clausius formula, an expression is obtained for the latent heat of vaporisation.

According to Mathias, $(D_l + D_v)/2D_k = 2 - \theta$, where D_l and D_v are the densities of liquid and saturated vapour respectively, and D_k is the critical density. The agreement between the experimental figures and the values calculated by this formula is in general very good, but, according to the author, the expression $1 + a'(1 - \theta)$ on the right-hand side, where a' is a constant for each substance, gives even better results, as shown by figures for fluorobenzene and ammonia. A formula is also developed for calculating the difference between the densities of liquid and saturated vapour, and is tested with satisfactory results by the available data for fluorobenzene and ammonia. Formulæ are further deduced for calculating the densities and volumes of liquid and saturated vapour in terms of θ and the various constants quoted above. J. C. P.

Sources of Error in the Ebullioscopic Method and Attempts to Remove Them. ERNST BECKMANN [With OTTO LIESCHE and THEODOR KLOPPER] (*Zeitsch. physikal. Chem.*, 1908, 63, 177—215).—An elaborate series of experiments has been made to determine the sources of possible error in ebullioscopic determinations. The influence of the external temperature is discussed, and is shown to be least for concentrated solutions; it is less than in the case of cryoscopic experiments. Direct electrical heating by means of a thin platinum spiral is very suitable for non-electrolytes, especially when the boiling point of the solvent is high. Electrolytes give abnormal results, even when an alternating current of high frequency is employed.

A method is described by which satisfactory measurements can be obtained with the bulb of the thermometer immersed only in vapour. The device employed keeps the bulb of the thermometer free from liquid, a layer of boiling liquid forming a jacket round the vapour space. In another form of apparatus, the bulb is immersed in liquid free from vapour, jacketed with the vapour from the same solution.

The influence of the nature and quantity of filling material (garnets or platinum tetrahedra) is also discussed. C. H. D.

Apparatus for Fractional Distillation under Reduced Pressure. WILHELM STEINKOPF (*Bull. Soc. chim.*, 1908, [iv], 3, 763—764).—Attention is directed to the author's apparatus for this

purpose (*Chem. Zeit.*, 1902, 26, 407), which resembles Delepine's (this vol., ii, 461), but differs in having the cylindrical receiver closed by a rubber stopper, through which the distributor, provided with a side-tube for attachment to a pump, passes.

T. A. H.

Modification of the Platinum Vessel of the Berthelot-Mahler Bomb. EDUARD TÓTH (*Chem. Zeit.*, 1908, 32, 608).—So as to minimise the wear-and-tear of the pastille, and to facilitate the arrangement of the fuse-thread, it is suggested that the bottom of the platinum vessel should be hollowed out in a pod-like form so that the fuse-thread can be introduced after weighing without disturbing the pastille.

J. V. E.

Heat of Neutralisation of Acetic and Benzoic Acids by Aniline in Benzene Solution. LÉO VIGNON and ÉVIEUX (*Compt. rend.*, 1908, 146, 1316—1318).—The molecular heats of dissolution of acetic acid, benzoic acid, and aniline, in benzene at $M/4$ dilution are -0.51 Cal., -3.54 Cal., and -1.09 Cal. respectively. When equal volumes of $M/4$ solutions of acetic acid and aniline are mixed, a fall of temperature (0.054°) is observed corresponding with an absorption of -0.16 Cal. per molecule. On the other hand, the formation of aniline acetate directly from the acid and base results in the development of heat, whilst the heat of dissolution of aniline acetate in benzene ($M/8$ dilution) is -3.63 Cal., from which the value $+1.87$ Cal. is deduced for the molecular heat of combination of acetic acid and aniline.

Similarly, by mixing equal volumes (200 c.c.) of $M/4$ solution of benzoic acid and aniline in benzene, a very slight elevation in temperature (0.024°) is produced, corresponding with a development of 0.08 Cal. per molecule. Aniline benzoate, however, has a heat of dissolution of -9.4 Cal. at $M/8$ dilution in benzene, giving the value $+4.77$ Cal. for the heat of formation.

Determinations of the molecular weights of aniline acetate and benzoate by the cryoscopic method give the values 111 and 151—153, which more nearly agree with those calculated for mixtures of the acid and base than for the salts.

The conclusions are drawn that aniline does not combine with acetic and benzoic acids in benzene solution, and that aniline acetate and benzoate are dissociated by dissolution in benzene.

E. H.

Heat of Neutralisation of Picric Acid by Different Aromatic Bases in Benzene Solution. LÉO VIGNON and ÉVIEUX (*Compt. rend.*, 1908, 147, 67—69).—Picric acid differs from benzoic and acetic acids (preceding abstract) in that it combines with aromatic bases in benzene solution.

The molecular heat of dissolution of picric acid in benzene at 20° and $M/8$ dilution is -3.8 Cal. The following are the heats of neutralisation of picric acid by various bases, and the characters of the salts formed. By aniline, $+14.75$ Cal.; *aniline picrate* forms small, yellow crystals, of which 100 parts of water dissolve 0.54 part and 100 parts of benzene 0.078 part at 22° . *o*-Toluidine, $+16.45$ Cal.;

o-toluidine picrate is precipitated as orange-yellow flocks, which quickly change into yellowish-white crystals. *m*-Toluidine, +15.98 Cal.; *p*-toluidine, +18.15 Cal.; *m*- and *p*-toluidine picrates form clear, yellow crystals. Methylaniline, +11.07 Cal. (solid salt); *methylaniline picrate* forms a golden-yellow, crystalline powder, *m. p.* 134°. Dimethylaniline, +14.1 Cal. (solid salt); *dimethylaniline picrate* is a granular, yellow powder, *m. p.* 142°. Ethylaniline, +12.6 Cal. (solid salt); *ethylaniline picrate* forms a clear yellow, crystalline powder, *m. p.* 132°. Dimethyl-*o*-toluidine, +9.45 Cal. (salt dissolved); the golden-yellow solution, after twenty-four hours' standing, deposits clear yellow crystals of *dimethyl-o-toluidine picrate*, *m. p.* 116—117°, of which 100 parts of benzene at 25° dissolve 1.35 parts. Phenylhydrazine, +19.03 Cal. (solid salt); *phenylhydrazine picrate* forms a bright yellow powder, *m. p.* 148—149°.

The molecular heat of dissolution of *o*-nitroaniline at 22° and *M*/8 dilution is -5.51 Cal., and its heat of neutralisation by picric acid is -0.35 Cal. The heat of dissolution of *o*-nitroaniline picrate, a brick-red, crystalline powder, in benzene at 22° and *M*/16 dilution is -8.40 Cal., whence the heat of formation in benzene solution is -1.2 Cal. A cryoscopic determination of the molecular weight in benzene solution also shows that no combination has taken place.

These results are an example of salt formation without ionisation. The electrical conductivity of the solutions either before, during, or after admixture is inappreciable.

Benzene solutions of phenol, nitrobenzene, and *m*-dinitrobenzene do not react with a benzene solution of *p*-toluidine.

The conclusions are drawn that (1) salt-formation in benzene differs from that in water, (2) that benzene having no appreciable ionising power is particularly useful for the thermal study of the formation of certain salts, (3) that the presence of several nitro-groups in the benzene nucleus greatly intensifies the acidic power of the hydroxyl group, and (4) that the acidity of picric acid becomes zero towards certain bases, such as *o*-nitroaniline.

Other acids, such as trichloroacetic acid, in which the acidic character is intensified by the presence of the three chlorine atoms, behave similarly to picric acid.

E. H.

Heats of Solution of the Three Forms of Lactose. C. S. HUDSON and F. C. BROWN (*J. Amer. Chem. Soc.*, 1908, 30, 960—971).—Lactose can be crystallised from solution in two forms, the monohydrate and the β -anhydrous modification. When the hydrate is heated at 125°, it is converted into the α -anhydrous form. Hudson (Abstr., 1904, i, 974) has determined the rate at which equilibrium is established between the hydrate and the β -modification, and the proportions of the two forms finally present. A study has now been made of the heats of solution of the three forms of lactose, keeping in view the fact that the solution of any one form is complicated by a second heat effect due to the change into the stable mixture of hydrate and β -form. The following terms are employed: The "initial heat of solution" is the heat produced when any form of the sugar is dissolved under such conditions that the change into the

mixture of hydrate and β -form is greatly retarded. The "final heat of solution" is the total heat developed when any form of the sugar dissolves to yield a solution containing the stable mixture. The "heat of passage" of one form into the other is the heat produced when a given quantity of one form changes in solution into an equivalent quantity of the other. The final heat of solution is thus the sum of the initial heat of solution and the heat of passage. The following results have been obtained by means of calorimetric measurements.

The initial heats of solution in gram-calories are: hydrate, -12.0 ; α -form, $+7.3$; β -form, -2.3 . The final heats of solution are: hydrate, -11.4 ; α -form, $+7.9$; β -form, -2.7 . The heats of passage to the β -form are: hydrate, $+1.0$; α -form, $+1.0$. The equality of the heats of passage of the hydrate and the α -form support the view that in solution the α -form instantly changes into the hydrate, which is then slowly converted into the β -form. The initial heat of solution of the hydrate increases about 0.1 gram-cal. per degree rise in temperature. On diluting strong lactose solutions (0.5 molal), a slight development of heat occurs, but the heat of solution is independent of the concentration when this is less than about 0.3 molal. The pure β -form has been prepared, and has $D^{20} 1.59$, whilst the hydrate has $D^{20} 1.54$. The thermochemical data now obtained show that the crystalline substance precipitated from aqueous solutions of lactose by alcohol and ether is a mixture of the hydrate and β -modification, the two forms being present in approximately the same proportions in which they occur in stable solutions. Observations of the rotatory power of stable solutions of the sugar indicate that the hydration is slightly increased with rise of temperature from 0° to 100° . The final heat of solution of the hydrate, calculated from the solubilities at 15° and 25° , is -11.5 , which agrees closely with the calorimetric determination at 20° .
E. G.

New Instrument for Reducing Gas Volumes to Standard Conditions. GRANT T. DAVIS (*J. Amer. Chem. Soc.*, 1908, 30, 971—973).—An apparatus is described for so adjusting the pressure on a gas that its volume is reduced to that which it would occupy under standard conditions of temperature and pressure, calculation being thus avoided. The pressure is applied by means of a column of water, and the method is therefore only suitable for gases which can be collected over water. For details, the description and diagram in the original must be consulted.
E. G.

Orthobaric Densities of Homologous Liquids. G. TERGAZARIAN (*J. Chim. Phys.*, 1908, 6, 492—499).—From the author's determinations of the densities and critical temperatures of acetonitrile and propionitrile, and from the corresponding determinations of Young for pentane, isopentane, hexane, heptane, and octane, it is shown that the difference between the temperatures of equal densities for two homologous liquids is equal to the difference of the critical temperatures of the same liquids. Hence, if the density curve (liquid) and the critical temperature of a single member of the

series is known, the density curve and critical temperature of all the other members can be calculated, if the density at a single temperature is known in each case.

The rule in question does not hold for the esters and alcohols studied by Young and Thomas (*Trans.*, 1893, 63, 1191). G. S.

The Unit-Stere Theory: Demonstration of a Natural Relation between the Volumes of the Atoms in Compounds under Corresponding Conditions and that of Combined Hydrogen. II. GERVAISE LE BAS (*Phil. Mag.*, 1908, [vi], 16, 60—92. Compare *Abstr.*, 1907, ii, 754).—The volume relationships of carbon and hydrogen in the liquid hydrocarbons of the olefine and acetylene series, and in aromatic and hydroaromatic compounds, have been examined in the light of the theory put forward in the earlier paper on the basis of data for the liquid normal paraffins.

At the melting point and at temperatures equally removed therefrom, the molecular volumes of the olefines may be represented by the expression: molecular volume $C_nH_{2n} = 6nS - 2.62 = WS - (=)$. Similarly, the molecular volumes of the acetylenes are given by: molecular volume $C_nH_{2n-2} = 6nS - 2S - 3 = WS - (≡)$. In these expressions, S is the value of the unit-stere = 2.97, W is the total number of valencies of the atoms in the hydrocarbon molecules, and the bracketed symbols represent the volume values corresponding with the unsaturated linkages.

At the boiling point, the molecular volumes of the olefines and acetylenes are given by the formulæ: molecular volume $C_nH_{2n} = 6nS$ and molecular volume $C_nH_{2n-2} = 6nS - 2S$ respectively. The value of S is approximately 3.7, but appears to vary slightly from one compound to another.

The data for aromatic compounds indicate that the atomic volumes in the nuclei are always less than the volumes of the same atoms in straight-chain molecules. The relative volumes of atoms are, however, the same in both cases. The atoms in aliphatic side-chains of aromatic compounds have the same volume as in the paraffins.

In the case of benzene and its homologues, it is shown that the critical coefficients are also subject to the valency law. H. M. D.

Torsional Elasticity of Liquids. L. LAUER and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1908, 63, 141—150).—An apparatus is described by means of which a known torque of short duration could be applied to a glass sphere immersed in the liquid to be examined. The duration of the impulse varied from 0.00000163 to 0.01956 second, and was regulated and measured by means of a Helmholtz pendulum. In other experiments, a steel rod of elliptical section was substituted for the glass sphere.

The liquids investigated were water, glycerol, and undercooled betol containing 1.5% sucrose. The last two gave positive indications of torsional elasticity, increasing with falling temperature. The temperature at which elasticity becomes marked is independent of the duration of the impulse, and almost independent of the moment of torsion. This

temperature is 63° for glycerol and 41° for betol. Water does not exhibit any elasticity above its melting point. C. H. D.

Weight of a Falling Drop and the Laws of Tate. Determination of Molecular Weights and Critical Temperatures of Liquids by the Aid of Drop Weights. II. J. LIVINGSTON R. MORGAN and ERIC HIGGINS (*J. Amer. Chem. Soc.*, 1908, 30, 1055—1068).—Morgan and Stevenson (this vol., ii, 356) have shown that the weight of a drop of liquid falling from the properly cut end of a glass capillary tube is proportional to the surface tension of the liquid, and can be employed for calculating the molecular weight and critical temperature.

In the present paper, an account is given of experiments which have been carried out with a bevelled tip similar to that used by Morgan and Stevenson, but attached to a burette of smaller diameter than that previously employed. The drop weights of carbon tetrachloride and the liquids studied in the earlier work have been determined at or near the temperatures at which their surface tensions have been measured by the rise of the liquids in a capillary tube. The results are tabulated. They confirm those obtained previously, and show that, for the determination of relative surface tensions, the drop-weight method is more accurate than the ordinary method depending on capillary rise, and, also, that the molecular coefficient of drop weight is a true constant. The drop-weight method is therefore the most accurate available for the determination of molecular weights, except that for permanent gases, which is based on the density. It is also shown that critical temperatures can be more readily and accurately calculated from drop weights than from capillary rise. E. G.

New Formulæ Correlating the Various Constants for Non-associated Liquids. ERIC HIGGINS (*J. Amer. Chem. Soc.*, 1908, 30, 1069—1074).—Morgan and Stevenson (this vol., ii, 356) and Morgan and Higgins (preceding abstract) have described a method of determining the volumes (and hence the weights) of drops of non-associated liquids delivered from the specially cut end of a capillary tube.

Since the drop volume is proportional to the surface tension, it is shown that $vM/T = K$, where M is the molecular weight of the substance in the liquid state, v the drop volume, and T the absolute temperature of the b. p. By means of these drop-volume constants of certain non-associated liquids (benzene, pyridine, chlorobenzene, aniline, and quinoline), the following can be calculated from a knowledge of the b. p., molecular weight, and density: the surface tension, critical temperature and pressure, vapour pressure at any temperature, latent heat of evaporation, and the value of a and b in van der Waals' equation. It is also shown that the drop weight and b. p. of a liquid enable its molecular weight to be ascertained, and hence all the constants already enumerated can be calculated. E. G.

Viscosity of Non-aqueous Solutions of Potassium Iodide. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1077—1084).—In earlier papers (Abstr., 1907, ii, 744; this vol., ii, 464), it has

been suggested that the cations of an electrolyte lower the viscosity of a solvent, whilst the anions and non-ionised molecules increase it. It has been considered desirable to test this hypothesis by working with non-aqueous solutions in which the degree of ionisation is less than in water. For this purpose, a study has been made of solutions of potassium iodide in methyl and ethyl alcohols, ethylene glycol, glycerol, furfuraldehyde, acetone, and pyridine. The density of the solutions at $25^{\circ}/4^{\circ}$, the absolute viscosity, and the ratio of the absolute viscosity of the solutions to that of the solvents are recorded.

The results show that all the solutions, except that in glycerol, exhibit positive viscosity. The negative viscosity of the glycerol solution is attributed to the association of the solvent. The value of the ratio of absolute viscosity to molecular volume has been calculated for fifty non-associated organic liquids, and found to be approximately constant for members of the same class of compounds in the same series. From this ratio, it is inferred that the degree of association of glycerol exceeds that of water. The conclusion that the cation of the electrolyte and the association of the solvent determine negative viscosity is confirmed.

E. G.

Critical Opalescence. VICTOR ROTHMUND (*Zeitsch. physikal. Chem.*, 1908, 63, 54—82. Compare Abstr., 1898, ii, 503; also Friedländer, Abstr., 1901, ii, 643).—Mixtures of *n*-butyric acid and water, for a short interval above the critical solution temperature, exhibit a peculiar bluish opalescence or turbidity. This opalescence is very markedly diminished by dextrose, as well as by a number of salts, but is increased by naphthalene.

The temperature-coefficients of viscosity of these ternary mixtures about the critical solution temperature have been determined, and it is found that in this respect there is no essential difference between dextrose and the salts, on the one hand, and naphthalene, on the other. The influence of these substances on the critical opalescence must therefore be optical in its nature.

According to Donnan (*Chem. News*, 1904, 90, 139), the interfacial tension at temperatures slightly above the critical solution temperature is still positive for very small radii of curvature, but negative for all ordinary curvatures. If this is so, then the critical opalescence is due to the presence of very fine drops, and a mixture may be really non-homogeneous above the critical solution temperature. The author accepts this explanation, and suggests that the influence of a third substance in diminishing or increasing the opalescence observed in mixtures of *n*-butyric acid and water is due to an alteration of the refractive index of one of the phases. The nearer the refractive indices of the two phases the more difficult will it be to detect the opalescence, and any substance which brings the index of the one phase nearer to that of the other will apparently diminish the opalescence.

J. C. P.

Cause of the Decoloration of Coloured Liquids by means of Various Charcoals. FRITZ GLASSNER and WILHELM SUIDA (*Annalen*, 1908, 361, 353—362).—It was shown previously (Abstr., 1907, ii,

932) that lampblack, although free from nitrogen and ash, decolorises certain, especially basic, dyes. As this is not in agreement with the behaviour of charcoals in general, the authors have further studied the decolorising action of two specimens of lampblack and one of acetylene-black, all of which were free from nitrogen and ash, and were in a state of fine division.

When boiled with water, lampblack has an odour of camphor; the evaporation residue, as also that from the alcoholic extract, does not absorb dyes. The benzene extract, on the other hand, contains an oil, which has a terpene- or camphor-like odour, and is partly volatile with steam; the evaporation residue absorbs basic dyes from aqueous solutions. The lampblacks differ from animal charcoals in that absorbed dyes are readily dissolved by dilute acids, alkalis, or alcohol, although not by water. As it was observed that the amount of dye absorbed by a lampblack varies with its percentage of oxygen, experiments were performed with a large number of phenols, carboxylic acids, and sulphonic acids, and it was found that these have mostly a high absorptive power for basic dyes. Moreover, it is found that aurine, rosolic acid, and hæmatoxylin form insoluble compounds with acid dyes. It is suggested that, whilst the absorptive power of animal charcoals results from the presence of substances containing the group $\text{N}\cdot\text{C}\cdot\text{N}$, that of the lampblacks depends on the presence of oxygen compounds, which form phenolic salts with basic, and oxonium salts with acid, dyes. The authors reply to criticisms by Rosenthaler (this vol., ii, 158). G. Y.

Diffusion of Albumin into Gelatin Jellies. G. MÖLLHAUSEN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 325).—When dry egg- or blood-albumin is placed on the top of a column of solidified gelatin solution containing 2–10% gelatin, the albumin forces its way into the jelly. After some days, a crack appears in the jelly, and this gradually increases in length. Rise of temperature favours the phenomenon. The albumin abstracts large quantities of water from the jelly during the diffusion process.

Addition of phenol to the albumin or jelly has no influence on the phenomenon. It also takes place when the albumin is dissolved previously in an equal weight of water, and when the jelly contains 10% of albumin. Diffusion of the mineral constituents and of the yellow colouring matter of the albumin into the jelly precedes the formation of the crack. The phenomenon cannot be ascribed to a tanning action. H. M. D.

Osmotic Pressure of Compressible Solutions of any Degree of Concentration. Part II. Cases in which both Solvent and Solute are Volatile. ALFRED W. PORTER (*Proc. Roy. Soc.*, 1908, 80, 4, 457–465. Compare Abstr., 1907, ii, 743).—The theory previously developed connecting osmotic pressure with vapour pressure in compressible solutions under any hydrostatic pressure is extended to the general case where the solute, as well as the solvent, has an appreciable vapour pressure. By means of a thermodynamic cycle, it is shown that the variation of vapour pressure of the solvent, and

also of the osmotic pressure, with variation of the hydrostatic pressure is expressed by the same equations as in the case where the solute is non-volatile. A simple proof is given that the vapour pressure of a pure liquid increases with hydrostatic pressure, by assuming that membranes can exist permeable to vapour, but not to liquid molecules. This proof cannot be extended to solutions, because a space variation of concentration would be set up by gravity under the conditions of the proof. The increased vapour pressure at a curved surface (Kelvin's formula), and also at an electrified surface, is supposed to originate in the higher hydrostatic pressure. R. J. C.

Osmotic Pressure of Sucrose Solutions at 10°. HARMON N. MORSE and H. V. MORSE (*Amer. Chem. J.*, 1908, 39, 667—680).—In view of the fact that the osmotic pressures of sucrose and dextrose solutions at 0° are somewhat in excess of the calculated gas pressures, whereas at 20° the two pressures are in agreement, it was considered desirable to determine the pressures of such solutions at several intermediate temperatures. The results of measurements of the osmotic pressure of sucrose solutions at 5° have already been recorded (Abstr., 1907, ii, 744), and in the present paper an account is given of determinations made at 10°.

It is found that the osmotic pressure of sucrose solutions at 10°, like those at 0° and 5°, considerably exceeds the calculated gas pressure; it diminishes slightly from the 0.1*N* to the 0.4*N* solution, and then increases with increasing concentration. On comparing the pressures at 0° and 10°, some indications of a temperature-coefficient are observable, and this fact will be alluded to again when the results obtained at 15° are recorded. E. G.

Vapour Pressure and Osmotic Pressure of Strong Solutions. HUGH L. CALLENDAR (*Proc. Roy. Soc.*, 1908, 80, A, 466—500).—A theory of solutions is developed on the basis of a simple hypothesis connecting vapour pressure and concentration.

Arguments are first adduced to show how osmotic and other properties of solutions may be explained quantitatively as the result of differences in vapour pressure. An equation is obtained connecting vapour pressure with hydrostatic pressure, according to which a hydrostatic pressure of 2000 atmospheres is necessary to increase the vapour pressure of water four-fold at 27° if its compressibility remains constant.

Consideration of the hypothetical vapour sieve apparatus of Poynting (*Phil. Mag.*, 1881, [v], 12, 40) leads to the result that if a solution and the pure solvent, each contained in a vapour sieve tube, are in equilibrium with the same vapour column, they are in equilibrium with one another. The solution is necessarily under greater hydrostatic pressure than the pure solvent in this case. No disturbance will ensue if the solution sieve be actually surrounded by the solvent column, that is to say, the liquids are in osmotic equilibrium also.

A semi-permeable membrane may therefore be considered as a vapour sieve, and osmotic pressure may be defined as the hydrostatic pressure which must be applied to increase the vapour pressure of a solution to

that of the pure solvent. Conversely, liquids in osmotic equilibrium necessarily have the same vapour pressure.

The osmotic pressure of a solution is independent of hydrostatic pressure only if the solvent occupies the same volume in the solution as in the pure state. In a column of solution, the increase in vapour pressure downwards will be the difference between the increase due to hydrostatic pressure and the decrease due to the concentration of the solute by gravity, so that the gravity effect can be evaluated in the case of sucrose solutions from Berkeley and Hartley's vapour pressure measurements.

All the foregoing relationships can be simply established by equating to zero the work done in taking unit mass of solvent round a closed "osmotic circuit," and the author prefers this method to the isothermal cycle method employed by Porter (Abstr., 1907, ii, 743). An equation is obtained connecting hydrostatic pressure with latent heat of vaporisation, from which it appears that a pressure of 42 atmospheres would increase the latent heat of water by 1 cal.

The author's theory of solutions is based upon the hypothesis that the vapour pressure of a solution should be proportional to the ratio of the number of molecules of free solvent to the total number of molecules in the solution, molecular aggregates and hydrates being considered as single molecules. Thus if in a solution of n molecules of solute in N molecules of solvent each molecule of solute appropriates a molecules of solvent, the number of free molecules of solvent will be $(N - an)$, and the total number of molecules will be $(N - an + n)$. If p' and p'' be the vapour pressure of solvent and solution, $p''/p' = (N - an)/(N - an + n)$. If sucrose be considered to hold 5 molecules of water of hydration, and if dextrose holds 2 molecules, this equation gives results which agree with Berkeley and Hartley's determinations of the osmotic pressure of these two substances within the limits of experimental error. The calculation must be made on a weight normal basis, and the hydration considered to be constant over the whole range of dilutions.

It is pointed out that the latent heat of fusion of ice has not the same value at temperatures below the freezing point as at 0° , and that the "molecular lowering" of the freezing point of water by a dissolved substance, which depends on the latent heat of fusion of the solvent, must also vary with the temperature; furthermore, the freezing-point lowering is generally tacitly assumed to be directly proportional to the ratio of the difference of vapour pressures of ice and water to the vapour pressure of water. Therefore the author considers that the usual method of comparing the found with the calculated freezing-point depressions is futile in the case of strong solutions with a freezing point far removed from 0° .

Owing to the uncertainty of existing data for the vapour pressure of water below 0° , an exact formula connecting the vapour pressures of water and ice is not possible. A number of possible formulæ are obtained by considering an "osmotic circuit," and the author finally adopts as the best approximation the simple expression $\log_e(p'/p) = -2.64t/273$, where p' and p are the vapour pressures of water and ice respectively, at t° Centigrade. On this basis, the

freezing-point depressions of sucrose solutions agree very well with the calculated values when the hydration (α) is taken as 5. The depressions of methyl- and ethyl-alcohol solutions containing upwards of 20 mols. per 100 of solvent agree very well with the theoretical when the hydration is taken as 1. Glycerol appears to have hydration 2, but the freezing-point diagrams of acetone and formic acid lie very near the curve plotted with $\alpha = -1$, which suggests that the molecules of these substances associate with each other.

The application of the theory to electrolytes is complicated by questions of electrolytic dissociation. Assuming the number of free ions to be proportional to the conductivity, the following hydrate values are deduced from freezing-point data: $\text{HCl}, 5\text{H}_2\text{O}$; $\text{CaCl}_2, 9\text{H}_2\text{O}$; $\text{MgCl}_2, 12\text{H}_2\text{O}$; $\text{KCl}, \text{H}_2\text{O}$; $\text{NaCl}, 2\text{H}_2\text{O}$.

When the rise of the boiling point of solutions is considered from the author's point of view, sucrose appears to have the same hydration at 100° as at 0° (namely, $5\text{H}_2\text{O}$), except in the strongest solutions, where it is somewhat less. Potassium and sodium chlorides, on the other hand, are calculated to be more highly hydrated at 100° ($\text{KCl}, 4\text{H}_2\text{O}$; $\text{NaCl}, 6\text{H}_2\text{O}$) than at the freezing point.

On thermodynamic principles, the hydration of a substance cannot remain constant on diluting its solutions unless the heat of dilution is zero, as in the case of sucrose. Consideration of the special case of hydrochloric acid with its great heat of dilution indicates that the variation in hydration is not necessarily very great, particularly as the heat developed on dilution may be partly the result of increased dissociation.

The author claims to have made out a good *prima facie* case for a modified form of the hydrate theory of solutions, and compares his results with those obtained by other advocates of the same hypothesis.

R. J. C.

The Solubility Product. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1908, 30, 946—954).—This paper contains a discussion of the principle of the solubility product which was enunciated by Nernst (*Abstr.*, 1890, 3). From the data obtained by Arrhenius (*Abstr.*, 1900, ii, 201) on the solubilities of silver acetate, propionate, butyrate, valerate, and chloroacetate in the presence of an excess of the corresponding sodium salt, the values of the solubility product ($C_{\text{Ag}} \times C_{\text{acid ion}}$) have been calculated. The results of Nernst's determinations (*loc. cit.*) of the solubility of silver acetate in presence of sodium acetate and silver nitrate respectively have also been re-calculated.

The results show that the solubility product has no theoretical foundation, and is only to be regarded as an approximate empirical principle. In the case of the organic silver salts, the principle is sufficiently in agreement with the observed facts to prove of some practical value, and this conclusion confirms the results obtained by other authors on the solubility of a salt in presence of other electrolytes having a common ion.

E. G.

Relationships between Chemical Composition, Crystalline Form, Hardness, and Density. I. VIKTOR PÖSCHL (*Zeitsch. anorg. Chem.*, 1908, 59, 102—107).—The author has found certain

relationships between the crystalline form, hardness, and density of polymorphic minerals. Of two such polymorphic forms, that which has the greater density and the greater crystalline symmetry is never less hard than the second modification. If the modification of a lower degree of symmetry has the greater density, this form is never less hard than the second form.

The densities of a number of mineral sulphides have been compared with those of the constituent elements. In all cases, the density of the mineral is intermediate between the densities of the elements. The former can be approximately calculated from the latter by means of the simple mixture rule. The calculated densities are, in nearly all cases, somewhat smaller than the experimental values. The deviation between the two values is shown to be a periodic function of the atomic weight of the metal.

H. M. D.

Relation between the Crystalline Form and Chemical Constitution of the Picryl Derivatives. GEORGE JERUSALEM and WILLIAM J. POPE (*Proc. Roy. Soc.*, 1908, 80, 4, 557—566).—The theory of Barlow and Pope as to the relation between crystalline form and chemical constitution (*Trans.*, 1906, 89, 1675; 1907, 91, 1150) has been further tested by application to a number of derivatives containing the 1:3:5-trinitrophenyl or picryl group.

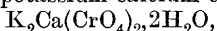
As regards crystalline structure, benzene and its simple derivatives belong to one of two types: one, derived from the closest-packed assemblage of equal spheres of hexagonal type, has the equivalence parameters $x:y:z = 3.101:3.480:2.780$; the other is derived from the closest-packed assemblages of equal spheres of cubic type. The direction of z is perpendicular to the two planes containing the centres of the two sets of hydrogen atoms ordinarily numbered 1:3:5 and 2:4:6 respectively. Of the thirteen picryl compounds for which data are now available, it is shown that nine belong to the hexagonal type, and that for these compounds the effect of substitution is to alter two of the dimensions only, the third, of relative length 2.780, corresponding with the z dimension of benzene, remaining practically unaltered.

Among the substances belonging to the rhombohedral arrangement are *s*-trinitrobenzene and picric acid. On passing from *s*-trinitrobenzene to the similarly-constituted tribromodinitrotoluene there is practically no change in the equivalence parameters, corresponding with the fact that the valencies of the groups displaced are the same as those of the original groups.

G. S.

Dimorphism of Potassium Calcium Chromate. A. V. RAKOWSKI (*Bull. Acad. Sci. St. Petersburg*, 1908, 10, 905—917).—The object of the research was to test the question whether two polymorphic forms of a substance can belong to the same crystalline system.

The β - and α -forms of potassium calcium chromate,



the crystalline characters of which are discussed in detail, are prepared by the action of unslaked lime on potassium dichromate, the quantity of each modification formed depending on the pressure and

temperature at which crystallisation occurs, and on the presence of other substances in the solution.

The α -modification belongs to the rhombic system [$a:b:c=2.3629:1:2.0946$], $D_{15}^{25} 2.449$ (2.413 for large crystals), molecular heat of solution 6993 Cal. The β -modification belongs to the hemihedral triclinic system [$a:b:c=0.7591:1:0.8915$; $\alpha=86^{\circ}10'$; $\beta=94^{\circ}4'$; $\gamma=81^{\circ}40'$], $D_{15}^{25} 2.611$ (2.600 for large crystals), molecular heat of solution 5458.8. Solubility curves and tables are given for both varieties, showing that the solubility of each increases with the temperature, and that the α -modification is unstable with reference to the β -form, the transition-temperature of the former being at about 0° .

At 97° the dry salt decomposes, thus: $K_2Ca(CrO_4)_2 \cdot 2H_2O \rightleftharpoons K_2CrO_4 + CaCrO_4 + 2H_2O$. A solution saturated at 20° becomes cloudy at $55-60^{\circ}$, and the precipitate formed at $90-100^{\circ}$ corresponds with the formula $K_2CrO_4 \cdot 4CaCrO_4 \cdot 2\frac{1}{2}H_2O$; at 260° , the water in this salt commences to separate. Z. K.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1908, 41, 1994—1998). **Clear Transparent Crystalline Liquids.** DANIEL VORLÄNDER (*ibid.*, 2033—2052).—See this vol., i, 640, 641.

Theory of Colloids. EDUARD JORDIS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 361—367).—A critical examination of the principles underlying a theory of colloids. In this first portion of the paper, the various possible types of homogeneous mixtures which may be classified under the head of solutions are discussed. A hydrosol regarded as a homogeneous mixture of solid and liquid particles is considered to satisfy the requirements of the definition of a solution.

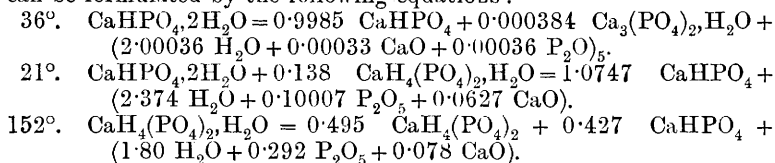
H. M. D.

Diagrammatic Representation of Equilibria between Acids and Bases in Solution. LAWRENCE J. HENDERSON (*J. Amer. Chem. Soc.*, 1908, 30, 954—960).—Diagrams have been constructed which express the requirements of the concentration law regarding the equilibrium in solution between strong acids and bases, and between strong bases and acids, of all strengths, but are not suitable for solutions of high acidity or alkalinity. These diagrams accurately define the conditions of equilibrium at all concentrations of hydrogen and hydroxyl ions, between all acids and bases, with the exceptions already mentioned, and in all mixtures of such substances. They also define all isohydric solutions of such substances in which this quality depends only on the equality of the concentration of hydrogen and hydroxyl ions.

E. G.

Calcium Phosphates. III. The System $CaO-P_2O_5-H_2O$. HENRY BASSETT, JUN. (*Zeitsch. anorg. Chem.*, 1908, 59, 1—55. Compare *Proc.*, 1906, 315).—By means of dilatometer experiments, the position of quintuple points on the space model of the three-component system $CaO-P_2O_5-H_2O$ has been determined. At these temperatures

changes take place which, on the basis of solubility measurements, can be formulated by the following equations:



The formulæ in brackets represent the composition of the solutions in equilibrium with the solid phases at the various quintuple points.

As the result of measurements of solubility at 25° , 40° , and 50.7° , isothermals have been obtained, on the basis of which the space model for the three-component system has been constructed.

The observation of van't Hoff, that the velocity with which changes in complicated systems take place diminishes with increasing basicity of the acid radicle and increasing valency of the metal, is confirmed by the author's observations.

The paper concludes with certain speculations as to the nature of the calcium phosphates which have been examined, and as to the condition of the phosphoric acid contained in soils. H. M. D.

The Ternary System: Mercuric Chloride, Ammonium Chloride, and Water at 30° . P. A. MEERBURG (*Zeitsch. anorg. Chem.*, 1908, **59**, 136—142; *Chem. Weekblad*, 1908, **5**, 429—435).—The three-component system has been examined according to the methods of the phase rule. Data are recorded representing the composition of the aqueous solutions in equilibrium with the various combinations of solid phases. Of the various double salts described in the literature, namely, $\text{HgCl}_2 \cdot \text{NH}_4\text{Cl}$; $\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$;

$\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$; $9\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl}$, and $3\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 4\text{H}_2\text{O}$, the first and last do not exist at 30° according to the author's experiments. These, however, indicate the existence of a double salt of the composition



Of the various double chlorides, $\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ is the only one which can be recrystallised from its aqueous solution. H. M. D.

Calculation of Hydrocarbon Equilibria. H. VON WARTENBERG (*Zeitsch. physikal. Chem.*, 1908, **63**, 269—272).—An error having crept into the calculation of the methane equilibrium in the earlier paper (this vol., ii, 26), this calculation is revised, with the result that the deviation between observed and calculated figures is greater than before. No complete explanation of the discrepancy can be expected until the equilibrium has been subjected to further experimental investigation. J. C. P.

Statics and Kinetics of the Transition which occurs in Liquid Sulphur. Heat of Fusion of Monoclinic Sulphur. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1908, **63**, 273—306).—The heat of fusion of monoclinic sulphur has been determined by an electrical method. A weighed quantity of sulphur was put in a glass

vessel inside an oil calorimeter, which in its turn was surrounded by an electric bath kept at 116° . When it was certain that the sulphur had been completely converted into the monoclinic variety, a known amount of energy was added by passing a current through a wire embedded in the sulphur; the added heat was so adjusted as to melt all the sulphur and to raise the temperature of the calorimeter about 5° , more or less. The value so found for the heat of fusion is 10.4 cal. for 1 gram of sulphur, with a possible error of $\pm 3\%$.

From this figure, the molecular depression constant for monoclinic sulphur is calculated by van't Hoff's formula; if further 42.5° is taken as the depression due to a gram atom of the insoluble variety (see Smith, Abstr., 1903, ii, 139) the number of atoms in a molecule of this insoluble sulphur works out to 6.9. The author, however, considers that 8 is more probably the correct number (see Smith, *loc. cit.*), and S_8 is accordingly taken as representing the molecular condition of both the soluble and the insoluble modifications.

The view that the two molecules have the same number of atoms, and that liquid sulphur is subject to a reversible isomeric change, $S_{8\text{ sol.}} \rightleftharpoons S_{8\text{ insol.}}$, is supported by Schaum's figures, which show how the freezing point of a sample of sulphur falls when it is kept for gradually increasing periods at temperatures above 120° . From these figures, it is possible to calculate satisfactory velocity-coefficients for the foregoing isomeric change, and from the values of the coefficient at different temperatures it is calculated that the heat absorbed when 1 gram of liquid soluble sulphur is transformed into the liquid insoluble modification is 21.1 cal.

From all this, it appears that the transition which occurs in liquid sulphur is an intramolecular rearrangement, which does not involve any change in the molecular weight (compare Smith, *loc. cit.*). J. C. P.

Affinity Constants of Organic Acids determined with the Help of Indicators. EDUARD SALM (*Zeitsch. physikal. Chem.*, 1908, 63, 83—108).—The affinity constants of sixty-eight organic acids have been determined by the indicator method already described (Friedenthal, Abstr., 1904, ii, 288; Salm, Abstr., 1904, ii, 536; 1906, ii, 218. Compare also Velej, Trans., 1907, 153, 1246). Solutions of hydrochloric acid were used as standards of comparison, and the indicators employed were dimethylaminoazobenzene, methyl-orange, and tropæolin-00. In the great majority of cases, the affinity constants deduced in this way are in good agreement with the values reached by the conductivity method. In the case of formic and oxalic acids, the value of the expression $a^2/(1-a)V$ falls off on dilution. J. C. P.

Saponification of Glycerides during Ester Exchanges in Homogeneous System. MILAN J. STRITAR and RICHARD FANTO (*J. pr. Chem.*, 1908, [ii], 78, 35—41. Compare Abstr., 1904, i, 843; 1907, i, 277).—The authors have calculated the results of their experiments on the saponification of rape-seed oil, as suggested by Wegscheider (this vol., ii, 165). If it is assumed that at the moment when the saponification is stopped the product is a mixture of diglyceride and ester, the mean partition coefficient for the second

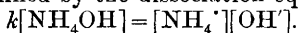
minute of the experiment is found to be 1.88, whilst that for the third minute is 1.02, hence in the second minute about twice as much glyceride as ester is saponified, whereas in the third minute the amounts are approximately equal. If, on the other hand, it is assumed that, at the moment of stoppage of the saponification, the combined glycerol is present as a mixture of tri- and mono-glycerides, the partition coefficient for the second minute is 2.35, and for the third minute, 1.28. Here, again, the saponification of the glyceride decreases in comparison with that of the ester. These results are in agreement with the authors' views as to the mechanism of the saponification of fats.

The remainder of the paper is a reply to Kremann (this vol., i, 120).
G. Y.

Schütz's Rule for Reaction Velocities. SVANTE ARRHENIUS (*Meddel. K. Vetensk. Nobelinstit.*, 1908, 1, No. 9, 1—17).—The author discusses a relationship pointed out by Schütz (Abstr., 1885, 1147) in connexion with the rate of action of pepsin on albumin. According to this, the quantity of albumin transformed in a given time by different amounts of pepsin is proportional to the square root of the pepsin concentration, provided that the reaction is not allowed to proceed too long. The same relationship has since been found in the action of trypsin and of lipolytic ferments.

It is shown that for the validity of Schütz's rule, the reaction velocity must be inversely proportional to the quantity of substance already transformed. This condition is fulfilled when one of the reacting substances is influenced by one of the products of reaction in such a way that the active mass of the former is inversely proportional to the active mass of the latter.

An example of such a reaction is afforded by the saponification of an ester present in large excess by a weak base, like ammonia. The reacting component to be considered is the OH' ion, and the active mass of this is determined by the dissociation equation



As saponification proceeds, the concentration of the NH_4^+ ions increases proportionally with the amount of ester saponified, and corresponding with the dissociation equation the concentration of the OH' ions diminishes in inverse proportion.

Measurement of the rate of saponification of ethyl acetate by ammonia, under the conditions specified, has shown that Schütz's rule is valid until about half the ammonia has been transformed. From this point, the deviations between experiment and the requirements of the rule increase very rapidly. The progress of the reaction was followed by determination of the electrical conductivity of the solution.

An action similar to that of an ammonium salt on ammonia is supposed to determine the similar progress of the action of pepsin on albumin. The cause of the action is supposed to be the combination of the reaction product with the ferment.
H. M. D.

Review of the Various Theories of Passivity. Fresh Observations on the Passivity of Iron, Nickel, and Chromium. CARL FREDENHAGEN (*Zeitsch. physikal. Chem.*, 1908, 63, 1—47. Compare Abstr., 1903, ii, 353; 1906, ii, 76; also Finkelstein, Abstr., 1902, ii, 81; Müller, Abstr., 1904, ii, 610).—The passivity of metals is supposed by some to be due to the formation of a film of oxide on the surface of the metal, and by others to be due to the change of the metal into another modification. The author rejects both these explanations, and argues in favour of the view, previously upheld by him (*loc. cit.*), that in the passive condition the metal is protected by a surface layer of gas.

The experiments recorded in the paper consisted in applying a gradually increasing or a gradually diminishing *E.M.F.* to an iron, nickel, or chromium electrode immersed in sulphuric acid, and determining (1) the *P.D.* at this electrode, and (2) the strength of the polarisation current. The *P.D.* of the metal electrode at the point where passivity or activity sets in is not well defined, and this supports the view that the passivity phenomena do not depend on the formation either of an oxide film or of another modification of the metal, but that they are ultimately related to the rate at which the metal becomes charged with oxygen. Further, the *P.D.* recorded when passivity or activity sets in is markedly affected by slight changes in the strength of the sulphuric acid, and rise of temperature has a notable influence in favouring the active condition. At an iron electrode immersed in sulphuric acid and subjected to anodic polarisation, some reactions take place which lead to the production of oxygen, and others use up oxygen. According to the author, the passive condition is reached when the oxygen polarisation extends uniformly over the whole surface of the electrode, and the reappearance of the active state on lowering the polarisation *E.M.F.* is due to the fact that the reactions which use up oxygen begin to overbalance those which produce oxygen. J. C. P.

The Excitation and Regulation of Catalytic Pulsations by means of an Electric Current. GEORG BREDIG and ERNST WILKE (*Biochem. Zeitsch.*, 1908, 11, 67—81).—Bredig and Weinmayer have shown that the catalytic decomposition of hydrogen peroxide into water and oxygen, a reaction discovered by Thénard, takes place under certain conditions in rhythmical periods. The influence of electrical currents on this rhythm has been studied. The peroxide solution was placed in a vessel, with mercury at the bottom, into which an electrode passed. The other electrode was placed in the peroxide solution. The apparatus was so arranged that the evolution of oxygen could be graphically recorded. It was found that by means of a constant current, alternating current, or induction shock, an α -periodic chemical change could be converted into a period change. Also, that a spontaneous rhythmical catalysis could be modified as regards its pulsation form, its period, or intensity by means either of a constant or alternating current. The relations of these phenomena to certain biological processes, such as nerve stimulation, are discussed. S. B. S.

Catalysis in Heterogeneous Systems. Decomposition of Chromous Chloride by means of Platinum. CASIMIR JABCYŃSKI (*Bull. Acad. Sci. Cracow*, 1908, 398—401).—The decomposition of chromous chloride between platinised platinum plates has been examined. Between 25° and 55° the reaction appears to be unimolecular. When smooth platinum foil is used, the velocity is some three times smaller than with platinised plates. The velocity of decomposition varies with the rate at which the liquid is stirred. The temperature-coefficient, 2.75% per 1°, is the same as for ordinary diffusion experiments, so that the velocity appears to depend entirely on diffusion, and the actual chemical reaction proceeds with enormous velocity. The effect of non-electrolytes, for example, alcohol and sugar, on the velocity is exactly the same as for other diffusion experiments.

The velocity depends on the amount of hydrochloric acid present, and is accelerated by the addition of potassium or calcium chloride, but diminished by the addition of chromic chloride. The reaction does not proceed in the presence of potassium chloride unless free acid is also present.

These phenomena are accounted for by the assumption of the formation of an additive compound of chromous and chromic chlorides, which has a slower rate of diffusion. Addition of hydrochloric acid, potassium chloride, or calcium chloride tends to decompose this compound, liberating chromous chloride, whereas increase in the concentration of the chromous chloride, or addition of chromic chloride, increases the amount of the additive compound.

Iodine and mercuric chloride do not affect the decomposition, whereas small amounts of hydrogen sulphide diminish the rate of decomposition; hydrocyanic acid acts less readily. J. J. S.

Catalysis. VI. Catalysis of Imino-esters. HERMANN I. SCHLESINGER (*Amer. Chem. J.*, 1908, 39, 719—771. Compare Stieglitz, this vol., ii, 167, 168; Derby, this vol., i, 419).—Measurements have been made of the velocity of hydrolysis of the hydrochlorides of methyl and ethyl iminobenzoates in 1/10 and 1/40 molar solutions, and also of the velocity of decomposition of methyl, ethyl, and *n*- and *iso*-propyl iminobenzoates, and of methyl *m*-nitroiminobenzoate, under the influence of varying proportions of barium hydroxide. A study has also been made of the decomposition of methyl iminobenzoate in aqueous solutions. The results are tabulated, and lead to the conclusions which have already been expressed by Stieglitz (*loc. cit.*). E. G.

Potential Energy of the Elements. DANIEL J. RANKIN (*Chem. News*, 1908, 97, 302—303).—An element is regarded as a system of energy which under normal conditions exist in two states, static or intrinsic energy and potential energy. The intrinsic energy is incapable of being freed, is inert, and is uninfluenced by any ordinary extraneous energy whatsoever. The potential or free existing energy permits of calculation in terms of thermal calories, and this the author has done for seventy-seven elements. In thermochemical measure-

ments, the "heat of formation" is the value of that portion of the potential which is lost or integrated, and the resulting compound undergoes diminution or increase in volume in a fixed ratio to the loss or gain of potential. For most elements the atomic weights of which are below 60, it has been found that the ratio of loss of potential to loss of volume = 1:1, except in the zinc, cadmium, mercury family, where it is 1:0.76, and with sodium, calcium, and potassium, 1:0.65 nearly. Examples are given showing that it thus becomes possible to calculate the density of a substance, such as solid oxygen or chlorine, when existing in a chemical compound; also, the specific gravity of a chemical compound when the heat of formation is given.

J. V. E.

Deduction of Stoichiometric Laws. F. WALD (*Zeitsch. physikal. Chem.*, 1908, 63, 307—324).—In replying to de Vries (this vol., ii, 366), the author maintains and extends his earlier views as to the possibility of deducing all quantitative chemical relationships from purely qualitative data. The limitations of the atomic hypothesis and of the theory of valency are emphasised. The author shows that of all the facts to which the name "stoichiometric" can be applied, the most general is this, that a qualitative analysis is possible without a quantitative.

J. C. P.

Safety Apparatus for Ovens, Baths, &c. LOUIS L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1908, 22, 192—195).—A modified form of H. Michaelis' apparatus (*Abstr.*, 1897, ii, 169) devised to automatically cut off the supply of gas to burners placed under baths, &c., provided with constant supply arrangements for water, in case the water supply is temporarily stopped, is described and figured.

T. A. H.

Simple Arrangement for Continuous Extraction with a Solvent of Inconstant Boiling Point. EMIL WÖRNER (*Chem. Zeit.*, 1908, 32, 608).—When using a Zuntz pattern Soxhlet apparatus for extracting with a solvent of no very definite boiling point, such as light petroleum, a mixture of alcohol and chloroform, &c., it is recommended that a wire spiral be placed round the extraction cup instead of the fragile glass tube. In this manner, the solvent of slightly lower boiling point is prevented from accumulating in the upper region of the tube, and by having intermediate porous layers of sand or wadding the extraction takes place quite rapidly.

J. V. E.

Circulation Stirrer for Liquids. ROBERT GOETZE (*Chem. Zentr.*, 1908, i, 1509—1510; from *Zeitsch. Chem. Apparatenkunde*, 1908, 3, 147).—A tubular glass stirrer having four short, horizontal open limbs is made to revolve rapidly in a flask-shaped vessel containing the liquid, so that the liquid is forced by the revolving limbs up a side-tube situated exactly opposite them, the action being similar to that of a centrifugal pump. The return liquid enters the vessel through the hollow spindle of the stirrer.

J. V. E.

Inorganic Chemistry.

Decomposition of Water Vapour by Electric Sparks. ALFRED HOLT, jun., and EDWIN HOPKINSON (*Phil. Mag.*, 1908, [vi], 16, 92—110).—The authors have examined the decomposition of water vapour and carbon dioxide by electric sparks, and the conclusion is drawn that the separation and distribution of the decomposition products noted by previous observers in the case of water vapour is not an electrical phenomenon, but is the result of gaseous diffusion. The decomposition effects cannot be explained by ordinary electrolysis.

When sparks are passed through water vapour contained in an apparatus of the type used by Chapman and Lidbury (*Trans.*, 1902, 81, 1301), hydrogen and oxygen are produced in the path of the spark. On account of its greater rate of diffusion, the hydrogen tends to become uniformly distributed throughout the apparatus, even when a rapid current of vapour is passing through it. The distribution of the oxygen depends on the relative position of the tube, through which the water vapour enters the sparking vessel, in reference to the anode and cathode. When the water vapour enters at the anode, the greater portion of the oxygen will be swept out at the cathode and vice versa. With the entrance tube near the centre of the spark-gap, equal quantities of oxygen are swept towards the separate poles. This view is supported by experimental data, and it is shown that, under like conditions, the products of decomposition of carbon dioxide, corresponding with their nearly equal rates of diffusion, are always distributed symmetrically.

The observation made by Chapman and Lidbury (*loc. cit.*) that the total quantity of water vapour decomposed, and the extent of the separation of the hydrogen and oxygen, is much greater when the current of water vapour enters the discharge tube in the neighbourhood of the cathode instead of near the anode is confirmed. To explain this, it is supposed that the metallic spray produced by the disintegration of the cathode exerts a catalytic action, which results in a greatly increased union of the products of dissociation. With aluminium electrodes, which do not yield such a metallic spray, the effect is not observed. Using platinum electrodes, the effect diminishes when thicker wires are used, corresponding with diminished disintegration; it is also smaller when the bulbs surrounding the electrodes are made larger.

The behaviour of other metallic electrodes has also been examined. Metals which oxidise when heated in air behave like aluminium; those which do not oxidise or which form a volatile oxide, as in the case of osmium, behave like platinum. Silver and palladium are exceptions. Although silver sprays readily, it does not appear to have any effect on the union of the dissociation products. The behaviour of platinum is traced to its exceptionally high catalytic activity.

On this view, J. J. Thomson's observation, that the pole at which the excess of hydrogen or oxygen appeared in his experiments depended on the length of the spark, can also be explained.

H. M. D.

Activity of the Halogens, Chlorine, Bromine, and Iodine in Relation to the Metals in General. M. C. SCHUYTEN (*Chem. Zeit.*, 1908, 32, 619—620. Compare this vol., ii, 31).—The chlorides of twenty-four metals have been digested with bromine and with iodine, and the bromides of twenty-three metals digested with iodine. After testing the residues from the metallic chlorides and showing the absence of free halogen, they were treated with chlorine water and again tested, when it was generally found that some bromine or iodine was liberated. In the case of the bromides digested with iodine, the dry test for iodine generally indicated the presence of small quantities of that halogen. Whether addition or substitution of halogen takes place under these conditions, the author is at present unable to decide.

J. V. E.

Variation of the Surface Tension of Sulphur with Rise of Temperature: $S\lambda^1$ and $S\lambda^2$. GEORGES CAPELLE (*Bull. Soc. chim.*, 1908, [iv], 3, 764—767).—Smith has shown (*Abstr.*, 1905, ii, 382, 580) that between the melting point (125°) and 160° a definite liquid form of sulphur ($S\lambda$) exists, and that at 160° this passes into a new form ($S\mu$). The author confirms and extends this view from observations on the anomalous change in the surface tension of sulphur as the temperature is raised from 125° to 160° . Between 125° and 142° a slight increase in surface tension takes place, and between 142° and 160° a large and rapid increase. At 160° the liquid becomes viscous, and observations cannot be carried further. It is suggested that Smith's $S\lambda$ is divisible into two species, one ($S\lambda^1$) existing between 125° and 142° , and the other ($S\lambda^2$) between 142° and 160° , but $S\lambda^2$ may be merely a mixture of $S\lambda^1$ with $S\mu$, the formation of the latter commencing at 142° and becoming complete at 160° . T. A. H.

Colloidal Sulphur. M. RAFFO (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 358—360).—Soluble colloidal sulphur is obtained when a concentrated solution of sodium thiosulphate is added very slowly to cooled concentrated sulphuric acid (D 1.84). If the addition of the thiosulphate solution is effected too rapidly, a large proportion of insoluble sulphur is formed. The changes taking place are represented by the equations: (1) $H_2S_2O_3 = SO_2 + H_2O + S$ (insoluble); (2) $H_2S_2O_3 = H_2S + SO_3$; $2H_2S + SO_2 = 2H_2O + 3S$ (soluble).

In order to separate the soluble and insoluble sulphur, the thick, cloudy liquid is diluted somewhat, heated to 80° , and filtered through glass-wool. It is then left in a cool place for twelve hours, again heated and filtered, and these operations are repeated until the whole of the insoluble sulphur has been removed. The end product is a cloudy, yellowish-white mass, which, on warming, yields a perfectly clear yellow liquid. On cooling, the colloidal sulphur separates, and is removed by centrifuging, washed with a little cold water, again centrifuged, and dissolved in the least possible quantity of water. The liquid is neutralised by addition of sodium carbonate, which causes the sulphur to separate, and, after centrifuging, a residue of very nearly pure soluble sulphur is obtained.

On removing the sodium sulphate from the neutralised solution by

dialysis, it is found that the solution became unstable and insoluble sulphur separates. The conclusion is drawn that a pure aqueous solution of colloidal sulphur cannot be obtained. Separation also takes place on addition of various electrolytes. The sulphur precipitated by sodium chloride or nitrate dissolves on warming or on dilution, and that precipitated by potassium chloride, nitrate, or sulphate is insoluble. Precipitation does not take place, in general, on the addition of ammonium sulphate, nitrate, or chloride, or of sodium sulphate. Dilute unneutralised solutions remain clear for long periods, although small quantities of rhombic and monoclinic sulphur are gradually deposited. Concentrated solutions become cloudy in consequence of the separation of insoluble sulphur.

H. M. D.

Spontaneous Oxidation of Sulphur and Sulphides. EGIDIO POLLACCI (*Boll. chim. farm.*, 1908, 47, 363—368).—Moist sulphur in a state of fine division oxidises in the air to sulphuric acid, the action being accelerated by light. In absence of oxygen, sulphur does not decompose water. Pure oxygen or hydrogen peroxide does not bring about the oxidation, and the active agent present in the air is considered to be ozone.

Metallic sulphides also oxidise in a moist state, the first products being the oxide and sulphur, the latter then oxidising to sulphuric acid. Solutions of hydrogen sulphide do not oxidise directly to sulphuric acid, the first process being the production of water and sulphur, followed by oxidation of the latter. The sulphides of iron, manganese, cobalt, gold, silver, platinum, antimony, and titanium oxidise rapidly, those of calcium, barium, strontium, potassium, arsenic, cadmium, mercury, and tin less rapidly, and those of zinc and copper very slowly.

C. H. D.

Preparation of Sulphur Trioxide. RUDOLF FRANK (D.R.-P. 194879).—One of the chief difficulties of the contact process for sulphuric acid is the sensitiveness of the contact material to impurities in the sulphur dioxide, and another is the maintenance of a definite temperature during the operation in order to avoid a reverse chemical change. These difficulties are overcome by compressing sulphur dioxide and oxygen under a pressure of 100 atmospheres, when a complete condensation to sulphur trioxide occurs. By rapidly releasing the pressure, the trioxide may be obtained in a solid condition without appreciable loss of vapour.

G. T. M.

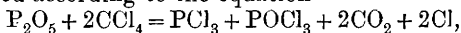
Preparation of Sulphuric Acid. OSKAR BENDER (D.R.-P. 195810).—A mixture of oxygen and sulphur dioxide is introduced into a generator furnace in which water-gas is being produced and then burnt. The heat generated induces the combination of these gases to form sulphur trioxide, and the water produced serves to hydrate this substance, forming sulphuric acid. When air is employed, a certain amount of nitric acid is also produced, which exerts its catalytic action on the mixture of gases and increases the formation

of sulphuric acid. The furnace is fed with sulphur or sulphur-containing materials.
G. T. M.

Quantitative Vaporisation of Phosphoric Acid from Phosphates in a Current of Chlorine and Carbon Tetrachloride or of Carbon Tetrachloride Only. PAUL JANNASCH and W. JILKE (*J. pr. Chem.*, 1908, [ii], 78, 21—28. Compare Abstr., 1907, ii, 864).—It is now found that phosphoric acid can be distilled quantitatively from calcium, sodium, or potassium phosphate if the phosphate is thoroughly ground with quartz powder and the mixture heated in a current of chlorine which has been passed through carbon tetrachloride. The calcium phosphate was heated for four hours at a dark red, and for two hours at a bright red, heat in a quartz boat, and the sodium and potassium phosphates for nine hours at a bright red heat in a gas-carbon boat, in a glass tube. The phosphoric acid distils the more quickly the slower the current of chlorine and carbon tetrachloride.

Phosphoric acid does not distil, even in traces, when magnesium phosphate is heated alone or in admixture with wood charcoal in a current of dry ammonia at a bright red heat (compare Heraeus, Abstr., 1903, ii, 82). Ammonium phosphate, on the other hand, volatilises partly in a current of ammonia, but does not attack the glass tube as when distilled in a current of carbon dioxide; the ammonium phosphate leaves a residue of vitreous phosphoric acid, which is almost insoluble in water or mineral acids.

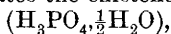
When heated in a current of carbon tetrachloride at a moderate red heat, ferric phosphate is completely volatilised; if the cool end of the tube is packed loosely with glass-wool, ferric chloride is here deposited quantitatively, whilst the mixture of phosphorus trichloride and oxychloride, formed according to the equation



is readily driven over into the receiver.

G. Y.

Hydrates of the Phosphoric Acids. HENRI GIRAN (*Compt. rend.*, 1908, 146, 1270—1272).—The freezing-point curve of aqueous solutions of orthophosphoric acid shows two minima and a single maximum. The minima characterise two eutectics of the composition ($\text{H}_3\text{PO}_4, 0.135\text{H}_2\text{O}$), m. p. 22.5° , and ($\text{H}_3\text{PO}_4, 3.205\text{H}_2\text{O}$), m. p. -81° . The maximum at 29° indicates the existence of the hydrate



for which Joly found m. p. 27° (compare Abstr., 1885, 482). The freezing-point curve for pyrophosphoric acid is similar in form. The two eutectics correspond with the formulæ ($\text{H}_4\text{P}_2\text{O}_7, 1.25\text{H}_2\text{O}$), m. p. 23° , and ($\text{H}_4\text{P}_2\text{O}_7, 6.87\text{H}_2\text{O}$), m. p. -75° . The maximum characterises the hydrate ($\text{H}_4\text{P}_2\text{O}_7, 1.5\text{H}_2\text{O}$), m. p. 26° . This compound has been isolated as unstable needles, readily undergoing conversion into orthophosphoric acid. Measurement of its heat of dissolution proves it to be less stable than the hydrate of orthophosphoric acid.

Only a small portion of the curve for metaphosphoric acid can be studied, since solutions containing less than 63% of water are converted on cooling into a vitreous mass, which refuses to crystallise.

W. O. W.

Molecular Weights of the Phosphoric Acids determined by Cryoscopy. HENRI GIRAN (*Compt. rend.*, 1908, 146, 1393—1396).—The molecular weights of metaphosphoric and pyrophosphoric acids in acetic acid solution diminish after a lapse of time, and finally reach a limit depending on the concentration of the solution. From extrapolation in the curve representing variation of molecular weight with age of solution, it is found that at the moment of solution, metaphosphoric acid has a molecular weight corresponding with the formula $5(\text{HPO}_3)$, whilst pyrophosphoric acid has the formula $3(\text{H}_4\text{P}_2\text{O}_7)$. The molecular weight of orthophosphoric acid varies only slightly with time; the values obtained varied from 111.9 to 127.1, according to the concentration of the solution. The acid should probably be represented by the formula $(\text{H}_3\text{PO}_4)_2$. Orthophosphoric and pyrophosphoric acids have the same molecular weights in the liquid as in the solid form.

W. O. W.

The Removal of Arsenic from Liquids and Gases. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 194864).—In order to free a liquid, such as concentrated sulphuric acid, from arsenic, it is treated with strong hydrochloric or hydrofluoric acid, and then mixed intimately with benzene. On drawing off the latter liquid, it is found to contain all the arsenic as chloride or fluoride, and, when freed from this impurity by treatment with water, it may be employed in removing arsenic from further quantities of sulphuric acid. Dichlorobenzene may also be employed for this purpose, and, owing to its higher boiling point, is preferably used in the removal of arsenic from gases by allowing it to flow down towers through which the gaseous mixtures are passing.

G. T. M.

Ammoniacal Arsenic Trichloride. ADOLPHE BESSON and GEORGES ROSSET (*Compt. rend.*, 1908, 146, 1266—1267. Compare Abstr., 1890, 1052; Hugot, Abstr., 1904, ii, 559).—When dry, gaseous ammonia acts on arsenic trichloride at -20° , a bright yellow solid, $\text{AsCl}_3 \cdot 4\text{NH}_3$, is formed; this sublimes completely when heated in a vacuum at 200° , forming a yellow, horn-like substance, $2\text{AsCl}_3 \cdot 7\text{NH}_3$. When the former compound is treated with liquid ammonia, it loses its colour, and remains colourless when the excess of ammonia is driven off. When extracted with liquid ammonia, ammonium chloride is removed and a white, insoluble residue obtained, the composition of which agrees with that of the imide, $\text{As}_2(\text{NH})_3$. On making an intimate mixture of the portions soluble and insoluble in liquid ammonia, a substance is obtained which differs from the original compound in that it is not completely volatile at 200° , and when treated with sulphuric acid yields only a small quantity of arsenic trichloride.

These experiments lead to the conclusion that liquid ammonia acts on the compound $\text{AsCl}_3 \cdot 4\text{NH}_3$ as a reagent, and not merely as a solvent. Arsenic trichloride also reacts with $\text{AsCl}_3 \cdot 4\text{NH}_3$, giving rise to ammonium chloride and a substance or mixture of substances, the composition of which is indicated approximately by the formula $\text{As}_4\text{Cl}_5\text{N}_2\text{H}_4$. The identity of this product has not been established.

W. O. W.

Tellurides of Arsenic and Bismuth. Cryoscopic Constant of Tellurium. HENRI PÉLABON (*Compt. rend.*, 1908, 146, 1397—1400).—Arsenic dissolves readily in molten tellurium. Examination of the freezing-point curve of the solution indicates the existence of the compound As_2Te_3 , characterised by a maximum at 362° . This telluride crystallises in long, silver-white needles having a pale yellow tint. The freezing-point curve for solutions of bismuth in tellurium has been completely followed. A maximum occurs at 583° , corresponding with the compound Bi_2Te_3 . The freezing points of solutions of these two tellurides in excess of tellurium have been determined, and the cryoscopic constant of tellurium calculated. The value $K=517$ was obtained from As_2Te_3 , whilst the bismuth compound gave $K=528$. These numbers agree closely with those already determined for this constant.

By applying Robertson's formula (*Trans.*, 1902, 81, 1233), the latent heat of fusion of tellurium is found to be 20—21 Cal.

W. O. W.

Synthesis of Boron Sulphide from Ferroboron and Manganoboron. JOSEF HOFFMANN (*Zeitsch. anorg. Chem.*, 1908, 59, 127—135. Compare *Abstr.*, 1907, ii, 82).—The formation of boron sulphide by passing a current of dry hydrogen sulphide over ferroboron and manganoboron at the melting point of antimony has been examined in detail. The ferroboron is more rapidly decomposed than the manganoboron, and a better yield is obtained with the former material. In both cases, only a portion of the contained boron can be converted into the sulphide.

Boron sulphide loses weight on exposure to the air, and hydrogen sulphide is evolved. It also changes when kept in the dark in closed vessels. Water, alcohol, and aqueous solutions decompose it rapidly. It is insoluble in carbon disulphide, and is decomposed slowly by ethyl ether and glycerol. Sulphuric acid reacts with the liberation of hydrogen sulphide and sulphur dioxide.

The author has attempted to ascertain whether borides of definite composition are present in the materials used in his experiments by decomposing these by treatment with aqua regia. The proportions of the constituents which pass into solution are supposed to indicate borides of the composition Fe_3B_4 and MnB .

H. M. D.

Preparation of Boron Nitride and Calcium Boride. ALFRED STOCK and WALTER HOLLE (*Ber.*, 1908, 41, 2095—2099).—Boron nitride, although easily prepared, is difficult to obtain in a pure state (Stock and Blix, *Abstr.*, 1901, ii, 650; Moeser and Eidmann, *Abstr.*, 1902, ii, 206). It is now found that boron nitride can be prepared by dropping boron bromide into liquid ammonia and gradually heating the resulting boronimide (Joannis, *Abstr.*, 1904, ii, 654) to 750° . Boron nitride, so prepared, reacts only slowly with water, being dissolved in boiling water in one day. In comparison with this, however, phosphorus nitride is highly stable, only about 1% being dissolved by boiling water in two hundred hours. In a glass tube at 180° ,

phosphorus nitride is completely dissolved by boiling water in a few hours, but in this case the alkali of the glass may be concerned.

The action of calcium on boron trioxide leads to the formation of almost pure calcium boride, and not to that of boron, as stated by Moissan (Abstr., 1899, ii, 153). G. Y.

Pure Carbon Dioxide. WALTER P. BRADLEY and C. F. HALE (*J. Amer. Chem. Soc.*, 1908, 30, 1090—1096).—In connexion with a study of the critical state of carbon dioxide (Bradley, Browne, and Hale, Abstr., 1905, ii, 75), it was necessary to prepare the gas in the highest possible degree of purity. A method was therefore devised, and is described in the present paper, by means of which carbon dioxide can be obtained of such purity that only 1 part in 30,000—40,000 parts is incapable of absorption by potassium hydroxide solution. The gas is evolved by the action of pure sulphuric acid on sodium hydrogen carbonate, and special apparatus has been devised for its purification and collection. For details, the description and diagram in the original must be consulted.

In the course of the experiments, it was observed that rubber tubing is slightly permeable to air, even against a pressure of 50 mm. of mercury. E. G.

Tschermak's Method of Preparing Silicic Acids. OTTO MÜGGE (*Centr. Min.*, 1908, 325—326. Compare this vol., ii, 277, 490).—A reply to Tschermak. L. J. S.

Preparation of Argon from Air by means of Calcium Carbide. FRANZ FISCHER and OSKAR RINGE (*Ber.*, 1908, 41, 2017—2030).—It is shown that argon can be obtained economically from air by means of calcium carbide. The nitrogen and oxygen are both absorbed when the air is passed over a mixture of calcium carbide (90%) and calcium chloride (10%) heated at 800° in an iron vessel. The nitrogen reacts with the carbide, yielding carbon and calcium cyanamide; the oxygen forms lime and carbon; carbon monoxide and dioxide are also formed, but these ultimately react with the carbide, yielding carbon. The carbide mixture is first heated under reduced pressure in order to remove moisture from the calcium chloride, and then dry air is passed over. The issuing gas contains small amounts of hydrogen, hydrocarbons, and carbon monoxide, and is therefore passed through a vessel containing heated copper oxide. By this process, some 11 litres of argon may be obtained in the course of two days, using about 7 kilograms of carbide.

Details of the apparatus and its use are given.

J. J. S.

Percentage of the Inactive Gases in the Atmosphere. A Correction to Previous Calculations. SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1908, 80, 4, 599).—The total weights of krypton and xenon in the atmosphere calculated from the volumes (Abstr., 1903, ii, 476) are ten times too small; the true values are 0.028% for krypton and 0.005% for xenon. The values for the proportion of helium and neon previously given (Abstr., 1905, ii, 817) are 100 times too small;

the true percentage of helium is 0.000056 by weight and 0.00040 by volume; of neon, 0.00086 by weight and 0.00123 by volume. G. S.

Preparation of Alcoholic Potassium Hydroxide Solution which will Keep. FRANZ RABE (*Zeitsch. Nahr. Genussm.*, 1908, 15, 730—731).—It is recommended that the required quantity of potassium hydroxide should be dissolved in its own weight of water, and the solution, when cold, poured into about 900 c.c. of 95% alcohol, with constant shaking. The whole is then diluted with alcohol to 1000 c.c., mixed, and placed aside until the oily drops of "aldehyde-resin" have separated. The solution is then decanted, and, at the end of about two days, is once more poured off from the separated precipitate (potassium carbonate, &c.). Filtration is unnecessary. W. P. S.

Electrolytic Production of Alkali Chlorates and Perchlorates. M. COULERU (D.R.-P. 195639).—In the ordinary electrolytic processes for chlorates, the production of free alkali hydroxide and hypochlorites diminishes the yield of the required salts. Increased efficiency is gained by the addition of calcium salts, chromates, or dichromates. The addition of chromate may be made in alkaline, neutral, or acid solution, the best effect being obtained in the last case and the worst in the first. Practically, however, the employment of an acid solution has two disadvantages, namely, corrosion of the platinum electrodes and formation of a highly-coloured product. Accordingly, the electrolytic solution is kept neutral by the addition of salts which will interact with any alkali hydroxide to furnish either a hydroxide not affected by hypochlorite, or one which will yield a technically important product when treated with this oxidising agent. Magnesium chloride is the best example of the first type of salt, and lead chloride of the second. In the first instance, the magnesium hydroxide which is precipitated by potassium or sodium hydroxide is not materially affected by hypochlorite, and in the second, the lead hydroxide precipitated by the alkali is oxidised by hypochlorite to lead dioxide. The yield calculated on the current employed is 90% for potassium chlorate and 85% for the corresponding sodium salt.

G. T. M.

Preparation of Anhydrous Sodium Thiosulphate and Hydrosulphide. VEREIN CHEMISCHER FABRIKEN IN MANNHEIM (D.R.-P. 194881 and 194882).—Dry pulverulent sodium hydrosulphide results when hydrogen sulphide is passed over sodium sulphide at 300°. If the gas contains carbon dioxide, the sodium sulphide is mixed with the calculated amount of powdered chalk.

Anhydrous sodium thiosulphate is produced by passing oxygen or air over sodium hydrosulphide at 100—150°; it is also formed when sodium sulphide is heated at higher temperatures in a current of hydrogen sulphide and oxygen.

G. T. M.

Preparation of Sodium Perborate. DEUTSCHE GOLD & SILBER SCHEIDE-ANSTALT (D.R.-P. 193722).—A 50% solution of sodium peroxide prepared in the cold is saturated with carbon dioxide and

then treated with a concentrated solution of sodium metaborate. Sodium perborate separates when the liquid is cooled to 2°, providing that sufficient water is present to keep all the alkali carbonate in solution.

G. T. M.

Manufacture of Lithia from Lepidolite. WILLIAM JAY SCHIEFFELIN and THOMAS W. CAPPON (*J. Soc. Chem. Ind.*, 1908, 27, 549—550).—A 97—99% decomposition of lepidolite can be effected by gradually heating a mixture of the ore with 10% more than its weight of sulphuric acid (66° B.) at 340°, the operation lasting about eight hours. The mass is leached with water and the silica separated; the solution is then treated with sufficient potassium sulphate to convert all the aluminium sulphate into alum. After six days, the mother liquor is decanted from the precipitated alum meal. In order to remove the alum still in solution, the liquid is first treated with whiting to neutralise the acid, and then boiled with freshly-precipitated aluminium hydroxide; practically all the alum is thereby precipitated as basic alum or alunite. A subsequent treatment with more whiting removes the last traces of alumina. The solution is then made alkaline with slaked lime and concentrated; it consists chiefly of lithium sulphate, a small amount of calcium sulphate, and traces of manganese and iron oxides. After removal of these impurities, the solution is added to potassium carbonate, and the precipitated lithium carbonate is then washed and dried.

P. H.

Electrolytic Production of Ammonium Persulphate. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 195811).—Hitherto a good yield of ammonium persulphate has been obtained electrolytically either by the use of a diaphragm or by the addition of a chromate in ammoniacal solution. It has now been found that a saturated solution of ammonium sulphate can be electrolysed so as to give a good yield of persulphate, provided that a current density of not less than 20 amperes per sq. decm. is employed, and that the solution is sufficiently acid not to develop an alkaline reaction in the neighbourhood of the cathode. With a current density of 300 amperes, a yield of 70% of persulphate is obtained without the use of a diaphragm.

G. T. M.

Double Chromates of Ammonium. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1908, 58, 412—426. Compare Abstr., 1907, ii, 94, 624).—The compounds in question were prepared almost exclusively by the gradual addition of 10 c.c. of a 2*N* solution of the appropriate salt to 50 c.c. of an approximately 2*N*-solution of neutral ammonium chromate; the precipitate was allowed to remain in contact with the mother liquor for some time, then filtered rapidly, and dried on a porous plate. As many of the salts are decomposed by water, they could not be purified by washing.

Ammonium barium chromate, $\text{BaCrO}_4 \cdot (\text{NH}_4)_2\text{CrO}_4$, forms light yellow, cubic crystals, and the corresponding *strontium* salt, light yellow, spherical, crystalline aggregates; both are decomposed by water. The corresponding *magnesium* salt, with $2\text{H}_2\text{O}$, forms yellow crystals, and is not decomposed by water.

From zinc chloride and neutral ammonium chromate solution, the compound, $4\text{ZnCrO}_4, 2(\text{NH}_4)_2\text{CrO}_4, 3\text{NH}_3, 3\text{H}_2\text{O}$, was obtained in transparent, dark yellow, spherical granules, but with a chromate containing ammonia in excess, the compound $\text{ZnCrO}_4, (\text{NH}_4)_2\text{CrO}_4, 2\text{NH}_3$, already described by Briggs (Trans., 1903, 83, 391), was obtained. Two double salts containing *cadmium*, of the probable formulæ $2\text{CdCrO}_4, 2(\text{NH}_4)_2\text{CrO}_4, \text{NH}_3, 3\text{H}_2\text{O}$ (deep-yellow prisms) and $\text{CdCrO}_4, \text{NH}_3, \text{H}_2\text{O}$

(small, granular crystals), were also prepared. When the chromate contains excess of ammonia, the compound $\text{CdCrO}_4, (\text{NH}_4)_2\text{CrO}_4, 2\text{NH}_3$ separates in light yellow, prismatic crystals (Briggs, *loc. cit.*). Two *mercury* salts were also prepared, but their constitution has not been elucidated, and they were probably impure.

With cupric chloride and the chromate containing excess of ammonia, the compound $\text{CuCrO}_4, (\text{NH}_4)_2\text{CrO}_4, 2\text{NH}_3$ was obtained (Briggs, *loc. cit.*); with the neutral chromate, the same salt in an impure condition was isolated. With nickel chloride and excess of ammonium chromate, a double salt, $2\text{NiCrO}_4, 2(\text{NH}_4)_2\text{CrO}_4, 3\text{NH}_3, \text{H}_2\text{O}$, has been obtained in small, reddish-brown prisms. Other double salts, obtained by interaction of these two reagents under different conditions, have been described previously. With cobalt chloride, the compound, $3\text{CoCrO}_4, (\text{NH}_4)_2\text{CrO}_4, 2\text{NH}_3, 3\text{H}_2\text{O}$, was obtained in dark reddish-brown granules, readily decomposed by water. With silver nitrate, the compound, $3\text{Ag}_2\text{CrO}_4, (\text{NH}_4)_2\text{CrO}_4$, was obtained in reddish-brown, granular crystals, and with lead acetate, the compound, $\text{PbCrO}_4, (\text{NH}_4)_2\text{CrO}_4$, as an amorphous precipitate; both compounds are decomposed by water. G. S.

The Solubility of Silver Iodide in Ammonia. HENRI BAUBIGNY (*Compt. rend.*, 1908, 146, 1263—1265; *Bull. Soc. chim.*, 1908, [iv], 3, 772—775).—The solubility of silver iodide in aqueous ammonia increases appreciably with rise of temperature. Failure to take this into account is responsible for the discordant results of previous observers. The author shakes known weights of silver iodide (free from chloride) with a definite volume of ammonia in sealed tubes at 50—60°, and, after allowing these to cool to the desired temperature, observes whether or no crystallisation has taken place. In this way, the coefficient of solubility of silver iodide at 16° in aqueous ammonia (D 0.926) is found to be of the order 1/6000, a value considerably lower than that obtained by previous workers.

W. O. W.

Simplest Method of Preparing Carey Lea's Photo-haloids. LÜPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 360—361).—When the halogen salts of silver are allowed to remain in contact, or are warmed, with colloidal solutions of silver, the so-called "photo-salts" are formed. These are separated by dissolving the excess of colloidal silver in nitric acid. The coloured halogen salts are also obtained when a suitable reducing agent is added to silver nitrate which is in contact with the ordinary silver halogen salts. Suitable reducing agents are (1) sodium citrate + ferrous sulphate; (2)

sodium potassium tartrate + ferrous sulphate; (3) tannic or gallic acid + alkali carbonate; (4) formaldehyde + sodium hydroxide; (5) sodium hypophosphite.

The method of preparation described supports the author's view that the coloured salts are adsorption compounds. H. M. D.

[Preparation of Calcium Hypochlorites.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 195896).—When a mixture of 1 part of quicklime and 6.4 parts of water is treated with chlorine until nearly all the lime is used up, a solution is obtained containing 180 to 190 grams of active chlorine and only 1 or 2 grams of chlorate per litre. This solution is then treated anew with lime and chlorine, when crystalline calcium hypochlorite is deposited. This operation may be repeated until nearly all the hypochlorite is precipitated, the action being accelerated by the addition of calcium chloride.

When milk of lime is chlorinated, a point is reached at which further introduction of chlorine does not increase the amount of active chlorine in solution, owing to the formation of basic hypochlorites of the type $\text{Ca}(\text{OCl})_2, x\text{Ca}(\text{OH})_2$. Two have been isolated in which x is 2 and 4; they cannot be obtained crystalline, owing to the circumstance that they are decomposed by water. G. T. M.

Colloidal Barium Sulphate. ALBERT RECOURA (*Compt. rend.*, 1908, 146, 1274—1276. Compare Neuberg, *Abstr.*, 1906, ii, 753).—The employment of pure glycerol as a solvent for the reacting salts when barium sulphate is prepared by double decomposition, results in the formation of a stable colloidal variety of the latter substance. The glycerol solution of the colloid can be diluted with several times its volume of water without bringing about precipitation of the insoluble form. The solution is, however, immediately coagulated on boiling. The addition of aqueous solutions of metallic salts (with the exception of mercuric chloride and salts of barium) likewise causes precipitation. Ammonia, baryta, and all monobasic acids, after several hours, bring about a gradual precipitation, whilst polybasic acids (boric acid excepted) cause immediate coagulation. Barium salts increase the stability of the colloid to a marked extent. A solution which has been rendered stable by the addition of barium nitrate can be kept for fifteen days to a month without depositing barium sulphate. Such a solution, however, is immediately coagulated by the addition of salts of polybasic acids; the salts of monobasic acids on the other hand are without action on it. W. O. W.

Langbeinite and Vanthoffite [$\text{K}_2\text{SO}_4, 2\text{MgSO}_4$ and $3\text{Na}_2\text{SO}_4, \text{MgSO}_4$]. RICHARD NACKEN (*Chem. Zentr.*, 1908, i, 1850; from *Nachr. K. Ges. Wiss. Göttingen*, 1907, 602—613. Compare *Abstr.*, 1907, ii, 530).—The author has studied the temperature-concentration diagram of the systems $\text{MgSO}_4\text{--K}_2\text{SO}_4$ and $\text{MgSO}_4\text{--Na}_2\text{SO}_4$ as in previous cases.

1. *Simple sulphates*.—Sodium sulphate and potassium sulphate are enantiotropic dimorphous, with transformation temperatures 234° and 595° , and m. p. 883° and 1076° respectively; they do not

appreciably decompose or volatilise. Magnesium sulphate is considerably decomposed below its m. p., 1124° .

2. *Magnesium sulphate-potassium sulphate system*.—The solidification curve shows a maximum at 33.3 mol.% K_2SO_4 and 930° . Both artificial and natural langbeinite exhibit simple refraction, D^{25} 2.829. The eutectic mixture, $MgSO_4$ + langbeinite, m. p. 884° , contains 22 mol.% K_2SO_4 . α - K_2SO_4 in the solid state is miscible with $MgSO_4$ to a limited extent. The eutectic mixture, langbeinite + saturated α - K_2SO_4 , mixed crystals, m. p. 747° , contains 62 mol.% K_2SO_4 .

3. *Magnesium sulphate-sodium sulphate system*.—The maximum concentration of this mixture has been found to be $Na_2SO_4, 3MgSO_4$, m. p. 813° , D^{25} 2.0345, double refracting granules, and not as is stated by Le Chatelier, $Na_2SO_4, 2MgSO_4$. Eutectic mixture, $MgSO_4 + Na_2SO_4, 3MgSO_4$, 808° and 23 mol.% Na_2SO_4 . α - Na_2SO_4 in solid form is miscible with $MgSO_4$ to a limited extent. Eutectic mixture, $Na_2SO_4, 3MgSO_4$ + saturated α - Na_2SO_4 , mixed crystals, 665° and 52 mol.% Na_2SO_4 . Natural vanthoffite shows an alteration in refraction at 489° , and has the same D^{25} 2.6955 as the artificial. J. V. E.

Double Chlorides and Bromides of Zinc and the Alkalis. FRITZ EPHRAIM (*Zeitsch. anorg. Chem.*, 1908, 59, 56—70).—The products obtained by crystallisation of solutions containing chlorides and bromides of zinc and sodium, potassium, ammonium, or lithium at temperatures between 20° and 100° have been examined.

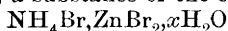
The salt, $2KCl, ZnCl_2, H_2O$, crystallises from a solution containing a slight excess of zinc chloride. On leaving the mother liquor for some days in contact with the air, the salt, $KCl, ZnCl_2$, separates in thick, monoclinic prisms. Solutions containing potassium chloride in considerable excess, deposit this on evaporation, and later the anhydrous double chloride, $2KCl, ZnCl_2$, appears.

The salt, $KBr, ZnBr_2, 2H_2O$, crystallises from solutions containing equal molecular proportions of the two bromides in elongated, six-sided tablets. Solutions containing 2 or more mols. of potassium bromide per mol. of zinc bromide yield very fine, hair-like needles of the composition $2KBr, ZnBr_2, 2H_2O$.

The already-described sodium zinc chloride, $2NaCl, ZnCl_2, 3H_2O$, is the only double chloride which can be separated.

The salt, $NaBr, ZnBr_2, H_2O$, crystallises from solutions containing zinc bromide in slight excess in hygroscopic prisms. The salt $2NaBr, ZnBr_2, 5H_2O$ is obtained in the form of small needles from solutions containing the two bromides in the same ratio.

In addition to the double chlorides and bromides of ammonium and zinc previously described, a substance of the composition



is obtained on evaporation of a solution containing equal molecular quantities of the simple bromides.

On evaporation of a solution containing 2 mols. zinc chloride per mol. lithium chloride, microscopic, six-sided leaflets of the basic salt, $ZnO, 3ZnCl_2, H_2O$, separate. By slow evaporation of the mother liquor over concentrated sulphuric acid, crystals of the composition $LiCl, ZnCl_2, 3H_2O$ are obtained. From solutions containing 2 mols.

lithium chloride per mol. zinc chloride, well-formed, hygroscopic, flat prisms of the composition $2\text{LiCl}, \text{ZnCl}_2, 2\text{H}_2\text{O}$ crystallise.

When a solution containing 6 mols. of lithium chloride per mol. of zinc chloride is evaporated on the water-bath and cooled, lithium chloride separates; on repeating these processes until no more lithium chloride crystallises on cooling, a syrupy liquid of the composition $3\text{LiCl}, \text{ZnCl}_2, 10\text{H}_2\text{O}$ is obtained. This liquid, which does not lose water at 100° and does not crystallise when cooled to -20° , is supposed to be a definite compound. The syrupy liquid, after having been kept in a desiccator for about six months, deposited crystals of lithium chloride.

H. M. D.

Rare Earths. HUGO ERDMANN and FRITZ WIRTH (*Annalen*, 1908, 361, 190—217).—The peculiar behaviour of cerium with 1 : 8-hydroxynaphthalenesulphonic acid (Erdmann and Nieszytka, this vol., i, 621) led the authors to study the salts of this acid with other rare earths, as also the malonates, which, like the oxalates, serve for the recognition and separation of rare metals, since the malonates of the cerium metals are isomorphous and microcrystalline, whilst those of the yttrium earths crystallise in long spears. The sulphides of samarium and gadolinium have also been prepared.

Neodymium and samarium are separated from lanthanum and praseodymium by a long series of fractional crystallisations of didymium magnesium nitrate, $2\text{R}(\text{NO}_3)_3, 3\text{Mg}(\text{NO}_3)_2, 24\text{H}_2\text{O}$, which crystallises in large plates (Demarçay, Abstr., 1900, ii, 346). Lanthanum is then separated from praseodymium by Welsbach's method of fractional crystallisation of the double salts with ammonium nitrate. Samarium and gadolinium nitrates were prepared from a euxenite and from the final filtrates from the preparation of neodymium, the samarium being precipitated as the double salt with potassium sulphate, $2\text{Sa}_2(\text{SO}_4)_3, 9\text{K}_2\text{SO}_4, 3\text{H}_2\text{O}$, which crystallises from concentrated potassium sulphate solution. Europium was removed from this precipitate by Urbain and Lacombe's method (Abstr., 1904, ii, 43). The gadolinium which remains dissolved in the potassium sulphate solution was purified by fractional precipitation of the nitrate from nitric acid. The examination of the arc spectra showed that the samarium nitrate was free from neodymium, and therefore from the metals of the cerium group, but contained traces of gadolinium, europium, and yttrium; the gadolinium fraction contained only traces of samarium, dysprosium, terbium, and yttrium.

Malonates of the Rare Earths.—As malonic acid does not form precipitates with the salts of the rare earths, malonates were prepared by the action of malonic acid on the hydroxides; on heating the aqueous solutions, the malonates separate in crystalline form. The following malonates are described (compare Holmberg, Abstr., 1907, ii, 90); the figures in brackets are the solubilities in 100 parts of water at 18° : $(\text{C}_3\text{H}_2\text{O}_4)_3\text{La}_2, 5\text{H}_2\text{O}$ (0.0455), white crystals; $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Ce}_2, 5\text{H}_2\text{O}$ (0.0141), white crystals, lose $2\text{H}_2\text{O}$ at 140° , and the remaining $3\text{H}_2\text{O}$ at 180° ; $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Pr}_2, 6\text{H}_2\text{O}$ (0.0179), green, crystalline powder; $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Nd}_2, 5\text{H}_2\text{O}$ (0.0354); $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Sa}_2, 6\text{H}_2\text{O}$ (0.0397), yellow,

granular powder; $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Gd}\cdot 8\text{H}_2\text{O}$ (0·0616), strongly refracting, yellow needles; $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Yt}_2\cdot 5\text{H}_2\text{O}$ (0·1076), white needles;
 $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Er}_2\cdot 10\text{H}_2\text{O}$

(0·1300), long needles. The malonates of the cerium group form prismatic, doubly refracting plates, and effloresce in air; those of the yttrium group form doubly refracting, rhombic needles. All of these salts dissolve in acids, and when boiled with alkalis form the hydroxide of the metal.

8-Hydroxynaphthalene-1-sulphonates of the Rare Earths.—The following 8-hydroxynaphthalene-1-sulphonates were prepared by the action of the acid on the carbonates of the rare metals; they separate from the boiling aqueous solution as heavy powders. The solubilities in 100 parts of water at 14° are given in brackets: $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{La}_2$ (0·0926—0·0987), white powder, dissolves in acids, forming bluish-red solutions; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Pr}_2$ (0·0709—0·0818), green powder, forms bluish-red solutions in acids; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Nd}_2$ (0·0171—0·0211), grey powder, forms yellowish-red solutions in acids; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Sa}_2$ (0·0496—0·0573), white powder, soluble in acids; $(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Gd}_2$ (0·117), white powder, forms bluish-red solutions in acids;

$(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Yt}_2$
 (0·0951), white powder, forms bluish-red solutions in acids;

$(\text{C}_{10}\text{H}_6\text{SO}_4)_3\text{Er}_2$
 (0·0339), white powder. These salts are not hygroscopic, but absorb oxygen, becoming black on exposure to air; when boiled with alkalis, they form metallic hydroxides.

Sulphides of the Rare Earths.—These are best prepared by heating the sulphates in a current of hydrogen sulphide (Muthmann and Stützel, Abstr., 1900, ii, 142).

Samarium sulphide, Sa_2S_3 , forms a yellow mass, D 3·7, burns when heated, forming the oxide and sulphate, is decomposed only slowly by boiling water, and dissolves in acids with evolution of hydrogen sulphide.

Gadolinium sulphide, Gd_2S_3 , forms a hygroscopic, yellow mass, D 3·8, and behaves in the same manner as the samarium salt.

G. Y.

Scandium. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1908, 80, A, 516—518).—As the result of spectroscopic examination of fifty-three rare-earth minerals, scandium has been detected in auerlite, cerite, keilhauite, mosandrite, orangite, orthite, pyrochlore, thorianite, thorite, and wiikite. All these minerals contain less than 0·01% of scandium, except wiikite, which contains more than 1%.

Wiikite is a black, amorphous mineral, which, when heated to redness in a silica tube, gives off helium, water, hydrogen sulphide, a white sublimate, and traces of hydrogen, carbon dioxide, and neon. An approximate analysis of wiikite gave the following figures: tantalic acid with some niobic acid, 15·91; titanic acid and zirconia, 23·36; earths of the cerium group, 2·55; earths of the yttrium group, 7·64; scandia, 1·17; thoria, 5·51; ferrous oxide, 15·52; uranic oxide, 3·56; silica, 16·98; water and gases, 5·83; calcium, manganese, tin, sulphur, &c., 1·97.

Scandium may be separated by fractional crystallisation from the crude earths, consisting chiefly of yttria, ytterbia, and scandia; its spectrum should be free from the lines of ytterbium.

A number of salts of scandium have been prepared and analysed.

R. J. C.

New Double Salt of Thallium. MORITZ KOHN (*Zeitsch. anorg. Chem.*, 1908, 59, 111—113).—When a hot concentration solution of thallous sulphate is added to a solution containing an equal molecular quantity of uranyl sulphate acidified with sulphuric acid, intensely coloured, yellow crystals of the double salt, $\text{Tl}_2\text{SO}_4 \cdot \text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, belonging to the rhombic system, separate on cooling. Solutions supersaturated with regard to the double salt are easily obtained.

H. M. D.

Freezing-point Diagrams of the Binary Systems, Cu-Cu₂Se, Ag-Ag₂Se, and Pb-PbSe. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1908, 5, 355—358).—The addition of selenium lowers the freezing point of copper, the eutectic point lying between 2 and 3% Se and 1063°. The curve then rises, soon becoming nearly horizontal. There is some separation into two liquid layers, the limits of which were not determined. The existence of copper selenide, Cu₂Se, melting at 1113°, is demonstrated. Copper does not form solid solutions with selenium.

Mixtures of silver with more than 7% Se separate into two liquid layers. The existence of the selenide Ag₂Se (m. p. between 834° and 850°) is indicated, but mixtures richer in selenium could not be prepared, owing to loss by volatilisation.

Only a single branch of the freezing-point curve of lead-selenium mixtures could be determined. The eutectic point lies close to the lead end. The existence of the compound PbSe, m. p. 1100°, is indicated.

C. H. D.

Non-electrolytic Solution of Mercury in Water and Other Liquids. A. CHRISTOFF (*Zeitsch. physikal. Chem.*, 1908, 63, 346—354).—Experiments show that mercury can dissolve in, and diffuse through, water which contains air, nitrogen, carbon dioxide, sulphuric acid, or potassium hydroxide, as also through benzene, nitrobenzene, and alcohol. The mercury was covered with a layer of water (or other liquid), and the fact of its diffusion was proved by the reduction of a gold chloride solution contained in a separate vessel (compare Barfoed, *Abstr.*, 1889, 346). In some cases, the mercury was exposed to the air, and the gold chloride solution was protected by a water seal. It is shown, also, that mercury left for a long time in contact with water suffers a slight loss in weight, although no mercury compounds can be detected in the water.

J. C. P.

Two Observations Relating to the Decomposition of Mercuric Iodide. MORITZ KOHN (*Zeitsch. anorg. Chem.*, 1908, 59, 108—110).—In alkaline solution, mercuric iodide is decomposed quantitatively by sodium arsenite, with the separation of metallic

mercury. After the solution containing an excess of arsenite has been heated to the boiling point, it is left for several hours, and the separated mercury can then be filtered off. Estimation of the iodide in the solution shows that the reaction is quantitative.

Hydrogen peroxide also liberates metallic mercury from mercuric iodide in alkaline solution. The mercury can be filtered off after one to two hours. The decomposition is not quite complete in this case.

H. M. D.

The Alumino-Silicate, $K_2Al_2SiO_6$. ZYGMUNT WEYBERG (*Centr. Min.*, 1908, 326—330).—Gorgen's method (Abstr., 1890, 13) for preparing the crystalline compound $K_2Al_2SiO_6$ was tried, but better results were obtained by fusing kaolin with a large excess of potassium dichromate. The minute, colourless, isotropic octahedra which result are, however, much contaminated by enclosures of crystallised chromic oxide. Attempts to obtain other salts of the acid, $H_2Al_2SiO_6$, were unsuccessful.

L. J. S.

The Potassium Alumino-Silicate, $K_2Al_2Si_2O_8$. ZYGMUNT WEYBERG (*Centr. Min.*, 1908, 395—402).—By fusing kaolin or a mixture of alumina and silica with a large excess of potassium salts (chloride, carbonate, sulphate, or chromate), a minutely-crystalline product with the composition $K_2Al_2Si_2O_8$ is obtained. The crystals appear to be of two kinds (possibly tetragonal and orthorhombic), and to differ from the hexagonal mineral kaliophilite.

L. J. S.

Preparation of Manganese Compounds. O. DIEFFENBACH (D.R.-P. 195523 and 195524).—The reactivity of naturally-occurring manganese dioxide is greatly increased when it is hydrated by heating under pressure at 188° with 30% sodium hydroxide solution. The product which is obtained in a voluminous form contains the hydrate $MnO_2 \cdot 2H_2O$.

The decomposition of an alkali manganate in aqueous solution into permanganate, manganese dioxide, and alkali hydroxide can be reversed when manganese dioxide suspended in 30% to 40% potassium hydroxide solution containing a small amount of manganate or permanganate is electrolysed in the anode compartment of an electrolytic cell. When the mixture is stirred and heated, the manganese dioxide is gradually converted into potassium manganate. Instead of manganate or permanganate, a small amount of potassium ferricyanide may be employed as the oxidising catalyst.

G. T. M.

Alloys of Iron and Carbon. GEORGES CHARPY (*Bull. Soc. chim.*, 1908, [iv], 3, i—xlvi).—A lecture delivered before the Chemical Society of Paris, in which a critical résumé of the results obtained in recent years in the study of iron-carbon alloys is given. The following principal lines of investigation are dealt with: (a) deduction of an equilibrium diagram by the application of the phase rule; (b) thermal investigations; (c) isolation of definite constituents from

the alloys by chemical processes; (d) microscopic examination, and (e) observation of the physical and mechanical properties of the alloys. The limits of applicability of each of these methods, and the special difficulties attending the prosecution of each, are discussed, and the bearing of the results obtained by the last four methods of research on the elaboration of a complete equilibrium diagram are considered in detail, and attention is directed to points still requiring investigation. A bibliography of the subject is appended. T. A. H.

Steels Containing Phosphorus. J. DE KRYLOFF (*Rev. de Métallurgie*, 1908, 5, 355—360).—The brittleness of steels containing small quantities of phosphorus may be removed by quenching in oil and re-heating to 750°. In this way, a uniform structure is obtained if the phosphorus does not exceed 0.07%. A larger proportion of phosphorus prevents the uniform distribution of ferrite and pearlite. C. H. D.

The Rusting of Iron. J. NEWTON FRIEND (*J. Iron Steel Inst.*, 1908, 77, i, 5—32. Compare Moody, *Trans.*, 1906, 89, 729; *Proc.*, 1907, 23, 84; Tilden, *Trans.*, 1908, 93, 1356).—Boiling pure iron or steel with distilled water in a Jena glass reflux apparatus for two hours does not dissolve any iron. The contrary result of Walker, Cederholm, and Bent (*Abstr.*, 1907, ii, 875) is to be attributed to the retention of some carbon dioxide by the water. An apparatus was devised in which water could be distilled from sodium hydroxide solution on to iron in a closed bulb, and in this case rusting did not take place. In another apparatus, iron was immersed in pure water, and a current of air free from carbon dioxide bubbled through the apparatus. Rusting did not take place if the iron was protected from contact with the glass, although the admission of ordinary air at once caused rusting. It is considered, in agreement with Moody, that the presence of an electrolyte is necessary to the formation of rust. Cast iron rusts even in pure air and water, probably owing to the oxidation of the sulphide and phosphide present. Pure steam is also without action on pure iron at 100°.

Neutral or alkaline hydrogen peroxide is without action on pure iron, although cast iron is rapidly attacked. Pure iron powder, freed from adhering films of gas, is not acted on by pure water at the ordinary temperature.

Neutral salts of the alkali metals exert a corrosive action, and, if the iron is in immediate contact with glass, local corrosion takes place at the point of contact. C. H. D.

Conductivity of Solutions of Ferric and Ferrous Chlorides and the Structure of Ferric Chloride. WLADIMIR JUFEREFF (*Zeitsch. anorg. Chem.*, 1908, 59, 82—86).—Measurements have been made of the electrical conductivity of concentrated solutions of the two chlorides of iron. The greater conductivity of the ferric solutions at dilutions greater than about 3.6 litres per mol. is interpreted in terms of an opinion expressed by Spring that ferric chloride in solution has the constitution $\text{Fe}_2\text{Cl}_4\text{Cl}_2$. Chlorine is supposed to be

set free, and the increased conductivity is attributed to the conversion of this into hydrochloric acid.

H. M. D.

Magnetic Oxides of Chromium. IVAN SHUKOFF (*Compt. rend.*, 1908, 146, 1396—1397).—Chromium trioxide decomposes at 330° with loss of oxygen and development of heat. If the decomposition is controlled so that the temperature does not rise above 500° , the oxides obtained are only feebly magnetic. On heating, however, to 500 — 510° , 13—14% of oxygen is evolved, and the black mass, which has the composition $2\text{CrO}_3, \text{Cr}_2\text{O}_3$, is strongly magnetic. An oxide of the same composition, but prepared at 485° , was very feebly magnetic. A crystalline magnetic oxide was obtained by the decomposition of chromyl dichloride; when ignited, it loses only 3.4—4% of oxygen.

W. O. W.

Molybdo-Uranic Compounds. ANDRÉ LANCIEU (*Chem. Zentr.*, 1908, i, 1763—1764; from *Bull. Sci. Pharm.*, 1908, 15, 132—140. Compare Abstr., 1907, ii, 697).—When uranium nitrate is added to an excess of ammonium heptamolybdate and the resulting precipitate boiled with molybdic acid, *uranium heptamolybdate*, $7\text{MoO}_3, 3\text{UO}_3$, is obtained as an amorphous, yellow powder. It is soluble in all mineral acids, giving a greenish-yellow, fluorescent liquid; it is decomposed by excess of water, and reduced to green uranium molybdate, $\text{U}(\text{MoO}_4)_2$, by alcohol and by acetic acid. The effect of sunlight on the heptamolybdate is to darken its colour, and to render it no longer reducible by alcohol or completely soluble in nitric acid, owing to the formation of insoluble anhydrous *uranium octamolybdate*, $8\text{MoO}_3, \text{UO}_3$. The hydrated compound, $8\text{MoO}_3, \text{UO}_3, 13\text{H}_2\text{O}$, is obtained as prismatic needles when ammonium heptamolybdate is precipitated by uranium nitrate and the product treated with excess of acetic acid; the substance obtained is extremely sensitive to light. A study has been made of the rate of change of this substance when exposed to light of various wave-lengths.

J. V. E.

A New Iodide of Titanium, Titanous Iodide, TiI_2 . EDOUARD DEFACQZ and H. COPAUX (*Compt. rend.*, 1908, 147, 65—67).—Titanium tetraiodide (Hautefeuille, *Bull. Soc. chim.*, 1867, [ii], 7, 201) is reducible by silver or mercury to a di-iodide. The reduction is most readily effected as follows: Two porcelain boats, the anterior one containing mercury and the posterior one titanium tetraiodide, are introduced into a porcelain tube and heated gradually in a current of hydrogen to dull redness. A sublimate of mercuric iodide and unchanged tetraiodide is formed in the cooled receiver, whilst fine brilliant black lamellæ of *titanous iodide*, TiI_2 , are formed near the exit end of the tube. The crystals, which are very hygroscopic, have D_{20}^{20} 4.3, are not acted on by organic solvents, are dissolved by concentrated hydrofluoric acid and by boiling hydrochloric acid, forming a blue solution, are violently attacked by nitric and sulphuric acids with loss of iodine, and are decomposed by water and aqueous alkali solutions. Titanous iodide forms additive compounds with dry ammonia and hydrogen chloride. It is reduced by hydrogen at a white heat, but

not at a red heat, giving amorphous titanium, which is very readily oxidised.

The analysis was carried out by the method described previously (Abstr., 1898, ii, 521). E. H.

Titanium Nitride and a New Class of Titanium Compounds, the Titanumnitrogenhaloids. OTTO RUFF and FRITZ EISNER (*Ber.*, 1908, 41, 2250—2264).—Wöhler showed originally that a nitride was formed on heating the compound of titanium tetrachloride and ammonia (*Annalen*, 1850, 73, 43), and described four nitrides. Friedel and Guérin (this Journ., 1877, i, 168) reduced this number to two, Ti_2N_2 and Ti_3N_4 . The latter substance has been found by Schneider (Abstr., 1895, ii, 169) to contain less nitrogen than that required by the formula, and he called it nitride A. A re-examination of the substance shows that Ti_3N_4 does not exist. The bluish-black product, obtained by heating the compound $TiCl_4 \cdot 6NH_3$ at the temperature at which Jena glass softens in a stream of ammonia, contains Ti = 72.1, N = 20.77, Cl = 2.64, O = 4.36 (Ti_3N_4 requires Ti = 72.0, N = 28.0). The total titanium was determined by dissolving the nitride in nitric and hydrofluoric acids, and precipitating the titanic acid by ammonia. When the substance is covered with dilute sulphuric and hydrofluoric acids and titrated with *N*/10 potassium permanganate, the nitride goes slowly into solution as the permanganate is reduced. The solution contains hydrochloric and some pertitanic acids; the latter is destroyed by potassium iodide, and the iodine separated estimated by thiosulphate. In this way, Ti, 52.7%, was found. As a blank determination with pure TiN gave 76.9 instead of 77.1, the conclusion is drawn that the 52.7 represents the titanium present in the tervalent condition, and, as the chlorine is supposed to exist as TiNCl, the composition of the Wöhler-Schneider nitride is deduced to be TiN = 68, TiNCl = 7.2, $(TiN)_2O ? = 13.3$, and $TiO_2 ? = 5.4$. When this mixture is heated in a current of ammonia at 1500° for six hours, the chlorine and oxygen are removed completely, and pure bronze-coloured titanium nitride, TiN, is obtained, D¹⁸ 5.1. It could not be converted into the chloronitride by chlorine either at 270° or in the liquid state.

An attempt to prepare the nitride, Ti_3N_4 , from the so-called titanamide (Stähler, Abstr., 1906, ii, 595) also resulted in failure. It is also shown that continued extraction of the compound $TiCl_4 \cdot 6NH_3$ with ammonia in a Stock and Blix apparatus (Abstr., 1901, ii, 650), moisture being excluded, does not give titanamide at all, but a titanochloroamide of the composition $Ti_{1.0}Cl_{1.43}N_{0.86} \cdot 3.5-5NH_3 \cdot 0.02TiO_2$. The ammonia is removed by careful heating in a vacuum at 270° , and a dirty green residue of *titanium chloronitride*, TiNCl, is obtained, containing, however, 1.3% nitride and 12—14% titanium oxynitride and titanium dioxide. It is extraordinarily reactive towards water, taking fire and giving ammonium chloride, nitrogen, and titanium dioxide. On further heating, it decomposes, thus: $4TiNCl = 3TiN + TiCl_4 + N$.

Although pure titanium chloronitride was not obtained, the corresponding *bromonitride*, TiNBr, is formed from titanium tetrabromide

(m. p. 39° , b. p. 230°) in a similar manner, the heating of the product obtained on extraction with ammonia being carried out at $200^{\circ}/4$ mm. It also reacts vigorously with water. W. R.

Preparation and Properties of Zirconium Tetrafluoride. LUDWIG WOLTER (*Chem. Zeit.*, 1908, 32, 606—607).—The method described by Marignac (*Jahresb.*, 1860, 136) for the preparation of zirconium tetrafluoride by heating zirconium dioxide mixed with twice its weight of ammonium hydrogen fluoride, has the disadvantage that this substance volatilises more readily than it attacks the zirconium dioxide. This, however, can be overcome by using, instead of the above mixture, pure zirconium ammonium fluoride, $\text{ZrF}_4 \cdot 2\text{NH}_4\text{F}$, which is readily prepared in a pure state by evaporating zirconium dioxide with excess of silica-free hydrogen fluoride and ammonia, and subliming the product in a platinum tube in a current of nitrogen.

Theoretical yields of the purest zirconium tetrafluoride are obtained by the action of anhydrous hydrogen fluoride on pure zirconium tetrachloride, the change readily taking place in accordance with the equation $\text{ZrCl}_4 + 4\text{HF} = \text{ZrF}_4 + 4\text{HCl}$. The product obtained is snow-white, crystalline, and practically insoluble in water. When sublimed, zirconium tetrafluoride forms small, strongly refracting, prismatic crystals having slightly curved facets, $D^{16} 4.4333$, and the molecular weight determined by Victor Meyer's method was found to be 166.1, in close agreement with ZrF_4 (166.7). Unlike the other elements of the carbon group, zirconium tetrafluoride is only sparingly soluble in water, 1.388 grams dissolve in 100 c.c. of water without hydrolysis taking place. When warmed to about 50° , the hydrate, $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$, is precipitated; in no case could any other hydrate or oxyfluoride be obtained. With liquid ammonia, zirconium tetrafluoride gives a white powder ($5\text{ZrF}_4 \cdot 2\text{NH}_3$), whilst with gaseous ammonia, pyridine, hydrogen sulphide, &c., practically no change takes place. It is suggested that this inactivity of the zirconium tetrafluoride compared with other members of the group is perhaps due to its small molecular volume: TiF_4 , 44.3; ZrF_4 , 37.5; SnF_4 , 40.7. J. V. E.

Oxides of Quinquevalent Bismuth. ALEXANDER GUTBIER and H. MICHELER (*Zeitsch. anorg. Chem.*, 1908, 59, 143—145. Compare Gutbier and Bünz, *Abstr.*, 1906, ii, 174, 234, 551, 678; Ruff, this vol., ii, 298).—The bismuthic acid described by Ruff is entirely different from the substance which is usually referred to by this name in the older literature. In order to avoid confusion, Gutbier and Bünz considered it necessary to retain the name bismuthic acid for a particular product obtained under specified conditions. This substance, which is formed from the dark brown oxidation products (obtained by oxidation of bismuth trioxide in presence of potassium hydroxide solution) by the action of hot concentrated nitric acid, has a colour which varies from scarlet-red to yellowish-red. It has no acid properties, and cannot be obtained from any of the sodium bismuthates which have been described.

In general, the substances obtained by Ruff cannot be compared with those obtained by Gutbier and Bünz. This view is expressed as a result of a repetition of Ruff's experiments by the authors.

H. M. D.

Use of Iridium Crucibles in Chemical Operations. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1908, 80, A, 535—536).—An account is given of the behaviour of pure wrought iridium crucibles during several months' use in ordinary quantitative estimations. Iridium is as hard as steel, and does not blister or alter in weight when repeatedly heated to redness. Heated for some hours in a Bunsen flame with insufficient air supply, the crucible is unharmed, as the deposit of carbon can be entirely burnt away. Sulphur in the gas is also without effect. Boiling aqua regia, fused micro-cosmic salt, or other phosphates with frequent additions of carbon, strongly heated silica or silicates with a reducing agent, boiling lead at white heat, boiling zinc, and molten nickel, iron, or gold are without effect on the crucible, which, after cleaning, retains its original weight. Fused potassium hydroxide attacks iridium less than platinum, and zinc run in with acid zinc chloride and then heated to boiling only superficially attacks the iridium. Prolonged heating with copper renders the crucible brittle when hot, but the copper can be burnt off.

A rhodium crucible is practically as resistant as an iridium one, and has the advantage of being cheaper and only half as heavy.

R. J. C.

Alkali Iridichlorides and Iridiochlorides. MARCEL DELÉPINE. (*Compt. rend.*, 1908, 146, 1267—1269).—The iridichlorides of potassium, rubidium, caesium, and ammonium, obtained from sodium iridichloride by double decomposition, conform to the type IrCl_6M_2 . The potassium and sodium salts are black. Large crystals of the ammonium salt are black, but small crystals have a red tint. The rubidium salt varies from brownish-red to brick-red, according to the size of the crystals. The *caesium* salt, IrCl_6Cs_2 , is bright red and sparingly soluble in water.

The iridiochlorides are readily prepared from the iridichlorides by reduction with a normal oxalate. Thus sodium iridichloride and sodium oxalate yield the very soluble sodium salt, $\text{IrCl}_5\text{Na}_3 \cdot 12\text{H}_2\text{O}$. Aqueous solutions of the *potassium* and *ammonium* salts are decomposed by water, thus, $\text{IrCl}_6\text{M}_3 + \text{H}_2\text{O} \rightleftharpoons \text{IrCl}_5(\text{H}_2\text{O})\text{M}_2 + \text{MCl}$; hence to obtain the trimetallic salts excess of an alkali chloride must be added. The crystals which separate are black, brownish-red, green, or yellow, according to size; on dehydration they become olive-green. The dimetallic iridiochlorides separate from the mother liquor on concentration. The *potassium* salt, $\text{IrCl}_5(\text{H}_2\text{O})\text{K}_2$, crystallises in needles; the *ammonium* salt in octahedra.

Dirubidium aquoiridiopentachloride, $\text{IrCl}_5(\text{H}_2\text{O})\text{Rb}_2$, forms small, thick crystals. The *caesium* salt, $\text{IrCl}_5(\text{H}_2\text{O})\text{Cs}$, crystallises in small, olive needles. Trirubidium iridiochloride crystallises in needles containing $1\text{H}_2\text{O}$, and not $1\frac{1}{2}\text{H}_2\text{O}$ as usually represented. The *caesium* salt, $\text{IrCl}_6\text{Cs}_3 \cdot \text{H}_2\text{O}$, forms bright olive needles.

In accordance with the requirements of Werner's theory for the

constitution of these salts, it is found that the trimetallic salts readily lose their water of crystallisation; the dimetallic salts of the type $\text{IrCl}_5(\text{H}_2\text{O})\text{M}_2$, on the other hand, undergo no change when heated at 150° .
W. O. W.

The Preparation of Alkali Iridiochlorides. MAURICE VÈZES (*Compt. rend.*, 1908, 146, 1392—1393).—A claim for priority (compare Abstr., 1899, i, 572, and Delépine, preceding abstract).
W. O. W.

Mineralogical Chemistry.

An Old Occurrence of Argyrodite at Freiberg. FRIEDRICH KOLBECK (*Centr. Min.*, 1908, 331—333).—A specimen in the A. G. Werner collection at Freiberg was labelled “dunkles Rotgülden,” and had been found in 1817 in the Bescheert Glück mine. It is a portion of a large, indistinct crystal with an iron-black colour. On examination, it proved to be the rare mineral argyrodite, in which germanium was discovered. Analysis by T. Döring gave the following results, agreeing with Penfield's formula Ag_8GeS_6 :

Ag.	Ge.	Sb.	Fe.	S.	Total
75.28	6.18	0.36	0.33	17.50	99.65

L. J. S.

Vanadium [Sulphide] from Minasragra. JOSÉ J. BRAVO (*Chem. Zentr.*, 1908, i, 1793; from *Oesterr. Zeitsch. Berg-Hüttenwesen*, 1908, 56, 166—168).—In an inclined strata of impure carbon of an asphaltic nature, there occur compact masses, 1—2 metres in diameter, composed of a mixture of sulphur, clay, coal-like substances, and vanadium sulphide. The colour of the fresh fracture is pale lead-grey, but the colour rapidly darkens when exposed to the air. An analysis gave:

SiO_2 .	Fe.	Al.	V.	S.	CaO.	Carbon, &c.
22.22	1.08	8.32	15.36	41.81	0.33	10.88

This previously unknown naturally-occurring vanadium sulphide is called *Rizopatronite*; it has D 2.456, hardness 3.5, amorphous with a transitory metallic lustre, and is soluble in cold alkali and aqueous ammonia.

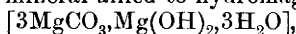
J. V. E.

The So-called Leesbergite. WILLY BRUHNS (*Mitt. Geol. Landesanst. Elsass-Lothringen*, 1908, 6, 303—307).—This name has been given by Blum (*Ann. Soc. géol. Belgique*, 1907, 34, *Bull.*, 118—120) to a white, chalky mineral from the Victor iron-mine, between Marspich and Hayingen, in Lorraine; from the analysis (I) he gave, the formula was deduced as $2\text{MgCO}_3\cdot\text{CaCO}_3$. The material

has much the appearance of hydromagnesite; in some parts it is harder and more compact, and in others, softer and looser in texture. In contact with water, the material soon falls to powder, but it does not absorb water as stated by Blum. Under the microscope, it is seen to consist of an aggregate of minute, strongly birefringent grains. Analyses II—IV are of different samples of material dried at 100°:

	CaO.	MgO.	CO ₂ .	H ₂ O.	Insol.	Al ₂ O ₃ + Fe ₂ O ₃ .	Total.
I.	21·06	29·89	49·43	—	0·05	0·52	100·95
II.	16·06	32·81	42·82	[5·17]	3·14		100·00
III.	19·79	29·81	45·85	3·72	0·67		99·84
IV.	15·00	n. det.	46·44	3·19	trace		—

The material is thus not constant in composition, and is without doubt a mixture of a mineral allied to hydromagnesite,



with calcite or dolomite.

L. J. S.

A Chemical Difference between Orthoclase and Microcline.

PHILIPPE BARBIER (*Compt. rend.*, 1908, 146, 1330—1332).—Twenty-five orthoclases and five microclines were decomposed by hydrofluoric and sulphuric acids, and the alkali chlorides examined spectroscopically. All the orthoclases contained small amounts of either lithium or rubidium, and sometimes both of these elements were present together, whilst in microcline they were absent. It is therefore considered that orthoclase and microcline are distinct species, and that they may be distinguished by this method.

L. J. S.

[Celadonite from the Færöes.] JAMES CURRIE (*Trans. Edinburgh Geol. Soc.*, 1907, 9, 1—68).—A detailed account is given of the topographical mineralogy of the Færöes. The following analysis, by T. F. Cowie, is given of celadonite from Stigafjall in the island of Strömö. The material lines amygdaloidal cavities in the basaltic rocks, being thicker at the bottom and colouring the associated heulandite up to a certain level in the cavities.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	H ₂ O.	Total.
52·39	20·82	5·09*	1·07	3·05	10·31†	5·72	98·45

* Including FeO.

† Including Na₂O.

At 100° the loss of water is 3·34%, and the remainder is expelled at 180°. This analysis differs considerably, especially in the large content of alumina, from those of material from other localities, suggesting that celadonite or "green earth" is not a definite mineral species.

L. J. S.

Japanese Zeolites. KOTORA JIMBŌ (*Beiträge zur Mineralogie von Japan*, 1907, No. 3, 115—120).—A description is given of analcite, apophyllite, heulandite, chabazite, and stilbite from Japanese localities. Analysis I, by Tsukamoto, is of optically anomalous crystals of analcite from Maze. [The original paper makes no comment on the fact that this composition is most unusual for analcite; probably there is some error.] II is of large, pale green, optically anomalous

crystals of apophyllite from Maze, where the mineral occurs with analcite, natrolite, and calcite in a basalt-agglomerate. III is of crystals of heulandite from Hatsuneura, in the island of Chichijima; and IV is of sheafs of stilbite from Obara.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	F.	Loss on ignition.
I.	49·87	10·24	12·53	0·99	11·03	—	14·26
II.	50·18	1·33*	26·10	3·16	—	0·95	17·83
III.	60·58	15·67	6·25	0·12	1·51	—	15·98
IV.	54·00	17·94	7·94	1·12		—	19·37

* Including a little Fe₂O₃.

L. J. S.

Chlorophyllite from Vizézy. PHILIPPE BARBIER (*Bull. Soc. chim.*, 1908, [iv], 3, 724—725).—A specimen of chlorophyllite from the Vizézy ravine, Montbrison, in the Loire valley, had the following composition:

SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	K ₂ O.	Loss.	Total.
42·43	33·21	10·58	traces	2·61	traces	4·75	6·26	99·87

T. A. H.

A New Mineral Occurring with Tourmaline in Madagascar. ALFRED LACROIX (*Compt. rend.*, 1908, 146, 1367—1371).—The pegmatite-veins intersecting crystalline limestones and mica-schists in the neighbourhood of Mt. Bity contain in their cavities crystals of smoky quartz, microcline, lepidolite, lithia tourmaline (often of gem quality and in very large crystals, which are often prominently zoned with different colours), beryl, and, in one instance, spodumene (colourless and the violet variety, kunzite). At Maharitra, the pegmatites contain a new mineral, which is described under the name *bityite*. It occurs as small, yellowish-white, hexagonal prisms, which are horizontally striated, and often aggregated in barrel-like shapes, in rosettes, or as a continuous crust over the other minerals. There is a perfect cleavage parallel to the basal plane. D 3·05, H 5½. Optically, the crystals are pseudo-hexagonal, showing a division into six sectors, each with a small angled negative bisectrix perpendicular to the basal plane. The refractive index is 1·62—1·64. Before the blowpipe, the mineral is readily fusible to an opaque, white, blebby glass; it is not attacked by acids. Analysis by F. Pisani gave:

SiO ₂ .	Al ₂ O ₃ .	CaO.	GlO.	MgO.	Li ₂ O.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
31·95	41·75	14·30	2·27	0·13	2·73	0·40	0·16	6·50	100·19

This gives the formula



The water is expelled only at a very high temperature, and the formula may therefore be written as $5\text{SiO}_2, 4\text{Al}_2\text{O}_3, 7(\text{R}_2\text{O} + \text{RO})$. The mineral may be classed as a basic orthosilicate in the staurolite and kornerupine group.

L. J. S.

Ilvaite from Shasta Co., California. BASIL PRESCOTT (*Amer. J. Sci.*, 1908, [iv], 26, 14—16).—Massive and crystallised ilvaite occurs at Potter Creek, in Shasta Co., in connexion with ore-bodies of

magnetite at a contact of limestone with diorite. The mineral is of contact-metamorphic origin, and is associated with hedenbergite. The crystals are bright, with a sub-metallic lustre and a greenish-brown streak. The following analysis by H. R. Moss agrees with the usual formula :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Cr ₂ O ₃ .	H ₂ O.	Total.
28·09	0·32	20·80	29·93	3·24	15·89	0·18	0·13	1·62	100·20

L. J. S.

Amount of Dissolved Organic Carbon Compounds in the Sea, and their Significance in its Internal Economy. MARTIN HENZE (*Pflüger's Archiv*, 1908, 123, 487—490; *Zeitsch. alg. Physiol.*, 7, 283, 321; *Abh. K. Ges. Wiss. Göttingen. Math.-physiol. Klasse*, [2], 6, 1).—Pütter has claimed that by the oxidation of the organic matter contained in sea-water, using Messinger's dichromate method, from 18 to 30 mg. of carbon dioxide per 100 c.c. can be obtained, and he stated that the organic matter to which this corresponds serves as nutrition for some of the lower organisms. The author has re-estimated the carbonic acid obtainable by the oxidation of organic matter in sea-water, using antimony for the absorption of the chlorine and other modifications of the Messinger method required in the case of sea-water. He only succeeded in obtaining from 0·4 to 3·5 mg. of carbon dioxide from 100 c.c., quantities which are within the limits of experimental error. He concludes, therefore, that Pütter's hypothesis entirely lacks experimental confirmation. S. B. S.

Physiological Chemistry.

Influence of Oxygen on Respiration. MARCUS S. PEMBREY and F. COOK (*Proc. physiol. Soc.*, 1908, xli—xlii; *J. Physiol.*, 37).—If a person breathes air or oxygen in and out of a spirometer, the breaking point is chiefly determined by the amount of carbon dioxide present. But after exercise, it is easier to breathe oxygen than air in this way, and the breaking point occurs when the amount of carbon dioxide reaches a higher level. This is regarded as supporting the old view that the hyperpnœa of muscular exercise is due in part to products of metabolism other than carbon dioxide. W. D. H.

Effects of Excess of Carbon Dioxide and Want of Oxygen on the Respiration and Circulation. LEONARD HILL and MARTIN FLACK (*J. Physiol.*, 1908, 37, 77—111).—Carbon dioxide at pressures from 15 to 30% causes hyperpnœa and convulsive breathing; above 30 to 35%, the excitatory effect is transient, and the narcotic effect produced may lead to respiratory arrest. Moderate doses raise the blood pressure and excite the vagus and vaso-motor centres. With higher concentrations, the blood pressure falls, owing to the depressant

effect on the heart. Pure air and massage lead to recovery of the heart. On account of the excitatory effect of the gas, a mixture containing 5% of it should be employed in resuscitating cases of carbon monoxide and nitrite poisoning. The effect of want of oxygen is a dyspnoea much more gradual in onset, and terminating in a convulsive stage of great intensity. The blood pressure is usually, but not always, raised, and the vagus centre is excited, especially in the convulsive stage. The pressure then falls. The heart is not so rapidly depressed as in carbon dioxide poisoning.

The inability to hold the breath depends more on want of oxygen than on excess of carbon dioxide. The power to hold the breath is increased by breathing excess of oxygen. Breathing in and out of a small closed space extends the power to resist alterations in the gases, because the circulation is not mechanically impeded as it is when the breath is held. In muscular exercise, excess of carbon dioxide rather than want of oxygen excites hyperpnoea. Haldane and Priestley are right in stating that normal breathing is regulated by carbon dioxide tension in the alveoli, but in cases of obstructed aëration of the blood, diminished oxygen tension is the more potent agent. W. D. H.

The Residual Nitrogen of the Blood. HERMANN HOHLWEG and HANS MEYER (*Beitr. chem. Physiol. Path.*, 1908, 11, 381—403).—The serum was coagulated in the presence of a mixture of equal parts of 1% acetic acid and 5% potassium phosphate solutions, so much of this mixture being added that the resulting liquid was distinctly acid to litmus, but neutral to Congo-red. Before coagulating this acidified mixture, it was diluted, and the diluted liquid half-saturated with sodium chloride. The blood was obtained from the femoral arteries of dogs. In one series of experiments, three samples of blood were withdrawn from each animal at three different periods, the first and last being withdrawn about seven hours after a meal, and the second during a period of starvation. In the second series of experiments, three samples were also withdrawn from each animal, the first and third during a period of starvation, and the second during the height of digestion. The total residual nitrogen was estimated in each sample, as well as that fraction which was precipitable with tannic acid; the urea was also estimated, the methods of Pflüger, Schöndorff, and Mörner-Sjögqvist being employed. It was found, as a mean of all the experiments, that the total residual nitrogen of serum obtained during periods of starvation was 0.0525 gram per 100 c.c., whereas in the serum obtained during digestion it was 0.0788 gram; of these quantities, 0.0384 and 0.0567 gram were due to urea. The fraction precipitable with tannic acid showed no definite relationship to the state of nutrition. There was a small increase of the fraction not precipitable with tannic acid (exclusive of urea) in samples from the well-fed as compared with those from starving animals (0.0130 gram and 0.0060 gram respectively). The increase is too small for any definite conclusions to be drawn as to the circulation of the end products of digestion on the serum. Neither could any very definite increase of such products be detected in the serum after the addition of amino-acids and albumoses to the ordinary diet. S. B. S.

Gürber's Phenomenon. J. DUNIN-BORKOWSKI (*Bull. Acad. Sci. Cracow*, 1908, 318—325).—If red blood-corpuscles saturated with carbon dioxide are placed in a sodium chloride solution, and then removed, it is found that the liquid has become distinctly alkaline (Gürber's phenomenon).

The author has repeated these experiments, and has attempted to measure the concentration of hydroxyl ions by physico-chemical methods, but finds that the concentration is less when the globules have been saturated with carbon dioxide than in the absence of the dioxide.
J. J. S.

The Action of Lipoid-soluble Substances on Red Blood-corpuscles. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1908, 10, 371—379).—If the theory already advanced as to osmosis (this vol., ii, 565) is correct, solutions with the same surface tension, excepting acids and bases which exert a chemical action, should have the same hæmolytic capacity. Experiments were made to test this theory, and the results seem to confirm it.

Substances which at a certain concentration were found to act hæmolytically, acted anti-hæmolytically below that concentration.

S. B. S.

The Complex Hæmolysins. H. TSURASAKI (*Biochem. Zeitsch.*, 1908, 10, 345—353).—Urea, the most important final product of metabolism, inhibits lipolysis, acting on the complement, but not on the amboceptor. Thiocarbamide and urethane also exert inhibitory action.

The conception of Sachs and Teruuchi that certain sera lose their hæmolytic capacity, owing to the presence of a ferment which destroys the complement at 37° and acts only in the diluted serum, was confirmed by some experiments on dogs' serum. After diluting the serum to 1 in 5, the complement was entirely destroyed by incubating for two hours at 37°.

S. B. S.

Lipolysis, Agglutination, and Hæmolysis. IV. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 11, 400—403).—An attempt was made to separate a substance producing lipolysis from one producing hæmolysis or agglutination, but without success. The experiments were carried out with ricin and with pancreatic juice. Red blood-corpuscles adsorb the agglutinin; after such treatment, however, the lipolytic function was also lost. Fibrin also adsorbs agglutinin, but a ricin solution treated with fibrin lost its lipolytic properties at the same rate at which it lost its agglutinating properties. Other adsorbents of agglutinins and hæmolysins, such as kaolin, lead to similar results. It seems probable from the experiments that the lipases play an important part in the phenomena of immunity.

S. B. S.

Hæmolysis. SVANTE ARRHENIUS (*Biochem. Zeitsch.*, 1908, 11, 161—171).—Hæmolysis by means of acids was investigated, and it was found that within certain limits there is a minimum action; both by increasing or diminishing the amount of acid above or below

this limit, the hæmolysis is increased. This is due to protein coagulation, which within these limits inhibits the setting free of the hæmoglobin from the corpuscles.

From experiments carried out with suspensions of corpuscles of varying concentration (suspensions of 0.1% to 5%), it was found that the quantity of substance necessary to produce hæmolysis was a linear function of the corpuscle concentration. The corpuscles take up the hæmolysing substance, and hæmolysis follows when a certain relationship exists between the concentration of this substance in the envelopes and that in the surrounding fluid. An equation can be found by means of which the relative quantities of various hæmolysins taken up by the envelopes can be ascertained from experimental data.

Lecithin was found to increase the hæmolytic action of acids, especially if allowed to remain in contact with the corpuscles before the acid was added. It has no action on the hæmolytic power of alkalis, and inhibits that of saponin. Alcohols and ether increase the hæmolytic action of cobra poison, and diminish that of saponin. Sodium oleate increases also the action of cobra poison, diminishing that of saponin. Calcium chloride diminishes the action of the sodium oleate on the cobra poison, this being due, as the author points out, to the formation of an insoluble salt. It is assumed that the lecithin action of acids is due, on the other hand, to increased solubility.

S. B. S.

The Mechanism of Hæmolysis by Saponin. KURT MEYER (*Beitr. chem. Physiol. Path.*, 1908, 11, 357—364).—The hæmolytic action of saponin (Merck) on different species of blood-corpuscles was investigated. It was found that those corpuscles containing the largest amount of cholesterol were most resistant to the hæmolytic action.

S. B. S.

Effect of Diet on the Amylolytic Power of Saliva. C. HUGH NEILSON and D. H. LEWIS (*J. Biol. Chem.*, 1908, 4, 501—506).—Previous results on the influence of diet on animals' saliva are contradictory. The present experiments were performed on human saliva. The amylolytic power rises with carbohydrate, and falls with protein, diet.

W. D. H.

Assimilation of Protein Introduced Parenterally. WILHELM CRAMER. **Assimilation of Protein Introduced Enterally.** HAROLD PRINGLE and WILHELM CRAMER (*J. Physiol.*, 1908, 37, 146—157, 158—164).—Evidence is adduced that egg-white introduced parenterally is partly assimilated and partly eliminated in the urine. The portion which is assimilated is believed to be taken up by the leucocytes. During ordinary absorption from the intestine, the leucocytes are also considered to play an important part. The intestinal mucous membrane is richer in non-coagulable nitrogen than during a fast, and this increase is most marked in the lymphoid nodules of the intestine. The blood of digesting animals shows a

small, but distinct, increase in residual nitrogen over that of fasting animals, and part of this is ascribed to the corpuscular elements.

W. D. H.

Influence on Internal Hæmorrhage on Protein Metabolism. FRED S. WEINGARTEN and BURRILL B. CROHN (*Amer. J. Physiol.*, 1908, **22**, 207—244).—Internal hæmorrhage was imitated in dogs by transferring blood to the extent of 2·8 to 3·5 of the body weight from the femoral artery into the abdominal cavity. There was a slight rise of the specific gravity of the urine on the days when this was done, and a very slight rise in the excretion of nitrogen, sulphur, and phosphorus. Many other points in metabolism, secretion, composition of urine, &c., were investigated, but with wholly negative results.

W. D. H.

The Occurrence of Urocanic Acid in a Pancreatic Digest. ANDREW HUNTER (*Proc. physiol. Soc.*, 1908, xxxvii—xxxviii; *J. Physiol.*, **37**).—From a long-continued pancreatic digest of plasmon, a substance having the elementary composition and other properties of Jaffe's urocanic acid ($C_{12}H_{12}O_4N_4$) was isolated.

W. D. H.

Relative Rate of Absorption of Optically Isomeric Substances from the Intestine. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, **4**, 437—438).—It is well known that isomerides differing in optical action are assimilated to varying degrees by the animal organism. The present experiments performed on intestinal loops with the optically differing lactic acids and other substances gave no evidence of any selection during the preliminary process of absorption.

W. D. H.

Theory of Chemical Energy in the Living Cell. OSCAR LOEW (*Centr. Bakt. Par.*, 1908, ii, **21**, 198—200).—Polemical against Bredig (*Abstr.*, 1907, ii, 943).

G. B.

The Difference between Isosmotic and Isotonic Solutions in Artificial Parthenogenesis. JACQUES LOEB (*Biochem. Zeitsch.*, 1908, **11**, 144—160).—The first question considered is how a hypertonic solution brings about parthenogenesis. The solution is not so much an exciting as a correcting agent. The excitant is the formation of an artificial membrane of lipid nature (principally lecithin) at the periphery of the egg. The second question dealt with is that isosmotic solutions for the egg are in general not isotonic.

W. D. H.

The Glycogenic Changes in the Placenta and the Fœtus of the Pregnant Rabbit; a Contribution to the Chemistry of Growth. J. LOCHHEAD and WILHELM CRAMER (*Proc. Roy. Soc.*, 1908, **80**, B, 263—284).—Analyses were made of the glycogen in the maternal and fœtal placenta of rabbits, as well as in the fœtal liver and the remaining part of the fœtal bodies, which were removed from pregnant animals in different stages of gestation from the fourteenth day

onwards. The placenta was mechanically separated into maternal and foetal parts, and the glycogen in each of these parts was estimated separately. The greater part of the placental glycogen was found in the maternal placenta. It was found that the percentage of this glycogen diminished from the eighteenth day onwards, whereas that in the foetal liver increased. It was also found that there is a distinct parallelism between the growth of the foetus and the amount of glycogen which it contains. The conclusion was drawn that the placenta of the rabbit has the function of depositing glycogen as a store of carbohydrate for the needs of the foetus. The investigation of the distribution of the glycogen-splitting enzyme led to the conclusion that the glycogen is absorbed from the maternal placenta in the form of a simpler carbohydrate, the transformation of the glycogen taking place in the placenta by the action of a secreted enzyme. In the earlier stages of intra-uterine life, the liver of the foetus does not appear to possess the power of storing glycogen; the power is not acquired until the last week of gestation. In the earlier stages of uterine life, therefore, the placenta fulfils the hepatic functions so far as glycogen is concerned. Investigations were also undertaken on the effect of variations of diet and of phloridzin injection, and it was considered from the results obtained that the glycogen metabolism of the placenta and foetus is independent of that by the mother, and is governed by conditions in many respects different from those which regulate the metabolism of the adult animal. The glycogenic metabolism of the rabbit is different from that of the sheep and cow.

S. B. S.

Temperature-coefficient of Rate of Conduction in Nerve.

KEITH LUCAS. **Temperature-coefficient of Rate of Conduction and Latent Period in Muscle.** W. J. WOOLLEY (*J. Physiol.*, 1908, 37, 112—121, 122—129).—Maxwell found the temperature-coefficient for conduction in molluscan nerve to be 1.78. The present figures for amphibian nerve give a mean of 1.79. Conduction in amphibian muscle gives a coefficient of 1.79 to 2.01. The conductive process is therefore probably similar in both tissues, but doubt is expressed whether the high coefficient is a necessary proof of a chemical as opposed to a physical process. The coefficient for the latent period of muscle is 3.26 to 3.3; this strengthens the supposition that conduction in muscle is a propagation, not of the contractile change, but of an independent disturbance, which calls up the contractile change at each point on its passage.

W. D. H.

Action of Nitrites and Atropine on Autonomic Nerves.

ALFRED FRÖHLICH and OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1908, 59, 34—56).—Certain autonomic nerves can be differentiated from those of sympathetic origin by their behaviour towards drugs, as shown in the following table:

Nerves.	Accelerator.		Inhibitory.	
	Stimulated by	Paralysed by	Stimulated by	Paralysed by
1. Autonomic.....	Pilocarpine	Atropine		Nitrites.
2. Sympathetic....	Adrenaline	Ergotoxin	Adrenaline	

These facts point to chemical differences in the nerve terminals.

W. D. H.

The Permeability of the Frog's Skin. WILLIAM M. BAYLISS (*Biochem. Zeitsch.*, 1908, 11, 226—237).—The physical examination of the frog's skin in the living condition shows that its properties are not so clearly defined as those of the homogeneous membrane of the red corpuscles (Hamburger) or of muscle fibres (Overton). Its properties are only partly explicable on the hypothesis that it is a semi-permeable membrane. Its most interesting property is its irreciprocal permeability to sodium ions.

W. D. H.

A New Function of the Pancreas and its Relation to Diabetes melitus. OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1908, 59, 83—94).—In normal men, cats, and dogs, adrenaline does not produce dilatation of the pupil, but this does take place in the following circumstances: (1) After total extirpation of the pancreas in dogs and cats; (2) in pancreatic insufficiency artificially produced in animals; (3) in many cases of human diabetes presumably of pancreatic origin; (4) in many cases of Basedow's disease.

It therefore appears that the pancreas has the power of inhibiting the sensitiveness to adrenaline in certain organs supplied by sympathetic nerves. In the last of the four cases, the susceptibility to adrenaline is possibly produced by hyperthyreodism.

W. D. H.

Contraction of Striated Muscle. JOHN S. MACDONALD (*Proc. physiol. Soc.*, 1908, xxv—xxvii; *J. Physiol.*, 37).—An attempt to explain the contraction of muscle by supposing that electrolytes make their appearance in the dark bands which raise the osmotic pressure there, and so water is attracted from the light bands. This is supported to some extent by changes in the distribution of the potassium salts as determined by Macallum's reagent, but the process of relaxation is admittedly left unexplained.

W. D. H.

Non-striated Mammalian Muscle. TADASU SAIKI (*J. Biol. Chem.*, 1908, 4, 483—496).—The non-striated muscle of the stomach and bladder is richer in water than striated muscle, and contains 2·8% to 3% of nitrogen. Traces of glycogen are present, and only 0·05% of lactic acid, although no precautions to avoid injury were taken. The creatine percentage is also low (0·8%); so is that of creatinine (0·024% to 0·052%). Hypoxanthine is the most abundant purine base; minute amounts of guanine and adenine are occasionally obtained, but never xanthine. The amount of hæmoglobin is 0·13% to 0·3%, which is less than in blood-free striated muscle (1% to 2·3%). The amount of connective tissue is greater than in striated muscle. Sodium, iron, calcium, and chlorine are more abundant than in striated muscle; the opposite is true for other elements, potassium, magnesium, &c. There is about three times as much sodium as potassium. The influence of such ions on the manner of contraction is discussed. As much, or almost as much, of the soluble proteins were obtained twenty-four hours after removal in muscles kept at room temperature

as in those kept in ice. No evidence of rigor mortis is therefore forthcoming. In spite of the low percentage of glycogen, evidence was obtained of its disappearance.

W. D. H.

Muscle Plasma. JOHN MELLANBY (*Proc. physiol. Soc.*, 1908, xxxiv—xxxv; *J. Physiol.*, 37).—Muscle plasma, prepared from bird's muscle, and containing 3% of added sodium chloride, clots on the addition of a little acid. This is prevented by dilution with water, but occurs immediately when more salt is added. It is soluble in excess of acid, but this is prevented by adding more salt. The coagulum produced by acid, when thoroughly washed, forms a gelatinous solution in water, which is acid to litmus, and is reprecipitated by small amounts of neutral salts. After careful precipitation of acid, the muscle plasma is practically free from protein.

Wide-reaching conclusions are drawn from these few experiments with salted muscle plasma to explain the coagulation of natural muscle plasma in rigor mortis. The combined action of salt and lactic acid is considered to cause rigor, and the development of more acid to produce its disappearance. The observations are also stated to indicate that there is only one protein in muscle, but in this preliminary communication no evidence is offered on this point.

W. D. H.

The Utilisation of Sugar during Muscular Activity. JOHANNES MÜLLER (*Chem. Zentr.*, 1908, i, 1567; from *Zentr. Physiol.*, 1908, 21, 831—833).—The author has succeeded in isolating lactic acid from the perfusion liquid by means of the zinc salt. In spite of a sufficient oxygen supply, the amount of acid isolated corresponded with the amount of sugar utilised.

S. B. S.

Mono-amino-acids in Meat Extract. KARL MICKO (*Zeitsch. physiol. Chem.*, 1908, 56, 180—211).—Meat extracts contain a small and unimportant percentage of mono-amino-acids (alanine 0.23, glutamic acid 0.08, taurine 0.2%); there is also 0.36% of inosite. Dipeptides were not found.

W. D. H.

A Phytin-splitting Enzyme in Animal Tissues. ELMER V. MCCOLLUM and EDWIN B. HART (*J. Biol. Chem.*, 1908, 4, 497—500).—Liver and blood contain a phytase, but not muscle and kidney.

W. D. H.

Influence of Inorganic Colloids on Autolysis. IV. M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1908, 10, 356—370. Compare this vol., ii, 121).—There is in the main an agreement between the action of colloidal silver on metabolism and on autolysis. Minimum amounts favour uric acid production. The uric acid-forming ferments are activated by colloidal silver, ferrous hydroxide, and arsenic sulphide. Larger amounts of the two last named inhibit uric acid formation. Uricolysis is delayed by colloidal silver; the other two colloids have no action on this phenomenon.

W. D. H.

The Autolytic and Hydrolytic Degradation of Protein under Normal and Pathological Conditions. W. GLIKIN and ADOLF LOEWY (*Biochem. Zeitsch.*, 1908, 10, 498—505).—The tissues were allowed to autolyse for several days in toluene water until the action practically ceased. The ammonia-nitrogen, mono-amino-acid-nitrogen, and diamino-acid-nitrogen, both in the dissolved part and undissolved part of the tissue, were then determined. The same factors were also determined for a portion of the same tissues which had been directly hydrolysed without previous autolysis. Normal organs were examined (liver and muscular tissue), as well as those from animals which had been poisoned by hydrochloric and hydrocyanic acids. The autolysis of muscular tissue from animals poisoned by acids appears to be somewhat below the normal. The results, however, do not permit of any very definite conclusions being drawn. S. B. S.

Available Alkali in the Ash of Human and Cows' Milk. JOSEPH H. KASTLE (*Amer. J. Physiol.*, 1908, 22, 284—308).—Although the amount of ash in human milk is much less than in that of cows' milk, the amount of alkali as detected by phenolphthalein, and available for nutritive purposes, is the same. Numerous analyses are given, and various subjects in relation to milk in infant feeding are discussed at length. Among the points raised, the view is acquiesced in that much of the indigestibility of cows' milk in children is due, not so much to its protein constituents, as to excess of fat. W. D. H.

Milk-serum. FR. LANDOLF (*Biochem. Zeitsch.*, 1908, 10, 486—489).—Fractional examination of the osazones obtained from the serum of cows' milk leads to the conclusion, not that several modifications of lactose are present, but that lactose is united in part to other carbohydrates, and this factor modifies the polarisation, reduction power, fermentation, and the properties of the osazones. W. D. H.

The Ferment which Destroys Lactose in Milk. ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1908, 11, 61—66).—Lactose is gradually destroyed in cow's milk when the latter has not been boiled. The reaction only takes place to a very slight extent in the presence of formaldehyde, but considerable change takes place when the milk is kept sterile by means of iodoacetone. Reducing compounds are formed which have not yet been isolated. S. B. S.

The Excretion of Sulphurous Acid on the Human Subject after Administration of Sodium Sulphite and Sulphurous Acid in Combination with Sodium Salt. FR. FRANZ and G. SONNTAG (*Chem. Zentr.*, 1908, i, 1477—1478; from *Arb. K. Gesundh.-Amt.*, 1908, 28, 225—260).—Experiments were made to determine the form of excretion of sulphurous acid after administration of neutral sodium sulphite and formaldehyde, acetaldehyde, and dextrose sodium sulphites. Under certain conditions, sulphurous acid was obtained from the urine. This acid can be estimated by

oxidation to sulphuric acid by hydrogen peroxide. Care, however, must be taken in drawing conclusions as to the presence of sulphites in urine, as the latter on distillation yields sulphur compounds of unknown nature. In men, as in dogs, by far the greatest part of the injected sulphite is oxidised to sulphate. In certain cases, after intervals of ten minutes or a quarter of an hour, sulphites can be detected in the urine. The quantity was, however, never more than 1% of the sulphite administered. S. B. S.

New Organo-mercury Compounds. "Iodoargyrum." GIULIO NARDELLI (*Chem. Zentr.*, 1908, i, 1572; from *Arch. Farm. Sperim.*, 1908, 7, 69—83).—The author finds that the mercury of this compound, $C_4H_4SHg_4I_4$ (Paolini, *Abstr.*, 1907, i, 788), is passed in the urine in larger quantities than in the faeces. Taken in small doses, the iodine is passed in twenty-four hours, and the third constituent, thiophen, could not be detected in the urine; it appears to become changed in the system. J. V. E.

Estimation of Reducing Substances in Infants' Urine. ROBERTO FUNARO (*Biochem. Zeitsch.*, 1908, 10, 463—466).—The total reduction in normal urine was estimated by Bang's method, the sugar by Bang's method, the uric acid by the Hopkins-Folin method, and the creatinine by Folin's method. After deducting the reduction due to sugar, uric acid, and creatinine, the remainder is due to isomaltose, dextrin, glycuronic acid, and unknown substances. Tables of analyses are given, and Lavesson's conclusion is confirmed that infants' urine contains a smaller amount of all these substances than the urine of adult men and women. W. D. H.

Amino-acids in the Urine during Pregnancy. E. C. VAN LEERSUM (*Biochem. Zeitsch.*, 1908, 11, 121—136).—The main difficulty in Pfaundler's method of estimating the amino-acids in urine is the removal of the phosphotungstic salts. They can, however, be entirely removed by the addition of potassium chloride without any loss in the amino-acids taking place. The amino-acid nitrogen varies in health from 2.7 to 7.7% of the total nitrogen. It is increased by administering amino-acids. In pregnant women, it rises to over 10% in 40% of the cases, and the highest point is usually reached just before parturition; in some cases, it occurs after delivery; this may be related to the process of uterine involution. W. D. H.

Origin of Endogenous Uric Acid. E. PROVAN CATHCART, E. L. KENNAWAY, and JOHN B. LEATHES (*Quart. J. Med.*, 1908, 1, 416—446).—A marked increase in the output of endogenous uric acid is found to occur in three conditions: (a) fever: here the increased output coincides and terminates with the rise of temperature. (b) Exposure to cold. (c) After severe exertion. In the last two cases the increased output outlasts its cause by many hours.

The high output in the morning is not due to retention of uric acid formed during the night (as Hirschstein considers), or to inactivity of the digestive organs in the night (and it is doubtful if

such inactivity really occurs), but to the quickened activity of all functions, especially of voluntary muscles, which occurs after rest. The more lively the performance of the bodily functions the greater does the output of uric acid tend to be, and it is suggested that uric acid has its origin principally in the metabolic processes of the voluntary muscles.

W. D. H.

Creatinine of Infants' Urine. ROBERTO FUNARO (*Biochem. Zeitsch.*, 1908, 10, 467—471).—Creatinine is always present in infants' urine. The individual differences are not great, even if the diet varies. The small amount present explains why those who used the zinc chloride method have been unable to detect it.

W. D. H.

Excretion of Pigments by the Urine. RUDOLF HÖBER and FELICJA KEMPNER (*Biochem. Zeitsch.*, 1908, 11, 105—120).—If pigments insoluble in lipoids were injected intravenously in frogs, they were in part taken up by the kidney cells and excreted. Such pigments are acid magenta, aniline-blue, Congo-red, and many others. Other pigments were not taken up, such as Berlin-blue, benzoazurin, &c. The difference partly depends on how far the pigments are in colloidal solution; those which are not taken up being highly colloidal, but there are exceptions to this rule, for instance, Congo-red.

W. D. H.

Urinary Constituents Precipitable by Phenylhydrazine. HUGO MILRATH (*Zeitsch. physiol. Chem.*, 1908, 56, 126—134).—If dogs' urine is warmed for two hours on the water-bath with phenylhydrazine and acetic acid, phenylsemicarbazide is not obtained. Four to five hours' heating is necessary for the purpose, although cats' urine will sometimes yield the product in two hours. In the case of human urine, two to five hours is necessary, and in ten hours 80% of the urea is converted into phenylsemicarbazide. Aqueous solutions of urea yield similar results.

W. D. H.

Arnold's Urinary Reaction with Sodium Nitroprusside. THEOPHIL HOLOBUT (*Zeitsch. physiol. Chem.*, 1908, 56, 117—125).—In people taking a meat diet, the urine gives a violet reaction with sodium nitroprusside and sodium hydroxide; this soon changes to purple, and finally yellow. If ammonia is used instead of sodium hydroxide, the colour lasts longer. The same coloration is obtained with dogs' urine when the animals are fed on cooked meat, cheese, eggs, and other protein-rich food, but not when they are fed on raw flesh, gelatin, or vegetable albumin.

W. D. H.

Molecular Concentration of Pathological Fluids. ADOLPHE JAVAL (*Compt. rend.*, 1908, 146, 1328—1330).—Hypoconcentration is relatively rare; hyperconcentration is fairly frequent in disease, especially in cases of cardiorenal insufficiency. This is mainly due to salts, and estimations of the amount of sodium chloride in different

fluids of the body are given. The increase of concentration is increased in some cases by the retention of nitrogenous catabolites.

W. D. H.

The Chemical Test for Diseases due to Nerve Degeneration. The Formation of Alkylamines. KOLOMAN BAUER (*Beitr. chem. Physiol. Path.*, 1908, 11, 502—514).—Concentrated urine was, after certain preliminary treatment, made alkaline, and the bases distilled over with steam into acid. The solution of the salts thus obtained was evaporated down and the residue treated with sodium hypobromite, whereby ammonia and primary and secondary bases were destroyed. The tertiary base trimethylamine was then distilled over with steam and isolated in the form of its platinichloride.

It was found that trimethylamine was a constant constituent of normal urine, due to the normal degradation of lecithin substances. Substances containing a choline complex, such as eggs and meat, added to the diet, caused an increase in trimethylamine elimination. The normal output of trimethylamine with a mixed diet is 18 to 26 mg. per day for an adult man. The base was also estimated in several cases of nervous disease. The average quantities found were: 51 mg. daily in the cases of tabes, 59 mg. in myelitis, and 37 mg. in progressive paralysis. In one case of neurasthenia, the amount of trimethylamine found gave no evidence of destruction of nervous matter, whereas in a second case it did. ; S. B. S.

Protein Metabolism in Cystinuria. CHARLES G. L. WOLF, PHILIP A. SHAFFER [with EMIL OSTERBERG and MICHAEL SOMOGYI] (*J. Biol. Chem.*, 1908, 4, 439—472).—The anomalies of metabolism in cystinuria consist in low ammonia, high undetermined nitrogen, and high neutral sulphur in the urine. The high undetermined nitrogen is partly, and the high neutral sulphur wholly, due to cystine. The ingestion of protein in a cystinuric person increases the neutral sulphur, and so presumably increases the cystine in the urine. If cystine or cysteine is given by the mouth, they are completely broken down to sulphates; it must, therefore, be assumed that the cystine group of the protein is not absorbed as such, but in combination as polypeptide or thio-proteose. These appear to be different types of cystinuria, but it is only in the more severe cases that tolerance for cystine or other amino-acids is diminished. If cystine is given subcutaneously, it is partly oxidised and partly excreted in the urine, but no controls were made on healthy people. Sulphur-free amino-acids are almost quantitatively catabolised to urea. Sodium cholate does not increase the cystine excreted. With regard to the time relations of the excretion after protein-feeding, no standards of comparison in normal persons are at present available. In the cystinuric patients, the maximum of nitrogen excretion occurred later than that of carbon, and the former was coincident with that of sulphur. The maximum excretion of ammonia was early. The curves for neutral sulphur and undetermined nitrogen were approximately parallel. The relationships of cystinuria to bile secretion are discussed, but without any very clear conclusions. In cases of cystinuria in which the excretion of cystine

stops from time to time, the sulphur of the urine returns to normal for these periods, but the undetermined nitrogen remains high on many days; this is possibly due to amino-acids. W. D. H.

Carbon Dioxide in Venous Blood and Alveolar Air in Cases of Diabetes. ARTHUR P. BEDDARD, MARCUS S. PEMBREY, and EDMUND I. SPRIGGS (*Proc. physiol. Soc.*, 1908, xxxix—xli; *J. Physiol.*, 37).—The results and figures given appear to show that with a prolonged and increasing acidosis in severe diabetes, a point is reached in which increased ventilation of the lungs occurs, which leads to a decrease of the carbon dioxide in the alveolar air and blood, notwithstanding that the blood is still capable, in spite of its reduced alkalinity, of taking up large quantities of carbon dioxide. The increased respiration is ascribed to the stimulation of the respiratory centre by acid substances, including carbon dioxide and other acids produced by metabolism, and prolonged acidosis appears to increase the sensitiveness of the centre. W. D. H.

Influence of Diuretics on Phloridzin Diabetes. OTTO LOEWI and E. NEUBAUER (*Arch. exp. Path. Pharm.*, 1908, 59, 57—63).—In contrast with other diuretics, the addition of sodium chloride does not increase the diuretic action of phloridzin, neither is the amount of sugar excreted increased by the administration of diuretics.

W. D. H.

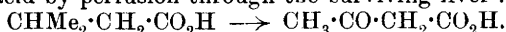
Influence of Calcium on Diuresis. OTTO PORGES and EGON PRIEBRAM (*Arch. exp. Path. Pharm.*, 1908, 59, 30—33).—If calcium chloride is introduced into the blood stream, its diuretic action is about equal to that of sodium chloride, unless doses sufficiently large to lower the blood pressure are given. W. D. H.

Physico-chemical Considerations as to the Pharmacological and Toxicological Actions of Mercury. LUIGI SABBATINI (*Biochem. Zeitsch.*, 1908, 11, 294—310).—The toxic effects of mercury on higher animals, just as in the case of bacteria, as shown by Krönig and Paul, depend on the concentration of mercury ions. Thus, by intravenous injection of sodium chloride, bromide, or iodide before the mercuric chloride, the toxic effect of the latter is depressed, owing to its decreased dissociation due to the presence of the sodium salts. The iodide is more effective than the bromide, and the bromide than the chloride, the iodide and bromide of mercury both dissociating less than the chloride. The lesions due to mercury poisoning can also be explained by the concentration of the mercury ions. These lesions occur chiefly in the secretory and excretory tracts. The concentration of the ions in the saliva, for example, would be great, owing to the absence of chlorides and proteins. In the stomach, on the other hand, the presence of chlorides and of protein would depress the dissociation of the chlorides; here the disturbance in mercury poisoning would be small. In the small intestine, the chlorides and peptones are still in large quantity, and again the dissociation would be small. Still lower in the intestinal tract, owing to absorption of chlorides and products

of tryptic digestion, the dissociation of mercury salts would be greater, and therefore the toxic effects can be observed. The lesions in the kidneys themselves, due to mercuric poisoning, occur almost exclusively in the convoluted tubules. Here, according to the Ludwig hypothesis, the urine is dilute, and becomes gradually concentrated in the passages, and here, also, the dissociation of the mercury salt and concentration of the ions can be great: hence the lesions. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body.

VII. The Formation of Acetoacetic Acid from *iso*Valeric Acid by Perfusion through the Liver. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 365—470. Compare this vol., i, 421; ii, 205).—Embden has shown that *iso*valeric acid is converted into acetoacetic acid by perfusion through the surviving liver:



To determine the mechanism of the reaction, perfusion experiments were carried out with the following acids. *iso*Valeric acid, α -hydroxy-*iso*valeric acid, β -hydroxy-*iso*valeric acid, pyrotartaric acid, and citramalic acid. Of these, only *iso*valeric acid and the β -hydroxy-derivative lead to the formation of acetone (and acetoacetic acid). From these results, the conclusion is drawn that the secondary carbon atom offers the first point of attack, and that the methyl group is not first oxidised. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body.

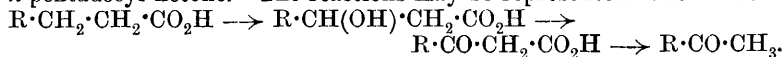
VIII. The Behaviour of $\alpha\beta$ -Unsaturated Acids when Perfused through the Liver. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1908, 11, 371—375).—Both dimethylacrylic and crotonic acids give rise to acetone by perfusion through the liver, whereas citraconic and mesaconic acids do not. The methyl group here does not offer the first point of attack, but the chemical change can be best explained by assuming that the addition of the elements of water at the double linking first takes place with the formation of β -hydroxy-acids. Dimethylacrylic acid, according to this hypothesis, would be converted into β -hydroxy-*iso*valeric acid, which readily gives rise to acetone (compare preceding abstract).

S. B. S.

Degradation of Carboxylic Acids in the Animal Body.

HENRY D. DAKIN (*Beitr. chem. Physiol. Path.*, 1908, 11, 404—405).—Friedmann has claimed (see this vol., ii, 205, and also preceding abstracts) that, on degradation of carboxylic acids, oxidation takes place first at the β -carbon atom with the formation of β -hydroxy-compounds. To this Knoop has objected, claiming that in normal fatty acids, oxidation generally takes place at the α -position, and that the formation of β -hydroxy-derivatives is an indirect process. Dakin, in support of Friedmann, shows, however, that *n*-butyric acid can yield acetone to the extent of 50% of the theoretical quantity when oxidised by hydrogen peroxide. This reaction can be best explained on the assumption that a β -hydroxy-derivative is first formed. Furthermore, all other fatty acids of the same series, up to stearic

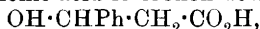
acid, undergo a similar oxidation. Octoic acid yields methyl *n*-amyl ketone; lauric acid, methyl *n*-nonyl ketone, and stearic acid, methyl *n*-pentadecyl ketone. The reactions may be represented as follows:



Further, phenylpropionic acid, when administered to an animal, yields, in addition to hippuric acid, β -hydroxyphenylpropionic acid and acetophenone, another example of β -oxidation. The reaction also takes place *in vitro* when hydrogen peroxide is employed as the oxidising reagent (see below). S. B. S.

The Oxidation of Fatty Acids. FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1908, 11, 411—414).—Reply to Friedmann on question of " β -oxidation" (see preceding abstracts of Friedmann and Dakin). S. B. S.

Oxidation of Phenyl Derivatives of Fatty Acids by the Animal Organism and by Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 419—435).—After hypodermic injection, β -phenylpropionic acid is broken down in dogs to



$\text{COPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, COPhMe , and PhCO_2H , the last substance occurring in the urine as hippuric acid. β -Hydroxy- β -phenylpropionic acid occurs as the laevorotatory variety, in close analogy to *l*- β -hydroxybutyric acid. Benzoylactic acid could not be isolated, but its production is inferred from the occurrence of acetophenone in the urine.

The oxidation of β -phenylpropionic acid and of β -hydroxy- β -phenylpropionic acid by hydrogen peroxide is very similar, acetophenone and benzoic acid being produced; the oxidation proceeds slowly even at 37°.

In order to test the hypothesis that phenylacetic acid owes its resistance to oxidation to its combination with glycine, β -phenylpropionylglycine, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (thick needles, m. p. 114—115°, more soluble in water than hippuric acid) was synthesised. After administration to dogs, it yields, however, the same degradation products as phenylpropionic acid. G. B.

[Physiological] Action of Optical Isomerides. III. Adrenaline. ARTHUR R. CUSHNY (*J. Physiol.*, 1908, 37, 130—138).—Neutral or *l*-adrenaline acts twice as strongly on the blood pressure as synthetic or *r*-adrenaline, and presumably also on the other organs affected by adrenaline. From this it is inferred that *d*-adrenaline is devoid of action on these tissues, and this was confirmed by the examination of a partly isolated *d*-adrenaline.

W. D. H.

Action of the Digitalis Group on the Kidneys. D. JONESCU and OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1908, 59, 71—82).—Substances of the digitalis group act as diuretics in doses insufficient to raise the blood pressure. They act by dilating the renal blood-vessels, and this is a specific effect on these vessels. W. D. H.

The Action of Strychnine on the Nerve Fibres of the Vagus to the Heart. V. FORLI (*Chem. Zentr.*, 1908, i, 1568; from *Zentr. Physiol.*, 1908, 21, 823—827).—Strychnine sulphate solution was allowed to act on the nerve fibres of the vagus of the heart in a cat; a diminution of conductivity and irritability of the affected position was observed, analogous to the action of the same substance on the sympathetic nerve fibres in the neck. S. B. S.

Sulphurous Acid in its Biochemical Relationship. LEO GRÜNHUT (*Biochem. Zeitsch.*, 1908, 11, 89—104).—Theoretical considerations are advanced as to the reason of the comparative toxicity of various solutions of sulphites, and compounds with salts of sulphites. The conclusion is drawn that the specific toxicity of a given sulphite solution depends on the quantity of $[H_2SO_3] + [SO_2]$ contained therein. S. B. S.

Chemistry of Phosphorus Poisoning. OTTO PORGES and EGON PRIBRAM (*Arch. exp. Path. Pharm.*, 1908, 59, 20—29).—In the phosphorus liver, a smaller part of the nitrogen is in the form of protein than in the normal liver. The lessening of hexone bases is still more marked. On autolysis, the nitrogen contained in substances precipitable by tannin is much greater than in autolysis of the normal liver. The nitrogen split off by hydrochloric acid is raised from 10% (the normal number) to 13%. How far these changes are due to differences in ferment action is discussed. W. D. H.

The Supposed Antidotes to Alkaloids and Artificial Antitoxins. H. DORLENCOURT (*Chem. Zentr.*, 1908, i, 1568; from *Bull. Sci. Pharm.*, 1908, 15, 82—88).—The statement of Baudran that antitoxins to alkaloids can be prepared by treating the latter with calcium permanganate was submitted to experimental investigation. It was found that a lethal dose of strychnine, injected intra-muscularly together with the substance produced by the action of calcium permanganate on the alkaloid, produced no toxic action. Heating the mixture to 120° produced no change in its action, and it was found that manganese salts, such as the chloride, act as an antidote to strychnine. There is, therefore, no question of a specific antitoxin. Similar results were obtained by intra-cerebral as by intra-muscular injections, and it is suggested that manganese salts might be employed as antidotes in therapeutic practice. S. B. S.

Cobra Poisoning and Hæmolysis. IVAR BANG (*Biochem. Zeitsch.*, 1908, 11, 520—537).—The importance of lecithin in cobra poisoning, as advanced by Kyes and others, is denied, and the existence of cobra-lecithids considered unproved. Kyes' cobra-lecithid is not a pure substance; it may be a mixture of poison and activator, or a chemical combination, but it is quite uncertain what the activator is; the mixture contains decomposition products of phosphatides, fats, and soaps. Lecithin itself, prepared from egg-yolk, was found to be wholly inactive as an activator to cobra venom in producing hæmolysis; the same is true for the monoamino-

phosphatide, cuorine, and the diaminophosphatide of egg-yolk. The kephalin fraction was found to be active, but the exact composition of this fraction is uncertain. Kossel's protagon, which consists largely of kephalin, is, however, inactive.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Action of the Zinc Ion on Media for Microbes. JOSEPH MENDEL (*Compt. rend.*, 1908, 146, 1290—1291).—Two electrodes, one of zinc and the other of platinum, were introduced into an infected gelatin tube, and a current of 1—5 milliamperes was passed through the medium for some minutes. An opaque zone developed round the zinc electrode, and the bacteria with which the medium had been infected grew well everywhere, except within this zone. S. B. S.

Nutrition of Nitrogenous Bacteria. MME. HÉLÈNE KRZEMIENIEWSKA (*Bull. Acad. Sci. Cracow*, 1908, 445—448).—The presence of potassium salts are essential for the nutrition of nitrogenous bacteria.

Gerlach and Vogel's statement (*Centr. Bakt. Par.*, ii, 10, 636) to the opposite effect is due to the fact that small amounts of potassium salts were always present in the media used in these experiments. J. J. S.

Formation of Acid by the Diphtheria Bacillus. C. LUBENAU (*Arch. Hygiene*, 1908, 66, 305—335).—The production of acid by Löffler's bacillus depends (as is well known) on the presence of carbohydrates in the broth; when the latter is free from carbohydrates, alkali is produced, but only under aerobic conditions. Diphtheroid organisms produce less acid on the whole, and do not form appreciable quantities of alkali. True diphtheria bacilli may produce acid, even in the absence of carbohydrates, if grown in a bouillon in which the proteins have been partly decomposed by a fourteen days' growth of *Bacillus coli*; the acid seems to be derived from the proteins. The addition of glycerol to the culture medium causes the diphtheria bacillus to accelerate its production of acid in the first few days, whilst in the case of diphtheroid organisms the acceleration does not occur until later. G. B.

Part Played by Yeasts in the Aldehydification of Alcohol. J. AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1908, 147, 77—80. Compare this vol., ii, 615).—Previous experiments have shown that living yeasts have a greater effect in the formation of aldehyde than yeasts sterilised by heat. Repetition of these experiments, in which the yeast was killed by antiseptics, gave similar results. Thus, living

yeast gave 1100 mg. of aldehyde per 100 grams of alcohol, yeast killed by mercuric chloride gave no aldehyde, that killed by formaldehyde gave traces, whilst after sterilisation by heating at 120° by means of salicylic acid, and by sodium fluoride, less than 100 mg. of aldehyde were formed. Moreover, increase in the proportion of alcohol present lowers the yield of aldehyde, the alcohol acting as an antiseptic. When yeast cells are killed by the action of chloroform and shaken with 10% alcohol, only traces of aldehyde are produced, and the clear filtrate produced when yeast is crushed in a Borrel apparatus is similarly inactive. If ethyl alcohol is replaced by methyl, propyl, butyl, isobutyl, or amyl alcohol, the corresponding aldehyde is never formed. The proportions of aldehyde and ethyl acetate formed depend on the duration of the experiment; thus immediately after agitation, 1100 mg. of aldehyde, but no ethyl acetate, were found, whereas after four days the amount of acetate was 316 mg., and of aldehyde less than 100 mg. This is probably to be explained by the formation of ethyl acetate from the acetic acid resulting from the oxidation of the aldehyde (compare Kayser and Demolon, *Abstr.*, 1907, ii, 714; this vol., i, 317). It is found, also, that yeasts accelerate the production of ethyl acetate in a solution of alcohol and acetic acid.

The rapid disappearance of the aldehyde previously described occurs only under the influence of living, not of dead, yeasts.

The conclusions are drawn that the production of aldehyde reaches its maximum in presence of the living yeast cell, that it is not effected by the juice contained in the cell, and that the phenomenon is peculiar to ethyl alcohol. E. H.

Malic Acid in the Production of Wine. Malo-lactic Fermentations. W. MESTREZAT (*J. Pharm. Chim.*, 1908, [vi], 28, 13—20. Compare *Abstr.*, 1907, ii, 903).—The malic acid of grape-juice partly disappears during fermentation, but no lactic acid is formed, and the "malo-lactic" fermentation of Rosenstiehl (*Rev. viticole*, 29, 509) does not exist. During the ripening of the wine, the malic acid undergoes a further slight diminution. G. B.

The Depression of Fusel Oil Formation, and the Part Played by Bacteria in the Formation of the Higher Alcohols during Fermentation. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 10, 490—497).—If ammonium sulphate is added as a source of nitrogen, the amount of amyl alcohol formed from leucine is diminished. The addition of 500 and 1000 grams of the sulphate to 2000 litres of mash, diminished the fusel oil yield from 5 to 2 litres; the addition of 250 grams of salt caused a diminution to 2.5 litres. In the fusel oil, *n*-butyl alcohol was found in very appreciable quantities when ammonium sulphate was added to the mash. In the fusel oil obtained when this addition was not made, isopropyl alcohol was found. These alcohols are probably due to the action of bacteria. S. B. S.

Transformation of Starch in Plants. WL. BUTKEWITSCH (*Biochem. Zeitsch.*, 1908, 10, 314—344).—The change of starch into sugar which is carried out by bark and wood is due to ferment action,

and the diastase was obtained in concentrated form by precipitation of aqueous extracts with alcohol. The bark also inverts maltose. Various conditions, such as changes of temperature on the activity of the ferments, are described.

W. D. H.

The Hydrolytic and Catalytic Ferments Acting during the Process of Ripening of Fruit. GIUSEPPE TALLARICO (*Chem. Zentr.*, 1908, i, 1563—1564; from *Arch. Farm. sperim.*, 1908, 7, 27—48).—Bananas were employed for the study; from this fruit, gathered in different stages of ripening, extracts were made. The catalytic action was determined by investigating the action of the extract on hydrogen peroxide; the amylolytic, by its action on starch; the proteolytic, by the action on gelatin, and the inverting, by the action on sucrose. The following enzymes were present: catalase, invertase, amylase, tyrosinase, and a proteolytic enzyme. The catalytic action is very intense so long as the fruit is green and during ripening; it weakens as the fruit gets black. The amylolytic action takes place when the fruit is green or at the beginning of the stage of ripening; it then disappears. The inverting action is almost entirely absent during the green stage, is intense during ripening, and then gradually disappears. The proteolytic action manifests itself during ripening, and then probably gets weaker.

S. B. S.

Carrotene from Carrots and the Substances which accompany it. HANS EULER and EBBA NORDENSON (*Zeitsch. physiol. Chem.*, 1908, 56, 223—235. Compare Willstätter, *Abstr.*, 1907, i, 865; Arnaud *Abstr.*, 1885, 670; 1886, 711; 1887, 859).—When fresh carrots are ground with sand, it is found that the expressed juice contains only a portion of the carrotene. The following substances have been extracted from carrots (23 kilos.): Phosphatides, lecithin, &c., 13; daucosterol, 0.5; phylosterol, 1.3; carrotene and xanthophyll, 0.7; oil of unknown composition, 3.5 grams. The following method of extraction is recommended: Boil with water, press, dry in absence of air, extract with carbon disulphide, and then with alcohol. Distil, dissolve in small amount of light petroleum, and precipitate the phosphatides with alcohol. The carrotene and xanthophyll can be thrown down by the addition of suitable salts to the solution, and can be separated by Willstätter's method.

Daucosterol, $C_{26}H_{42}O_4$ (?), crystallises from boiling alcohol in flocculent masses consisting of microscopic needles, m. p. 283° , and gives the Salkowski-Hesse reaction.

An analysis of the purified phosphatides gave the ratio N : P = 1 : 0.6.

When carrotene is oxidised with a small amount of an acetic acid solution of chromic anhydride, care being taken that the temperature does not rise above 30 — 40° , an oil, $C_{40}H_{56}O_8$ or $C_{40}H_{60}O_8$, which does not solidify at -10° is obtained. Phytosterol was not obtained when the carrotene employed was quite free from this compound.

J. J. S.

The Endo- and Ekto-invertase of the Date. A. E. VINSON (*J. Amer. Chem. Soc.*, 1908, 30, [vi], 1005).—The invertase of the date remains insoluble in all ordinary solvents throughout the green stages,

but becomes readily soluble on ripening, that is, it changes from an endo- to an ekto-form. The change in the behaviour of the invertase towards solvents coincides very closely in point of time with the passage of the tannin into the insoluble form. Evidence is, however, adduced to show that the two phenomena are not causally connected; thus glycerol will dissolve date invertase in presence of soluble tannin, but it fails to extract invertase from green dates. Tannin, however, renders invertase insoluble in water.

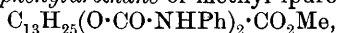
It does not appear that the invertase is altered in changing from the insoluble to the soluble form. The rates of inversion of sucrose by equivalent amounts of green and of ripe date pulp are practically identical. Picric acid, chromic acid, and formaldehyde retard the action of green and ripe pulp to approximately the same degree. The living protoplasm does not appear to be directly connected with the inversion, since neither ether, chloroform, nor acetone render inactive the green tissue.

The author explains the difference in solubility by supposing that in the case of the green date the enzyme forms an insoluble compound with some constituent of the protoplasm; on ripening, the protoplasm undergoes profound change, and the enzyme is liberated. He examines and rejects the alternative view, that the cell wall of the green tissue is semi-permeable, whilst that of the ripe tissue is not. E. J. R.

Transitory Presence of Hydrogen Cyanide in Ferns. MAURITS GRESHOFF (*Pharm. Weekblad*, 1908, 45, 770—773).—The author has detected hydrogen cyanide in ferns, such as *Gymnogramme aurea*, *G. lastrea*, and *G. athyrium*. The percentage varied between 0.056 in very young fronds and 0.006 in old fronds, and always diminished with increase in the age of the material examined. A. J. W.

Chemical Examination of Ipomœa purpurea. FREDERICK B. POWER and HAROLD ROGERSON (*Amer. J. Pharm.*, 1908, 80, 251—286).—The chief constituent dissolved by alcohol is a resin, from which by extraction with various solvents the following substances were obtained: pentatriacontane, a phytosterol ($C_{27}H_{46}O$, m. p. 132—133°, $[\alpha]_D -32.1^\circ$, probably identical with sitosterol; compare Abstr., 1903, ii, 517), several fatty acids, a new crystalline alcohol, *ipuranol*, $C_{23}H_{38}O_2(OH)_2$, m. p. 285—290°, and a new acid, termed *ipurolic acid*, $C_{13}H_{25}(OH)_2 \cdot CO_2H$, silky needles, m. p. 100—101°.

Ipuranol yields an *acetyl* derivative, m. p. 160° (not analysed); from the acid, the *sodium* salt, $C_{13}H_{25}(OH)_2 \cdot CO_2Na \cdot H_2O$, the *silver* salt (m. p. 160°), the *methyl* ester, $C_{13}H_{25}(OH)_2 \cdot CO_2Me$, m. p. 68—69°, the *monomethyl ether* of methyl ipurolate, $OH \cdot C_{13}H_{25}(OMe) \cdot CO_2Me$, m. p. 64—65°, and the *diphenylurethane* of methyl ipurolate,



m. p. 96—97°, were prepared. By decomposition of the various resin fractions with potassium hydroxide and with barium hydroxide, there were obtained a number of acids, including α -methylbutyric acid, $[\alpha]_D +17.95^\circ$, α -hydroxylauric acid, $C_{12}H_{24}O_3$, m. p. 69—70°, and probably azelaic acid. The drug also contains a minute quantity of an essential oil. G. B.

"Bourgou" (*Panicum stagninum*); a Sacchariferous Grass. E. PERROT and EUGÈNE TASSILLY (*Bull. Soc. chim.*, 1908, [iv], 3, 740—742).—A sample of this grass collected in Upper Senegal was found to contain 10% of sucrose, 7% of reducing sugars, calculated as dextrose, some emulsin, but no invertase or glucosides capable of being hydrolysed by emulsin. T. A. H.

Influence of Manures and Soil Moisture on the Disposition and Perfection of the Ears and the Club Shape of Göttingen Square-head Winter Wheat. W. OHLMER (*J. Landw.*, 1908, 56, 153—171; from *Inaug. Diss. Göttingen*, 1907).—The wheat was grown in zinc vessels and pots containing loam, with different manures; the amounts of water were 45% and 70% of the water capacity of the soil.

It is shown that the club shape becomes more marked when the nitrogen supply is increased, whilst a high percentage of moisture in the soil is unfavourable. N. H. J. M.

The Storage and Transportation of Sucrose in the Beet (*Beta vulgaris*). FRIEDRICH STROHMER (*Chem. Zentr.*, 1908, i, 1469—1470; from *Oesterr.-ung. Zeitsch. Zuckerind. Landw.*, 37, 18—21).—In the second year of growth, at the time of flowering, the cane sugar disappears from the roots, and is employed for building up the parts of the plant above the earth. At this time, both in the main stem and in the branches, more invert sugar is found than sucrose, so that hydrolysis into monosaccharides of the latter first takes place, when it is transported, the hydrolysis being followed by re-synthesis. The exposure to light has great influence on the store of sugar; plants which have been kept in the shade half the day during the whole period of growth yield only one-fourth to one-half as much sugar as those which, growing under otherwise similar conditions, have been exposed to full light for the whole day. The plants grown in the shade yielded larger quantities of other products of non-carbohydrate nature, and had consequently considerably less technical value. S. B. S.

Manuring Experiments with Calcium Cyanamide for Potatoes. ALBERT STUTZER (*J. Landw.*, 1908, 56, 141—144).—The potatoes were grown on plots of 100 square metres, without nitrogenous manure, and with 250, 500, and 750 grams of sodium nitrate, "Stickstoffkalk," and ammonium sulphate respectively. Sodium nitrate gave lower yields than "Stickstoffkalk," probably owing to the large amount of rain; the percentage of starch was, however, highest when sodium nitrate was employed. The highest yields per acre of dry matter and starch were obtained on the plot which received 500 grams of "Stickstoffkalk." N. H. J. M.

[Nutritive Value of Non-Proteins in Hay.] MAX MÜLLER (*J. Landw.*, 1908, 56, 192—193. Compare this vol., ii, 220).—The hay extract employed in the feeding experiments previously described (*Abstr.*, 1907, ii, 645) contained 1.87% total N by Jodlbaur's method

and 1.84% by Kjeldahl's. The results obtained with blood-albumin have been confirmed by further determinations. N. H. J. M.

Persistence of the Nitrogen of Green Manure in a Light Sandy Soil. CONRAD VON SEELHORST (*Mitt. deut. landw. Ges.*, 1908, 23, 83—89, 139—144).—Experiments with different plants grown with green manures in a sandy soil in iron boxes having an area of 1 square metre. The nitrogen in the crops was determined, and also the amount per month and nitrogen content of the drainage. The experiments commenced in 1904 (compare *ibid.*, 1906, 21, 289—292, 295—299).

The decomposition of green manure in sandy soil is so rapid that, when applied in October, half the nitrogen may be washed out in the drainage by February or March when the winter has been mild and wet. When applied in February, the decomposition would be still more rapid; the loss of nitrogen is then, however, reduced partly by its being taken up by the growing crop and partly by the amount of drainage being diminished.

The amount of nitrogen was determined in the rain collected in Göttingen in 1906, and the following results obtained:

Rainfall.			Nitrogen.			Rainfall.			Nitrogen.		
mm.			per million. kg. per hec.			mm.			per million. kg. per hec.		
January...	48.7		1.40		0.68	July	124.1		0.72		0.89
February	47.9		1.40		0.67	August ...	79.3		1.26		1.00
March ...	78.3		0.47		0.37	September	59.7		1.85		1.10
April	28.9		0.91		0.26	October...	25.1		1.47		0.37
May	95.6		1.26		1.20	November	53.1		0.84		0.45
June	84.3		1.25		1.05	December	46.8		1.41		0.66

The rainfall for the year was 771.8 mm., and the total nitrogen 8.718 kilos. per hectare, or 1.13 per million of rain water.

N. H. J. M.

Action of Organic Nitrogen Manures as Compared with Sodium Nitrate. MAX POPP (*Landw. Versuchs-Stat.*, 1908, 68, 253—300).—Blood meal and horn meal in quantities containing (1) 0.2 and (2) 0.4 gram of nitrogen in each case were mixed with soil (250 grams), and the amounts of nitrogen as ammonia and nitrates determined in water extracts at the commencement and after two, six, and twelve weeks. The following amounts of nitric nitrogen, as percentages of total N, were found:

	At commencement.		2 weeks.		6 weeks.		12 weeks.	
	1	2	1	2	1	2	1	2
Blood meal	0	0	17	8	70	66	72	72
Horn meal	0	0	10	1	54	45	59	57

The amounts of ammonia were very small, except after two weeks, when the nitrogen in that form amounted to 6—13%. Similar experiments, in which calcium carbonate was also added, generally gave very slightly higher results.

Vegetation experiments extending over five or six years are

described, in which different crops were grown successively in large cylinders and manured with a variety of organic manures. The approximate values of the different manures as compared with sodium nitrate were found to be as follows: blood meal and horn meal, 70; fish meal, ricinus meal, and meat meal, 60; Bremer poudrette and bone meal, 55; molasses manure, 40; wool dust, 25, and leather meal, 10.

N. H. J. M.

Gaseous Compounds produced by the Decomposition of Calcium Cyanamide and their Action on Plant Growth. EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1908, 68, 189—228).—Calcium cyanamide mixed with soil and basalt sand gave off 3.78 and 4.26% of the total nitrogen as ammonia in eight days. In three days, 50 grams of the manure yielded 0.00068 gram of hydrogen phosphide, but no hydrogen sulphide, and in the same length of time 10 grams gave 0.0795% of acetylene.

Results of experiments on germination in presence of the different gases make it probable that the injurious action of calcium cyanamide is due to free ammonia and perhaps also to hydrogen phosphide. Acetylene was found to have no injurious action on germination.

Experiments were also made in soil and water culture on the action of the different gases. The results showed that small amounts of free ammonia, hydrogen phosphide, and hydrogen sulphide are injurious to growth.

N. H. J. M.

Absorption of Calcium Cyanamide in Soil. HUBERT KAPPEN (*Landw. Versuchs-Stat.*, 1908, 68, 301—331).—The absorptive power of soils causes the decomposition of calcium cyanamide into lime and cyanamide. The latter compound is also produced by the action of carbon dioxide, and its production is rapid when both actions occur simultaneously. The formation of cyanamide is favourable to vegetation, since it is more readily attacked by bacteria than the strongly alkaline calcium compound.

In soils of low absorptive power, the transformation of calcium cyanamide is slower, and, under these conditions, injury to germination and plant growth, due to poisonous cyanamide compounds, may occur.

The influence of absorption is only indirect, conditions being produced which are favourable to the rapid conversion of poisonous compounds into harmless substances.

N. H. J. M.

Factors which Influence the Manurial Action of Sparingly Soluble Phosphates. HENRIK G. SÖDERBAUM (*Landw. Versuchs-Stat.*, 1908, 68, 433—450).—Oats and barley were grown in pots in a sandy soil, deficient in nitrogen and phosphoric acid, manured with different phosphates in conjunction with nitrogen in different forms.

Oats manured with tricalcium phosphate gave slightly lower results with ammonium nitrate and slightly higher results with ammonium sulphate than when sodium nitrate was employed. In the case of barley manured with bone meal, ammonium nitrate caused a similar depression as compared with sodium nitrate, whilst ammonium sulphate

reduced the yield 46·6%. A mixture of sodium nitrate and ammonium sulphate, however, increased the yield (4·1%) as compared with sodium nitrate alone. Tricalcium phosphate, ammonium sulphate, and potassium sulphate gave somewhat higher results (with oats) than when potassium chloride was employed, whilst bone meal, ammonium sulphate, and potassium chloride gave distinctly better results (with barley) than when potassium sulphate was used.

In a subsequent series of experiments, ammonium salts (both nitrate and sulphate) in conjunction with tricalcium phosphate and bone meal respectively considerably increased the yield of oats as compared with sodium nitrate. Barley manured with bone meal and ammonium nitrate gave higher results than with sodium nitrate, whilst tricalcium phosphate and ammonium nitrate gave lower results. Both phosphatic manures (especially tricalcium phosphate) gave much lower results with ammonium sulphate than with sodium nitrate. Addition of equivalent amounts of sodium carbonate to ammonium sulphate in conjunction with bone meal increased the yield of barley, the total produce being then slightly higher (1·1%) than with sodium nitrate and bone meal. In the case of tricalcium phosphate, addition of sodium carbonate with ammonium sulphate nearly doubled the yield obtained with ammonium sulphate and tricalcium phosphate; the yield, however, was still more than 50% below that obtained with sodium nitrate and tricalcium phosphate.

Sodium carbonate in conjunction with ammonium sulphate and phosphates very slightly reduced the yield of oats as compared with ammonium sulphate and phosphates alone.

The changes in the physiological reaction caused by different nitrogenous compounds will not only vary with different plants, soils, and with different amounts and kinds of the other manures employed, but may even be reversed.

N. H. J. M.

Analytical Chemistry.

Absorption Bulbs for use with Bottles containing Standard Solutions, &c. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 1077).—A piece of apparatus is described which may be fitted to bottles containing standardised alkali solutions in order to prevent the entrance of carbon dioxide, &c., to the bottle when the solution is drawn off into a burette. It consists of a bulb provided with a side-tube reaching to the bottom of the bulb; the air enters by this tube and, after bubbling through potassium hydroxide solution or other absorbent placed in the bulb, leaves through a tube at the top of the bulb. This tube is bent downwards so that it can be fixed through a hole in the cork of the bottle. By slightly altering its form, the bulb may be used to absorb the gases formed during fermentation experiments, and for other purposes.

W. P. S.

Replacement of Hydrogen Sulphide in Chemical Analysis. EDUARD DONATH (*Chem. Zeit.*, 1908, 32, 629—630, 645—647).—The author recommends the process used by Vortmann chiefly on hygienic grounds.

This process is, briefly, as follows: the solution is made alkaline with sodium hydroxide and then heated with excess of pure sodium sulphide, which dissolves the metals of the tin group. The insoluble matter is then treated with dilute hydrochloric acid, which dissolves all but the sulphides of those metals which are precipitated in the usual course with hydrogen sulphide; cobalt and nickel are also left undissolved. For further details, Vortmann's brochure is referred to.

In order to prepare ammonium sulphide without using a hydrogen sulphide apparatus, distillation of sodium sulphide with ammonium chloride solution is recommended.

L. DE K.

Use of Certain Organic Acids and Acid-Anhydrides for the Standardisation of Alkali and Acid Solutions. ISAAC K. PHELPS and L. H. WEED (*Zeitsch. anorg. Chem.*, 1908, 59, 114—119).—Experiments are recorded which show that succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride can be used, with phenolphthalein as indicator, for the titration of sodium and barium hydroxide solutions with the same degree of accuracy as a solution of hydrochloric acid standardised by precipitation with silver nitrate.

H. M. D.

Comparison between Succinic Acid, Arsenious Oxide, and Silver Chloride for the Standardisation of Solutions in Iodimetry, Alkalimetry, and Acidimetry. ISAAC K. PHELPS and L. H. WEED (*Zeitsch. anorg. Chem.*, 1908, 59, 120—126. Compare preceding abstract).—Succinic acid can be accurately employed for the standardisation of sodium thiosulphate solutions. The authors' method consists in standardising a pure sodium hydroxide solution by means of succinic acid. This solution is used to titrate a solution of a mineral acid, a known quantity of which is added to an excess of solution containing potassium iodide and iodate. The thiosulphate solution is then used to titrate the liberated iodine. Results quite as accurate as those yielded by the estimation of iodine with a standard arsenious oxide solution are obtainable. The liberation of iodine by mineral acids from an iodide-iodate solution is not complete in very dilute solution.

H. M. D.

Separation of Chlorine, Bromine, and Iodine by means of Hydrogen Peroxide in Acid Solution. PAUL JANNASCH (*J. pr. Chem.*, 1908, [ii], 78, 28—34).—In continuation of the study of the separation of the halogens by means of hydrogen peroxide, a method has been worked out for the quantitative separation of chlorine, bromine, and iodine from each other. The haloid mixture is made acid with acetic acid and treated with hydrogen peroxide; the iodine is then distilled off in a current of carbon dioxide, collected in an

aqueous solution of ammonium hydroxide and hydrazine sulphate, and estimated as described previously (Abstr., 1906, ii, 194). The bromine and chlorine in the distillation residue are separated and estimated as before (Abstr., 1906, ii, 894), with the difference that the bromine is collected in a solution of sodium, instead of ammonium, hydroxide and hydrazine sulphate. The analyses quoted show that the method gives good results for chlorine and iodine, but that bromine is found slightly too low. G. Y.

Detection and Estimation of Chlorites and Hypochlorites in Chlorates. BIRGER CARLSON and JULIUS GELHAAR (*Chem. Zeit.*, 1908, 32, 604—605, 633—634).—*Qualitative Examination of Chlorates.*—Five grams of the sample are dissolved in 100 c.c. of cold water and a drop of zinc iodide-starch solution is added. If no immediate blue colour is noticed, hypochlorites are absent. Two c.c. of *N*/10 sulphuric acid are now added, and if there is no immediate coloration, neither hypochlorites nor chlorites are present. These directions must be strictly adhered to.

Quantitative Estimation.—The following is an outline of the method employed: The hypochlorite is titrated in the usual manner with arsenious acid, the excess of which is then titrated with iodine. To another portion of the solution is now added the requisite amount of arsenic solution to destroy the hypochlorite, and, after diluting to 250 c.c. and heating to 95°, the solution is titrated as quickly as possible with indigo solution; if neutral or alkaline, the liquid should be acidified faintly with dilute sulphuric acid. The indigo solution is prepared by dissolving about 6 grams of sodium indigotinsulphonate in a litre of water, and should be checked with a solution of chlorite, checked in turn with standard iodine and thiosulphate. L. DE K.

Estimation of Sulphur in Iron and Steel. MAX ORTHEY (*Zeitsch. angew. Chem.*, 1908, 21, 1359—1364, 1393—1399).—The following published processes may be recommended. They are all based on the evolution of the sulphur as hydrogen sulphide and absorption of the latter in cadmium acetate solution; the cadmium sulphide is converted by means of copper sulphate into copper sulphide, which is then burnt to oxide (1, 2, 3, 4), or the cadmium sulphide is estimated iodometrically (5, 6):

(1) The sample is treated with hydrochloric acid, D 1·19. (2) The gases are passed through a red-hot tube. (3) The hydrochloric acid fumes are condensed in a little water, which is afterwards boiled to expel any hydrogen sulphide. (4) A mixture of zinc and cadmium acetate is used. (5) An ammoniacal solution of cadmium acetate is used. (6) An acetic acid solution is employed.

In the case of steel, the following methods may be used also: (7) The sample is dissolved in dilute hydrochloric acid (1:2), and the gases passed through a red-hot tube. (8) Acid, D 1·124, is used, and the gases ignited. (9) The same, but a mixture of dilute hydrochloric acid (1:2) and dilute sulphuric acid (1:4) is used instead. For reference, analyses 3, 4, 5, and 6 should be used.

Good results are obtained also by the following methods, where the sulphur is finally weighed as barium sulphate: (a) The sample is dissolved in strong hydrochloric acid, and the heated gases are passed through ammoniacal hydrogen peroxide. (b) The sample is oxidised with nitric acid, D 1.42, the nitric acid is expelled by excess of hydrochloric acid, and the ferric chloride removed by shaking with ether; or the iron is precipitated with ammonia, and, after adding barium chloride, the ferric hydroxide is re-dissolved by hydrochloric acid. (c) The iron is treated with copper-ammonium chloride, and the residual matter oxidised with nitro-hydrochloric acid and potassium chlorate.

L. DE K.

Decomposition of Certain Minerals and Industrial Products by means of Sodium Peroxide and Metallic Sulphides. JAMES H. WALTON, JUN., and HERMAN A. SCHOLZ (*Amer. Chem. J.*, 1908, 39, 771—789).—A method is described for decomposing certain mineral substances, and is particularly applicable to sulphide ores and products containing a large proportion of silica, such as glazes and slags. The decomposition is effected by fusing the material in a nickel crucible with a mixture of sodium peroxide, zinc sulphide, and potassium persulphate. In the case of basic substances, such as franklinite and chrome iron ore, iron pyrites is added in order to increase the temperature.

The method yields accurate results, and is very rapid; the silica is brought into solution, and therefore does not tend to clog the filters, and the use of platinum crucibles is obviated.

E. G.

Colorimetric Estimation of Phosphorus in Steel. G. MISSON (*Chem. Zeit.*, 1908, 32, 633).—The reagents required are (1): Pure nitric acid, D 1.2. (2) Potassium permanganate, 8 grams per litre. (3) Pure hydrogen peroxide, prepared by introducing gradually 40 grams of sodium peroxide into a cold mixture of 900 c.c. of water and 100 c.c. of nitric acid. (4) Ammonium vanadate, prepared by dissolving 2.345 grams of the salt in 500 c.c. of water, adding 20 c.c. of nitric acid, and diluting, when cold, to one litre. (5) A freshly-prepared 10% solution of ammonium molybdate.

One gram of the sample is dissolved in 20 c.c. of reagent (1), and boiled and mixed with 10 c.c. of reagent (2). After boiling a few seconds longer, 10 c.c. of reagent (3) are added to redissolve the manganese precipitate, then 10 c.c. of reagent (4), and the excess of peroxide is removed by boiling. When cold, the liquid is diluted to 60—65 c.c., 10 c.c. of reagent (5) are added, and the whole is diluted to 800 c.c. exactly. After two or three minutes, the coloration is compared with that of a standard sample treated similarly; the colour is stable for several days.

L. DE K.

Estimation of Phosphoric Acid in Foods. EMIL WÖRNER (*Zeitsch. Nahr. Genussm.*, 1908, 15, 732—734).—According to the process described, the organic matter of the food is destroyed by heating with sulphuric and nitric acids, the phosphoric acid is then precipitated by the addition of ammonium molybdate solution, and the amount of phosphoric acid in the precipitate is estimated volumetrically.

From 1 to 5 grams of the dry sample are heated in a flask with 5 c.c. of concentrated sulphuric acid and 5 c.c. of nitric acid until the nitric acid has been expelled and fumes of sulphuric acid are evolved. If the remaining solution is dark in colour, a little more nitric acid is added and the heating continued. The solution is cooled, diluted with 20 c.c. of water, boiled for a short time, and filtered to remove silica and any trace of undecomposed fat. The filtrate, amounting to 100 c.c., is then treated with 30 c.c. of 50% ammonia, heated to a temperature of about 80°, and 25 c.c. of 10% ammonium molybdate solution are added. The mixture is shaken for a short time and, after the lapse of fifteen minutes, filtered, and the precipitate washed with water by decantation until free from acid. The filter is next placed in the flask containing the precipitate, 150 c.c. of water are added, a measured quantity of $N/2$ sodium hydroxide solution (about 5 c.c. more than is required to dissolve the precipitate) is introduced, and the contents of the flask are boiled until all the ammonia has been expelled. The excess of sodium hydroxide is then titrated back, using phenolphthalein as indicator. Each c.c. of $N/2$ sodium hydroxide solution is equivalent to 0.001268 gram of phosphoric anhydride or to 0.000556 gram of phosphorus.

W. P. S.

Estimation of Phosphates in Urine. ANNIBALE FERRARO (*Boll. chim. farm.*, 1908, 47, 399—400).—In the estimation of phosphates in urine by Neubauer's method, the uranium solution must be run in in drops throughout, with brisk agitation, the solution to be tested being kept at the temperature of the boiling-water bath. The last reading should be taken after six to seven minutes of rapid stirring. When much calcium phosphate is present, it is better to run the solution to be tested from a burette into the uranium solution. Potassium ferrocyanide is to be preferred to cochineal as an indicator.

C. H. D.

The Dyer Method for the Determination of Plant Food in Soils. FRANK T. SHUTT and A. T. CHARRON (*J. Amer. Chem. Soc.*, 1908, 30, [iv], 1020).—Experiments are recorded showing the effect of (1) the time of digestion and (2) the volume of the solvent in making analyses of soil by Dyer's method (*Trans.*, 1894, 65, 115). The authors used a rich black loam from the prairie at Tisdale, Sask., described as typical of large areas in the Canadian north-western wheat belt, and characteristically rich in nitrogen and organic matter. Four sets of determinations were made: samples weighing 100 grams of soil were extracted for (a) seven days, (b) five hours, with 1000 c.c. of 1 per cent. citric acid, and (c) seven days, (d) five hours, with 500 c.c. of 1 per cent. citric acid; the results were:

		P ₂ O ₅ , per cent.	K ₂ O, per cent.	CaO, per cent.
Seven day digestion, 1000 c.c. solvent	(a) ...	0.02287	0.03818	0.5320
" " " 500 c.c. "	(c) ...	0.01999	0.03355	0.2718
Five hour digestion, 1000 c.c. "	(b) ...	0.01807	0.03958	0.5210
" " " 500 c.c. "	(d) ...	0.01599	0.03089	0.2285

A reduction in the volume of the solvent has materially reduced the percentages of phosphoric acid, potash, and especially of lime

obtained; reduction in the time of digestion has caused a falling off in the amount of phosphoric acid, has scarcely affected the lime, and not at all the potash. It is evident that the volume of the solvent is a more important matter than the time of digestion. E. J. R.

Detection of Arsenic in Urine. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, 56, 95—114).—The paper is mainly concerned with methods for oxidising the urine prior to the application of Marsh's test. The method recommended is to oxidise the evaporated alcoholic extract of the urine by treatment with 15 c.c. of nitric acid (D 1.48), and then to heat the mixture with 10 c.c. of sulphuric acid in a Kjeldahl flask, occasionally adding 0.5 c.c. of nitric acid until oxidation is complete. Various other practical details are discussed.

G. B.

Iodometric Estimation of Arsenic and Antimony in the Presence of Copper. F. H. HEATH (*Amer. J. Sci.*, 1908, [iv], 513—519; *Zeitsch. anorg. Chem.*, 1908, 59, 87—93).—The solution, which must contain the arsenic or antimony in the higher state of oxidation, is mixed with 1—2 grams of citric acid and then with potassium iodide (3 grams to 50 c.c., 5 grams to 100 c.c.). The iodine liberated, which represents the copper, is then titrated with standard thiosulphate. The filtrate from the cuprous iodide is treated with 1 c.c. of bromine and boiled in order to expel the iodine, if necessary with further addition of bromine, which is then in turn boiled off completely. The whole is now diluted to 100 c.c., and, after adding 2 grams of potassium iodide, the solution is boiled down to half its bulk. When cold, any free iodine is decolorised with sulphurous acid, using starch as indicator. After diluting again to 100 c.c., iodine solution is added until the liquid is coloured, and then very dilute sulphurous acid to make the colour disappear. Excess of sodium hydrogen carbonate is now added, and the arsenic or antimony titrated with standard iodine in the usual way.

When both arsenic and antimony are present, the copper estimation is not quite so satisfactory. L. DE K.

Parr's Method of Determining the Heat of Combustion of Coal. EMIL J. CONSTAM (*Zeitsch. angew. Chem.*, 1908, 21, 1414).—Polemical. A reply to Parr (this vol., ii, 533). P. H.

Volumetric Estimation of Carbon Dioxide and other Acids in Air. H. HENRIET and M. BOUYSSY (*Compt. rend.*, 1908, 146, 1100—1101).—The air is passed through standardised sodium or potassium hydroxide solution, and the latter is then diluted to a definite volume. One-half is next titrated with acetic acid, using phenolphthalein as indicator, and the decrease in titre of the solution multiplied by 2 is equivalent to the amount of carbon dioxide in the air; the neutral point is reached when the normal carbonate formed has been converted into hydrogen carbonate. The second half of the solution is then treated with barium chloride, and titrated with acetic acid without removing the barium

carbonate. The quantity of alkali required to neutralise the total acidity of the air is thus obtained, and the amount of the acids other than carbon dioxide may be calculated. W. P. S.

The Autolysator, an Apparatus for the Automatic Estimation of Carbon Dioxide. CHARLES A. KEANE and HARRY BURROWS (*J. Soc. Chem. Ind.*, 1908, 27, 608—610).—The apparatus is used for the automatic analysis of furnace gases. The absorption of the carbon dioxide is effected by means of soda-lime, and the pressure of the gas before and after the absorption is measured by differential manometers. The gas to be analysed is drawn by water suction of constant pressure through two similar capillary tubes, each of which is connected with a manometer. By interposing the absorbent substance between the two capillaries, the difference in pressure due to the absorption of the carbon dioxide is indicated on the manometer, provided that the flow of gas be so regulated that a constant volume flows through the apparatus. A full description, with diagrams, of the apparatus is given in the original paper. W. P. S.

Application of the Cobaltinitrite Method to the Estimation of Potassium in Soils. W. A. DRUSHEL (*Zeitsch. anorg. Chem.*, 1908, 59, 97—101. Compare this vol., ii, 66).—The method already described is applied to the estimation of potassium in soils. A weighed quantity of soil is extracted on the water-bath with 20% hydrochloric acid. The acid is then removed by evaporation, and the bases separated by addition of sodium carbonate or ammonia and ammonium oxalate. After removal of the ammonium salts and the organic matter by heating to redness, the residue is dissolved in water, acidified with acetic acid, and evaporated with excess of sodium cobaltinitrite. The further procedure is exactly the same as that previously described (*loc. cit.*). H. M. D.

Estimation of Lead in Alloys. W. ELBORNE and C. M. WARREN (*Chem. News*, 1908, 98, 1).—One gram of the alloy in fine shavings is put into a flask with 50 c.c. of hydrochloric acid, and a slow current of chlorine is passed for twenty-four hours. When all is dissolved (sometimes heat must be applied towards the end), the solution is transferred to a small weighed porcelain dish, evaporated to dryness on a water-bath, and the residue cooled in a desiccator.

The mass is then treated repeatedly with absolute alcohol; this dissolves all the chlorides present except the lead chloride, which is then dried at 100° for three hours and weighed. For fear any lead chloride may be lost, the filtrate and washings are passed through a weighed filter, which is then also dried at 100°. L. DE K.

Rapid Valuation of Pastilles of Mercuric Chloride and Cubes of Sodium and Potassium Iodides. PAOLO FIORA (*Boll. chim. Farm.*, 1908, 47, 401—402).—The mercuric chloride pastille (1 gram) is dissolved in water, and a solution of 1.162 grams of potassium iodide added. After filtering, a 1% solution of mercuric

chloride is added, the formation of a precipitate indicating a deficiency in the pastille. The quantity given allows a margin of 0.05 gram. For 1 gram cubes of potassium and sodium iodides, 0.776 and 0.859 gram of mercuric chloride are added respectively, a very dilute solution of potassium iodide being used for titrating back.

C. H. D.

Estimation of Cerium in the Presence of Other Rare Earths by the Action of Potassium Ferricyanide. PHILIP E. BROWNING and HOWARD E. PALMER (*Amer. J. Sci.*, 1908, [iv], 26, 83—84; *Zeitsch. anorg. Chem.*, 1908, 59, 71—73).—To a measured portion of the cerous sulphate (containing about 0.1 gram of cerium), which may contain also the sulphates of the other rare earths, are added 20 c.c. of 2% ferricyanide solution, and then a slight excess of aqueous potassium hydroxide. The precipitate is filtered off, and the filtrate and washings, amounting to about 200 c.c., are slightly acidified with dilute sulphuric acid, and the ferrocyanide formed by the reducing action of the cerous salt is then titrated as usual with standard permanganate; 2 mols. of ferrocyanide = 1 mol. of cerous oxide.

L. DE K.

Estimation of Iron and Vanadium in the Presence of Each Other. GRAHAM EDGAR (*Amer. J. Sci.*, 1908, [iv], 26, 79—82; *Zeitsch. anorg. Chem.*, 1908, 59, 74—78).—The process is based on the fact that ferric iron is reduced to the ferrous state both by the action of sulphur dioxide and amalgamated zinc, but in the case of vanadic acid, the reducing action of sulphur dioxide goes as far as V_2O_4 only, but that of zinc to V_2O_3 . The difference in permanganate used for re-oxidation after reduction with sulphur dioxide and the second reduction with zinc is a measure for the amount of vanadium present.

The solution is saturated with sulphur dioxide, a few c.c. of dilute sulphuric acid are added, and the liquid boiled in a current of carbon dioxide free from air. When all the sulphur dioxide has been removed, the flask is cooled rapidly, and the liquid titrated with standard permanganate until the colour changes from blue to yellowish-green; the liquid is then heated to 70—80°, and the titration continued. The liquid is now passed through a column of amalgamated zinc contained in a long Jones' reductor, being preceded by 150 c.c. of hot dilute 2½% sulphuric acid. After washing the zinc with 100 c.c. of the acid and then with 200 c.c. of water, the contents of the receiving flask (into which some pure ferric sulphate had been introduced, and which has been kept cool) are mixed with syrupy phosphoric acid and titrated with permanganate until the reaction is nearly at an end; the temperature is then raised to 70—80°, and the titration continued.

L. DE K.

Simultaneous Volumetric Estimation of Iron and Vanadium [in Ferro-Vanadium]. T. WARYNSKI and B. MDIVANI (*Ann. Chim. anal.*, 1908, 13, 210—212).—Three to four grams of the alloy are treated several times with nitrohydrochloric acid and nitric acid and evaporated to dryness, and the residue is boiled with dilute nitric acid and filtered

off from any silica. The filtrate is then evaporated with addition of hydrogen peroxide, and then again several times with sulphuric acid to expel the nitric acid. The mass is then dissolved in very dilute sulphuric acid, and diluted to 500 c.c.; 100 c.c. are taken for the estimation of the vanadic acid only by Bunsen and Mohr's method (distillation with hydrochloric acid, collecting the distillate in potassium iodide, and determining the iodine liberated). Another 100 c.c. are then taken for the joint estimation of the ferric oxide and vanadic acid by the authors' stannous chloride method (compare this vol., ii, 636).
L. DE K.

Estimation of Chromium as Silver Chromate. FRANK A. GOOCH and L. H. WEED (*Amer. J. Sci.*, 1908, [iv], 26, 85—86; *Zeitsch. anorg. Chem.*, 1908, 59, 87—93).—Chromium in the state of chromate or dichromate may be accurately estimated by adding to the solution an excess of silver nitrate, then a slight excess of ammonia, and finally acetic acid to slightly acid reaction. The silver chromate is collected on a Gooch filter, washed first with a dilute solution of silver nitrate to remove any soluble impurities, and then with small portions of water, 20—30 c.c. in all. The precipitate may be dried at 135°, or gently over a naked flame.
L. DE K.

Estimation of Tungstic Acid and its Separation from other Substances by means of a Mixture of Chlorine and Sulphur Chloride. FRANÇOIS BOURION (*Compt. rend.*, 1908, 146, 1102—1104).—It has been shown previously (Abstr., 1904, ii, 341) that tungsten trioxide when heated strongly in a mixture of chlorine and sulphur chloride yields volatile oxychlorides, and the method now proposed is based on this reaction; it is applicable to the estimation of tungsten trioxide in sodium tungstate, silicotungstic acid, &c. A portion of the sample is placed in a porcelain or silica boat, and is then heated in a glass tube through which a current of chlorine containing a little sulphur chloride is passed. The volatile substances are collected in a receiver containing water, and, when the operation is at an end, the contents of the receiver are evaporated with nitric acid, heated to remove sulphuric acid, the residue is taken up with ammonium nitrate solution, and the tungsten trioxide is collected on a filter and weighed. If any of the oxychloride condenses on the sides of the glass tube, the latter may be rinsed with ammonia and the solution added to the contents of the receiver. The silica may be recovered by extracting the contents of the boat with water and weighing the residue.
W. P. S.

A New Method of Separation of Silica and Tungsten Trioxide. EDOUARD DEFACQZ (*Compt. rend.*, 1908, 146, 1319—1320. Compare Abstr., 1907, ii, 475; Marignac, *Ann. chim. Phys.*, 1864, [iv], 3, 9; Friedheim, Henderson, and Pinagel, Abstr., 1905, ii, 614; Bourion, preceding abstract).—This is based on the facts that silica is unattacked, but tungsten trioxide is reduced by hydrogen at 600—900° either to lower oxides or to the metal, and that the latter are converted by chlorine into the volatile hexachloride

or oxychlorides. The mixture of silica and tungsten trioxide contained in a boat is heated to redness in a current of hydrogen. When the reduction is complete, the boat is introduced into a glass tube bent so as to admit of the condensation of volatile products, and heated in a current of dry chlorine. If the reduction has been complete and all the air has been expelled, a mixture of tungsten hexachloride and oxytetrachloride is volatilised, otherwise the product consists of a mixture of the red and yellow oxychlorides.

The receiver is washed out with dilute ammonia, and the tungsten estimated in one of the known ways. The silica remains in the boat, and should be quite white; it should give no colour reaction when fused with potassium hydrogen sulphate.

The method is generally applicable to mixtures of two oxides, only one of which is reduced by hydrogen to a metal, forming with chlorine a volatile chloride. E. H.

Tables for Converting Percentages of Alcohol by Volume into Percentages by Weight. A. BLONDEAU (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 1032—1045).—The tables given show the weights of alcohol corresponding with volumes of alcohol as determined by Gay-Lussac's hydrometer in mixtures of alcohol and water containing from 1 to 100% of alcohol by volume at any temperature between 0° and 30° W. P. S.

Estimation of Alcohol and Extract in Spirits by means of the Refractometer. JOSEPH RACE (*J. Soc. Chem. Ind.*, 1908, 27, 547—548).—A table is given showing the refractive indices of mixtures of alcohol and water containing from 1 to 100% of alcohol, the indices being given for each difference of 1%. Using this table, it is possible to estimate the quantity of alcohol and extract in a spirit. The refractive index of the spirit is taken at a temperature of 15·5°, and also that of the liquid obtained by evaporating 25 c.c. of the spirit almost to dryness and diluting the residue to the original volume. The difference between these results is due to the alcohol and other volatile constituents, and the difference between the refractive index of the extract and that of water is due to the extractive matters contained in the spirit. W. P. S.

Messinger and Vortmann's Method of Estimating Phenols. Separation of Salicylic Acid. J. BOUGAULT (*Compt. rend.*, 1908, 146, 1403—1405).—The violet-red compound obtained by Messinger and Vortmann (*Abstr.*, 1889, 1150) by the action of iodine and potassium hydroxide on phenol, and formed in these authors' method of estimating phenol (*Abstr.*, 1890, 1473), is not a di-iododiosobenzene, $C_6H_3I_2 \cdot OI$, but a mixture of 2:4:6-tri-iodophenol with the red substance obtained by Lautemann (*Annalen*, 1861, 120, 309), and shown by Benzinger and Kämmerer (*Abstr.*, 1878, 574) to be tetraiododiphenylenequinone.

Similarly, the substance obtained by Messinger and Vortmann from salicylic acid is a mixture of the same red substance with potassium 3:5-di-iodosalicylate. The extreme insolubility of Laute-

mann's red substance furnishes a means of estimating and separating salicylic acid. For example, a mixture of 0.1 gram of salicylic acid and 0.2 gram of cinnamic acid is dissolved in 50 c.c. of water and 1 gram of sodium carbonate. Excess of iodine is added, the whole heated on the water-bath for twenty minutes, and finally boiled for ten minutes under reflux, iodine being added from time to time to ensure excess being present. The latter is removed by sodium sulphite, and the precipitate collected on a Gooch crucible. The weight multiplied by 138/344 gives the weight of salicylic acid.

Lautemann's red substance is produced by the action of iodine on a solution of 2 : 4 : 6-tri-iodophenol in sodium carbonate.

J. C. C.

Estimation of Orcinol in Orchella "Weed." HENRY EDGAR WATT (*J. Soc. Chem. Ind.*, 1908, 27, 612).—The following method of estimating orcinol in Orchella weed (the name usually given to the lichen *Rocella tinctoria*) is given. Two grams of the powdered lichen are mixed in a mortar with 2 grams of sodium carbonate, and water is then added gradually until the mixture has a volume of 100 c.c. After being stirred occasionally for twenty minutes, the mixture is poured on a filter, and 50 c.c. of the filtrate are treated with an excess of standardised sodium hypochlorite solution. An excess of *N*/10 arsenious acid solution is immediately added, and the excess is titrated back with sodium hypochlorite solution, using as indicator starch-iodide solution acidified with acetic acid. The sodium hypochlorite solution must be standardised on pure orcinol. Four samples of orchella weed from the Seychelles were found to contain 11.5%, 1.6%, 8.8%, and 9.3% of orcinol respectively. In addition to the instantaneous reaction between orcinol and sodium hypochlorite on which the above method is based, a secondary and slower reaction appears to take place, and is not completed within twenty-four hours.

W. F. S.

Estimation of Sugar. IVAR BANG (*Biochem. Zeitsch.*, 1908, 11, 538—540).—Further details of the author's method are given, and Jessen-Hansen's remarks on the theory of the reaction criticised.

W. D. H.

Detection of Dextrose in Urine. ANDREAS OTTO (*Pharm. Weekblad*, 1908, 45, 809—813).—Kowarsky's phenylhydrazine test may be recommended, but the precipitate should be recrystallised from alcohol in order to obtain the typical crystalline form of the glucosazone; a slight excess of acetic acid does not influence the result. A rapid crystallisation does not affect the nature or the size of the crystals. Two minutes boiling with the reagent is not necessary, although desirable; addition of sodium chloride is not always necessary. The reaction with alkaline bismuth solution (Nylander's test) is accelerated and rendered more delicate by adding a few drops of platinic chloride, but attempts to make this a quantitative process by measuring the volume of the precipitate utterly failed, although there is no doubt as to the complete elimination of the dextrose. The addition of

platinic chloride is particularly of service if the phosphates have not been removed previously.

The ordinary Fehling test for sugar is not influenced by platinic chloride.
L. DE K.

Detection of Sucrose. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 1078).—A portion of the solution under examination is placed in a test-tube, and about 10 c.c. of concentrated sulphuric acid are then introduced, the test-tube being inclined so that the two liquids do not mix. If sucrose is present, a coloured ring appears at the junction of the liquids; the ring is red below and yellow above. The test will detect the presence of 0.00005 gram of sucrose. The reaction is also given by other carbohydrates, but it is most sensitive in the case of sucrose.
W. P. S.

Detection of Glycuronic Acid by B. Tollens' Method in Human Urine. KARL TOLLENS (*Zeitsch. physiol. Chem.*, 1908, 56, 115—116. Compare B. Tollens, this vol., ii, 639).—To 5 c.c. of urine, 0.5 c.c. of a 1% alcoholic solution of naphtharesorcinol and 5 c.c. of hydrochloric acid (D 1.19) are added; the solution is boiled for one minute over a small flame, left for four minutes, cooled, and extracted with ether. When glycuronic acid is present, the ether is coloured intensely blue, and when examined spectroscopically, shows a band near the sodium line.
G. B.

Estimation of Tartaric Acid in Argol and Wine Lees. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1908, 146, 1031—1032; *Ann. chim. anal.*, 1908, 13, 266—269; *Bull. Soc. chim. Belg.*, 1908, 22, 218—221; *Bull. Assoc. chim. Sucr. Dist.*, 1908, 25, 964—967).—The method proposed depends on the insolubility of barium tartrate in alcohol, and on the solubility of barium bromide in this medium. A weighed quantity of about 1 gram of the sample is treated with an excess of potassium carbonate solution, and the mixture is boiled and diluted to a volume of 100 c.c. Twenty-five c.c. of this solution are acidified with hydrochloric acid, boiled to remove carbon dioxide, and then rendered alkaline with ammonia. Forty c.c. of *N*/10 alcoholic solution of barium bromide and about 75 c.c. of 95% alcohol are added, the mixture is stirred, and the precipitate, consisting of barium tartrate, is collected on a filter and washed with alcohol. The precipitate may then be converted into barium sulphate and weighed as such, the tartrate being calculated from the weight of sulphate found, or the excess of barium bromide may be estimated in the filtrate. For this purpose, the filtrate is diluted with water, ammonium oxalate is added, the barium oxalate is collected on a filter, washed with dilute ammonia, then decomposed with hot dilute sulphuric acid, and the oxalic acid in the solution titrated with potassium permanganate solution. The difference between the quantity of barium bromide added and that found as oxalate in the filtrate is equivalent to the tartaric acid in the sample.
W. P. S.

Viscosity and Lubrication. CHARLES F. MABERY and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1908, 30, 992—1001).—The viscosity of lubricating oils is usually regarded as a standard of quality, but probably does not afford a trustworthy indication of the comparative durability of oils differing widely in composition. If the viscosity constant is supplemented by chemical data and frictional durability tests, it may no doubt be depended on as giving accurate information for commercial purposes. A large number of hydrocarbons obtained by the fractional distillation of petroleum have been examined, and a series of frictional tests have been carried out with them in comparison with castor, sperm, and rape oils.

The lubricating value depends on the temperature reached during the frictional test, the degree of friction, and the time for which the oil continues to lubricate. The durability of the individual hydrocarbons increases with decrease in hydrogen, and in a similar ratio to the increase in specific viscosity. A hydrocarbon of the series C_nH_{2n-4} was found to be more efficient in reducing friction than castor, sperm, or rape oil. It was equal to sperm oil in temperature and coefficient of friction, and superior to castor and rape oils in durability.

With regard to the comparative value of the various series of hydrocarbons in petroleum from which lubricating oils are prepared, those of the C_nH_{2n+2} series have a low lubricating value. Lubricating oils from Pennsylvania petroleum consist chiefly of the C_nH_{2n} and C_nH_{2n-2} series, whilst those from the heavier oils are composed largely of hydrocarbons of the C_nH_{2n-2} and C_nH_{2n-4} series.

Comparative examination of distillates from South American and Pennsylvania petroleums has shown that neither sp. gr. nor b. p. can be depended on as indicating the lubricating value unless the source of the oil is known.

Nothing is at present known as to the constitution of the series of hydrocarbons in lubricating oils. E. G.

Analysis of Hyposulphites and their Compounds with Formaldehyde. W. F. GREAVES (*J. Soc. Dyers*, 1908, 24, 195—196).—For the estimation of formaldehyde in the formaldehyde compound of sodium hyposulphite, the method described by Cross, in which the compound is heated with chromic acid, is recommended as being trustworthy. A Lunge's nitrometer is employed for measuring the carbon dioxide produced. The inner tube of a Lunge bottle is filled with 5 c.c. of cold saturated chromic acid solution, and 10 c.c. of a 10% solution of the compound under examination are placed in the part of the bottle surrounding the tube. The bottle is then connected with the nitrometer, the contents of the bottle are mixed and gently heated until the mixture just boils, the bottle is next cooled by placing it in cold water, and, at the end of one hour, the volume of the carbon dioxide is read off, the usual corrections for temperature, pressure, &c., being made. The method described by Knecht and Hibbert (*Abstr.*, 1907, ii, 907) for the estimation of sodium hyposulphite can be applied to the analysis of hyposulphite compounds which are not decomposed by water. W. P. S.

Folin's Method for Separating Acetone and Acetoacetic Acid in Urine. T. STUART HART (*J. Biol. Chem.*, 1908, 4, 473—476. Compare Abstr., 1907, ii, 588).—Folin's method was found to be a valuable one. In cases where acetone is excreted, the amount is far more constant than that of acetoacetic acid. If the total amount of the two substances increases, the increase is largely due to the acetoacetic acid. W. D. H.

Separation of Ammonia and Amines by means of Boiling Absolute Alcohol. JEAN BERTHEAUME (*Compt. rend.*, 1908, 146, 1215—1217; *J. Pharm. Chim.*, 1908, 28, 8—13. Compare Jarry, Abstr., 1899, ii, 738; Brochet and Cambier, *Bull. Soc. chim.*, [iii], 13, 533).—In order to determine the trustworthiness of the method of separating amine hydrochlorides by means of boiling absolute alcohol, the author has determined the solubilities of methylamine hydrochloride, ammonium chloride, and a mixture of the two in this solvent. The amine hydrochloride was prepared from bromoacetamide, and purified from ammonia by yellow mercuric oxide.

The quantities of the salts dissolved separately were determined by evaporation of the solutions and desiccation at 110°; in the case of the mixture of the two salts, François' method of analysis (Abstr., 1907, ii, 503) was employed. The values obtained were:

100	grams	absolute	alcohol	at	82°	dissolve	23.01	grams	NH ₃ MeCl.
100	"	"	"	"	78.5	"	1.538	"	NH ₄ Cl.
100	"	"	"	"	0	"	0.778	"	NH ₄ Cl.
100	"	"	"	"	82	"	{ 25.0	"	NH ₃ MeCl and
							{ 2.266	"	NH ₄ Cl.
100	"	"	"	"	0	"	{ 6.0	"	NH ₃ MeCl and
							{ 0.65	"	NH ₄ Cl.

From these results, it is obvious that the solubility of each salt in boiling alcohol is increased in the presence of the ether, that when a mixture of methylamine and ammonium hydrochlorides is extracted with boiling alcohol the two salts are dissolved in the proportion 11:1, and that on cooling to 0° the solution deposits 1.616 grams of ammonium chloride per 19 grams of methylamine hydrochloride, that is, a mixture containing 85% of the latter salt.

Employing François' method of analysis, the author finds (1) that if a saturated aqueous solution of pure methylamine hydrochloride is saturated with ammonium chloride at 15°, the product deposited on evaporation contains 9.2% of the latter salt; (2) that the crystals first deposited by a boiling alcoholic solution of Brochet and Cambier's crude methylamine hydrochloride contain 10.8% of ammonium chloride, and (3) that a saturated solution of ammonium and methylamine hydrochlorides in boiling absolute alcohol deposits, on cooling, crystals containing 8.5% of ammonium chloride.

These results are contrary to the general opinion that ammonium chloride is insoluble in saturated aqueous or alcoholic solutions of methylamine hydrochloride.

The conclusion is drawn that the method of separation is of very little use. E. H.

A Rapid and Delicate Method of Detecting Bile-pigments in Urine. WILLIAM MACADIE (*Pharm. J.*, 1908, [iv], 26, 686).—A modification of Gmelin's test. The urate precipitate, produced by adding a saturated solution of calcium chloride to the faintly acid urine, contains the bile-pigments; it is dissolved in a mixture of 1 part of hydrochloric acid (D 1.16) and 3 parts of alcohol, and while still in the centrifuge-tube, 5—6 drops of nitric acid, D 1.42, are added. G. B.

Proposed Method for the Routine Valuation of Diastase Preparations. WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1908, 30, 798—805).—Commercial potato-starch is washed, pressed dry, and dried gradually finally at 80°. The remaining water, generally about 10%, is then estimated. Other starches should not be employed. A quantity corresponding with 20 grams of anhydrous starch is then stirred with 100 c.c. of water, and poured into a flask containing 800 c.c. of boiling water; the boiling is continued for ten minutes, and hot water is added up to 1000 grams.

Fifty grams of the starch solution are weighed out into a series of flasks kept at 40°. To each are added increasing portions of the diastase solution (for instance, liquid malt ten times diluted). After ten minutes each bottle is tested for free starch with dilute iodine solution. This then gives an idea of the strength of the diastase product, as it shows how much is wanted to convert the starch into dextrin and sugar in a given time. The operation is then repeated, using double the quantities of starch solution and diastase solution. As a check, the sugar formed may be estimated. L. DE K.

Colorimetric Method Applicable to both Peptic and Tryptic Enzymes. HERBERT E. ROAF (*Bio-Chem. J.*, 1908, 3, 188—192).—Grützner's method of estimating the rate of proteolysis by the amount of carmin liberated from fibrin stained with that pigment has the disadvantage that it is only applicable to enzymes which, like pepsin, act in an acid medium; if used for trypsin, the dye is liberated by the alkali employed. Congo-red may be substituted for carmin, and fibrin stained with it may be used for both peptic and tryptic ferments. W. D. H.

Ferments and Anti-ferments. VII. Detection of Trypsin. MARTIN JACOBY (*Biochem. Zeitsch.*, 1908, 10, 229—231. Compare Abstr., this vol., i, 236).—A solution of ricin or a suspension of edestin remains cloudy in the absence of trypsin, and becomes clear when trypsin is present in an alkaline medium. W. D. H.

Süchting's Method for Estimating Acidity of Soils. A. J. VAN SCHERMBEK (*J. pr. Chem.*, 1908, [ii], 77, 489—497).—In Tacke's method for estimating soil acidity (Abstr., 1908, ii, 103), it is assumed that no acid is produced during the four hours required for

the determination. It is pointed out that, whilst under natural conditions the production of acids in the soil is checked when the acidity reaches a certain limit, the soil water is greatly diluted in the process referred to, and conditions are thus produced which are favourable to increased decomposition of the organic matter; the error is further increased by addition of calcium carbonate. Süchting's modification (this vol., ii, 231) has the advantage that the time required is reduced to about half; nevertheless, it yields results which may be far too high. A peaty sand, for example, showed an amount of acid corresponding with 1.44% HCl in the soil water, which is fifty to sixty times the amount in which it is possible for roots to live.

Correct results can only be obtained under conditions of sterilisation.
N. H. J. M.

Separation of Clay in the Estimation of Humus. C. A. MOOERS and H. H. HAMPTON (*J. Amer. Chem. Soc.*, 1908, 30, 805—807).—Determinations of the humus by evaporating the ammoniacal extract to dryness on a water-bath, so as to coagulate the clay, redissolving in 4% ammonia, and filtering, shows that this method gives more uniform results than direct filtration through a Pasteur-Chamberland filter, which gives low results, chiefly owing to loss of humus in the filter. Peter and Averitt's method (*Kentucky Stat. Bul.*, No. 126, 63—126), in which a factor is employed for correcting for loss in the clayey residue, was also found to be unsatisfactory; the results were not concordant, and the factor (10%) too low for the soils examined.

A number of determinations of humus in soils limed three years previously, and in the unlimed soils, showed that the small differences due to lime can be detected by the evaporation method described above.
N. H. J. M.

The Action of Heat on the Lecithin-Phosphoric Acid Contained in Pastry. W. LUDWIG (*Zeitsch. Nahr. Genussm.*, 1908, 15, 668—680).—It is shown that a considerable decrease in the amount of lecithin-phosphoric acid present in pastry takes place when the latter is heated for some time at a temperature of 102°. The loss is particularly marked in samples containing but little egg-material, and may amount to as much as 40%, calculated on the quantity present before the heating. The decrease is not due to loss of volatile phosphorus compounds, but to a portion of the lecithin being rendered insoluble in the solvents employed in the estimation of the lecithin-phosphoric acid. The total amount of phosphoric acid is the same after as before the heating. A small decrease in the amount of lecithin-phosphoric acid was also noticed when the pastry was kept for a few months. The author finds that practically the whole of the lecithin-phosphoric acid may be obtained in solution by boiling the pastry three times with absolute alcohol, the boiling being continued for twenty minutes each time.
W. P. S.

General and Physical Chemistry.

Magnetic and Electric Double Refraction of Nitrobenzene. Variation with Wave-length. A. COTTON and HENRI MOUTON (*Compt. rend.*, 1908, 147, 193—195. Compare Abstr., 1907, ii, 727; this vol., ii, 2).—The differences between the ordinary and extraordinary indices of refraction of nitrobenzene in the magnetic field increase regularly when the wave-length of the light diminishes. Measurements have been made with the yellow, green, and indigo mercury lines, and with the *C* and *F* lines of hydrogen. Kerr's phenomenon has been studied in the case of pure nitrobenzene, using small differences of potential, and it is found that the dispersion is the same in the case of electric as in the case of magnetic double refraction; the temperature-coefficient is also approximately the same for each. The two phenomena therefore appear to have a common origin, and this may be sought in molecular orientation. W. O. W.

Spectrum of the Discharge from a Glowing Lime Cathode in Mercury Vapour. F. HORTON (*Proc. Camb. Phil. Soc.*, 1908, 14, 501—507).—The spectrum of the discharge between an electrically heated Wehnelt cathode and an aluminium anode exhibits five new lines, which are shown to be due to mercury. The wave-lengths of the lines are 6912, 6715, 6232, 6121, and 6070. The fact that these have not been described previously is supposed to be due to their absence from the ordinary arc or spark spectrum. H. M. D.

Spectra of the Calcium Flame. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1908, 147, 188—190).—A spectrophotographic study of the calcium flame obtained by the apparatus previously described (this vol., ii, 336). The spectra are considerably richer in lines than the flame spectra hitherto obtained. A table is given showing the wave-lengths of the lines and also their relative intensities when the spark is used in conjunction with air-gas, air-hydrogen, oxygen-coal gas, and oxyhydrogen flames, and also when the de Watteville pulverisation method with an air-gas flame is employed. W. O. W.

Absorption Spectra of some Compounds obtained from Pyridine and Collidine. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1908, 14, 435—440. Compare Baker and Baly, *Trans.*, 1907, 91, 1122).—The absorption band of 3:5-dichloropyridine is found to be displaced towards the red end of the spectrum when compared with that of pyridine. The amount of the displacement and the persistence of the band are, however, smaller than has been found in the case of 3:4:5-trichloropyridine. These effects are in agreement with previous observations relating to the influence of the introduction of chlorine into the pyridine nucleus.

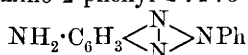
The absorption band of collidine hydrochloride is also displaced towards the red end relatively to that of the free base, and the persistence of the band is increased by union with hydrochloric acid.

Observations have also been made with the heptachlorolutidine obtained by Sell and Foster from the enneachlorocollidine previously examined. Compared with that of the latter substance, the absorption band of heptachlorolutidine is displaced towards the red, and its persistence is considerably greater.

H. M. D.

Change of the Colour of Fluorescence with the Solvent.

HEINRICH LEY and K. VON ENGELHARDT (*Ber.*, 1908, 41, 2509—2516).—It has been observed repeatedly that the colour of fluorescence depends on the nature of the solvent in which the fluorescent substance is dissolved. Kehrman and Messinger (*Abstr.*, 1892, 889) and Kauffmann and Beisswenger's investigations (*Abstr.*, 1905, ii, 131) point to a relation between the colour of fluorescence and the dielectric constant of the solvent, whilst Stark (*Abstr.*, 1907, ii, 147) draws attention to the relation of fluorescence to selective absorption. The present authors have now studied the changes in the absorption spectra of substances with varying fluorescence when dissolved in various solvents, the absorption curves being carried into the ultra-violet. As objects of study were chosen 5-amino-2-phenyl-2:1:3-benzotriazole,



(Kehrman and Messinger, *loc. cit.*), and dimethylnaphtheurhodine (Kauffmann and Beisswenger, *loc. cit.*) in methyl-alcoholic, ethyl-alcoholic, ethereal, chloroform, ethyl acetate, and carbon disulphide solutions. The results are tabulated and expressed in curves.

It is found that with the benzotriazole, the fluorescence changes from bluish-green through blue to bluish-violet, and the absorption is shifted towards the ultra-violet when the base is dissolved in alcohol, ether, and chloroform in the order named. That the solution in carbon disulphide is not fluorescent is to be ascribed to the formation of an additive *compound*, in agreement with which it is found that the solution in carbon disulphide is stable towards light, whereas the solutions in other solvents, especially in chloroform, are rapidly decomposed on exposure to light. The fluorescence is weakened by addition of acids, but disappears only in presence of an excess of hydrochloric acid; this change also is expressed in the absorption curve. It is probable that the hydrochloride fluoresces in the ultra-violet.

With the eurhodine base, also, the colour of the fluorescence changes with the shifting of the absorption towards the ultra-violet, but in the order of solvents: alcohol, chloroform, ethyl acetate, ether, from reddish-yellow through yellowish-green to yellow.

G. Y.

Fluorescence and Photo-electric Sensitiveness of Organic Substances. JOHANNES STARK and W. STEUBING (*Physikal. Zeitsch.*, 1908, 9, 481—495. Compare *Abstr.*, 1907, ii, 147, 417; this vol., ii, 138).—The authors have made experiments on a large number of

substances to ascertain the relationship between fluorescence, on the one hand, and the nature of the banded absorption spectrum and the photo-electric effect, on the other.

Benzene and derivatives of it containing no other chromophoric group exhibit fluorescence bands which, like the corresponding absorption bands, decrease in intensity with increasing wave-length. The fluorescence spectrum of benzene is situated in the region of smallest wave-lengths, substitution of one or more hydrogen atoms leading to a displacement of the spectrum towards greater wave-lengths. The same phenomenon is met with in the case of condensed or coupled ring compounds. The displacement produced by successive substitution shows a gradual decrease. Of the various substituting groups investigated, the methyl group produces the least displacement and the amino-group the greatest. The fluorescence spectrum of benzene, naphthalene, anthracene, phenanthrene, and certain other aromatic hydrocarbons consists of several distinct bands, but if hydrogen in the ring is substituted by another element or group, or if two benzene rings are coupled by other atoms than carbon and hydrogen, a continuous spectrum is obtained. Substances containing a chromophoric group, but not a benzene ring, do not exhibit fluorescence.

As a result of the examination of the photo-electric properties, the conclusion is drawn that substances which fluoresce are also photo-electrically active. The greater the photo-electric effect the more intense is the fluorescence. Quinine sulphate is an exception, and it is suggested that this is due to a difference in the constitution of the solid and the dissolved substance.

The fluorescence of benzene derivatives containing another chromophoric group has been examined. The behaviour of these can be anticipated from that of the two simpler classes of substances.

An explanation of the phenomena of fluorescence and of photo-electric activity is given in terms of the electronic theory discussed in the authors' previous papers.

H. M. D.

A Case of Anomalous Rotatory Dispersion. Application of Measurements of Rotatory Dispersion to the Study of the Composition of Oil of Turpentine. EUGÈNE DARMOIS (*Compt. rend.*, 1908, 147, 195—197).—French levorotatory turpentine has practically constant properties, and probably contains *l*-pinene. Other oils are usually dextrorotatory, and probably contain *d*-pinene. The rotatory dispersion of certain lævo- and dextro-oils has been studied, and it is found that the dispersion is normal, but varies with the oil examined. Certain mixtures of dextro- and lævo-oils, however, exhibit anomalous dispersion, the results not being in accordance with those calculated from Biot's law of mixtures. These mixtures can, moreover, be produced by distillation of any dextro-oil, by stopping the operation at the right point. The conclusion is drawn that the two dextro- and lævo-oils are not chemically homogeneous. Crystallisable *l*-pinene has been isolated from the lævo-oil. The dextro-oil probably contains *d*-pinene together with an unknown substance having less dispersive power than *l*-pinene.

W. O. W.

Triboluminescence of Racemic Compounds. DÉSIRÉ GERNEZ (*Compt. rend.*, 1908, 147, 11—15. Compare Tschugaëff, *Abstr.*, 1905, ii, 132).—A number of *d*- and *l*-tartrates and the corresponding racemates have been examined with the object of testing Tschugaëff's theory, that when the two active forms are triboluminescent the racemic compound is not. In confirmation of the theory, the author finds that *l*-tartaric acid, like the dextro-modification, is triboluminescent and racemic acid is not. Dextro- and lævo-potassium tartrates and potassium racemate, and *d*- and *l*-ammonium tartrates and ammonium racemate, obey the rule, as also does the double racemate of sodium and potassium, the constituents of which are both triboluminescent. Contrary to Tschugaëff's statement, acid potassium racemate is triboluminescent as well as the acid potassium tartrates.

The following substances are all triboluminescent and contrary to Tschugaëff's theory: the normal tartrates and racemates of rubidium, sodium, and thallium; the acid tartrates and racemates of ammonium, potassium, rubidium, sodium, and thallium, and the double racemates of ammonium-lithium, antimonyl-potassium, caesium-lithium, lithium-potassium, lithium-rubidium, lithium-sodium, lithium-thallium, rubidium-sodium, sodium-thallium. Lithium racemate is triboluminescent, but the lithium tartrates could only be obtained in a non-crystalline condition, and appeared to give no light when crushed.

The *d*- and *l*-tartrates and the racemates of quinine, strychnine, and brucine, and the acid *d*- and *l*-tartrates and acid racemates of cinchonine, strychnine, and brucine, are all crystalline substances exhibiting triboluminescence.

There are only six authentic cases in favour of Tschugaëff's rule as compared with a large number in opposition to it. No general relation can be detected between molecular symmetry and triboluminescence.

R. J. C.

Thermodynamic Treatment of Photochemical Processes. FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1908, 63, 458—466).—Various formulæ are deduced by the author, and their bearing on the experimental results obtained by Luther and Weigert (*Abstr.*, 1905, ii, 785) are discussed. He reaches the result that in the system anthracene-dianthracene the energy which is chemically utilised in unit time is in all cases practically proportional to the light absorbed by the anthracene. If this is accepted, then it is possible on a thermodynamic basis alone to interpret all the experimental results observed by Luther and Weigert. The electrochemical theory recently propounded by Byk (this vol., ii, 339) appears to be unnecessary.

J. C. P.

Emission of Electricity from the Induced Activity of Radium. WILLIAM DUANE (*Amer. J. Sci.*, 1901, [iv], 26, 1—13).—The rate of decay of the induced activity of radium has been investigated by measurements of the quantity of electricity carried by the α - and β -rays instead of the ions produced by these. The induced

activity was deposited on the surface of a small metallic cylinder, which, during the electrical measurements, was supported co-axially inside a tube of the same metal in such a way that the distance between the outer surface of the cylinder and the inner surface of the tube only amounted to 0.44 mm. The current flow between the cylinder and the tube was measured by means of a quadrant electrometer.

The decay curves obtained in this way do not coincide with the curves corresponding with the diminution of the ionisation, and this is attributed to the emission of negative rays by radium-*B*. From the variation of the rate of discharge with the time, the conclusion is drawn that the same quantity of electricity is discharged when radium-*B* changes into radium-*C* as when radium-*C* changes into radium-*D*.

In a magnetic field parallel to the active surface, or an electrical field normal to the surface, the rate of discharge is altered; the magnitude of the observed effects is what would be expected if the charge were carried by electrons moving with velocities, normal to the active surface, of, or less than, 4×10^8 cms. per second.

The number of ions produced by the α -rays in air is less than 9000 times, and probably less than 3600 times the number of β -particles emitted by the active deposit in the same time. Assuming that each α -particle from radium-*C* produces 180,000 ions, it follows that at least 20, and probably more than 50, electrons are emitted from an active (brass) surface for every α -particle which is expelled from radium-*C*.

The experiments also show that the ionisation caused by radium-*B* and radium-*C* in the air in the immediate neighbourhood of the active surface is approximately the same.

H. M. D.

Coefficient of Absorption of Radioactive Emanations in Different Liquids. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 319—320).—A claim for priority (compare Koder, this vol., ii, 80).

W. A. D.

Photographic Impressions Produced by Radium Emanation. JOSÉ MUÑOZ DEL CASTILLO and FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 322—323).—Radioactive solutions having an activity of 2,100,000 volts per hour per litre produce very good radiographs with an exposure of thirty hours; solutions with an activity of 2100 volts per hour per litre in the same circumstances do not affect the plate.

W. A. D.

Radioactivity of Swedish Spring Waters. HJALMAR SJÖGREN and NAIMA SAHLBOM (*Arkiv. Kem. Min. Geol.*, 1908, 3, i, No. 2, 1—28).—The authors have examined about sixty spring waters from central and southern Sweden, and find in all cases evidence of the presence of a radioactive emanation. The samples of sea-water examined were found to be inactive. The degree of activity of a spring water depends on the chemical character and quantity of the water and on the depth of the spring. In some waters the emanation

is found to be more abundant in winter than in summer. A close connexion exists between the radioactivity and geological character of a well, water from the granite showing the highest and that from sedimentary rocks the lowest activity. In all cases, the radioactivity observed was found to correspond with that of radium. The ochre deposited by some of the springs exhibits slight radioactivity, but the mud deposits are quite inactive. T. H. P.

Radioactivity of the Waters of Lerez. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 237—242).—An investigation of the rate of decay of the radioactivity of the highly active waters of Lerez (compare Abstr., 1907, ii, 218). The initial activity probably exceeds 10,000 volts per hour per litre, and diminishes according to an exponential equation similar to that characteristic of radium; after about fifty days, however, a nearly constant residual radioactivity of about 20 volts is reached. It is probable that the radium emanation is responsible for the greater part of the radioactivity of these waters, but some other active substance is also present. W. A. D.

Radioactivity of Waters of Agaete (Canary Islands). FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 242—243).—The chalybeate water of the thermal springs of Agaete has a temperature of 25° and is decidedly radioactive, one sample having an activity of 8.9 volts per hour per litre. W. A. D.

Radioactivity of Water from Cucho. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 350).—The water of the San Roque spring, in the valley east of Cucho, province of Burgos, contains hydrogen sulphide, and has a temperature of 15° and an initial activity of about 74 volts per hour per litre. W. A. D.

Radioactivity of Mud from the Baths of Fitero Viejo. FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 344—350).—From the character of the radioactivity of the mud, it is concluded that radium is present partly in a form soluble in hydrochloric acid and partly in an insoluble form. Thorium is entirely absent, but actinium may be present. W. A. D.

Radioactivity of Potassium and other Alkali Metals. J. C. MCLENNAN and W. T. KENNEDY (*Physikal. Zeitsch.*, 1908, 9, 510—512.* Compare Abstr., 1907, ii, 217, 597).—The radioactivity of a large number of potassium salts and of certain salts of sodium, ammonium, lithium, rubidium, and calcium has been examined by measuring the saturation current produced by the various salts when distributed in thin uniform layers on the base of an ionisation chamber. All the potassium salts and metallic potassium were found to be radioactive, but when the activities are divided by the percentages of potassium in the various compounds, numbers are obtained which vary in the ratio of one to thirty-three. The author considers that this precludes the possibility that the radioactivity is a normal property of the potassium atom. With the exception of one

* and *Phil. Mag.*, 1908, [vi], 16, 377—395.

sample of rock salt out of three examined, all the sodium salts and metallic sodium were found to be inactive. Ammonium chloride was found to be slightly active, rubidium alum and caesium chloride still less so, and the other salts showed no trace of activity. The activity of the salts other than those of the alkali metals is supposed to be due to traces of radioactive impurities.

The activity of the potassium salts is unchanged on heating, and attempts to separate active impurities by electrolysis, recrystallisation, solution in ethyl ether, and by precipitation with ammonium carbonate gave no positive result.

H. M. D.

Nature of the γ -Rays. JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 540).—Of the two views which have been advanced as to the nature of γ -rays: (1) that they are pulses of electromagnetic disturbance propagated through the ether; (2) that they are electrical doublets travelling with great velocity and possessing energy and momentum, it is pointed out that these approximate closely if it is supposed that the electromagnetic disturbance is distributed, not uniformly, but in patches over the wave-front. According to the pulse theory, the velocity of propagation of the rays should be equal to that of light, which is the case according to available experimental data. Barkla's measurements of the polarisation of the secondary rays produced by the γ -rays are also in accord with the pulse theory. By means of these two factors, it is possible to differentiate between the two theories.

H. M. D.

Velocity of Secondary Cathode Rays from Gases. JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 541—545).—The blue pencil of cathode rays emanating from a Wehnelt cathode, on which the lime is confined to a small area, is surrounded by a blue haze. This is due to secondary rays produced by impact of the primary cathode rays against the gas molecules. If a piece of metal is inserted in the region occupied by the haze and the metal is negatively charged to a moderate potential, the negative particles of the haze are repelled and the metal is surrounded by a well-defined dark space. Experiments are described the object of which was to determine the difference of potential required to stop the negative particles. It is found that this potential difference is independent of the potential of the primary discharge, indicating that the energy of the secondary rays is independent of that of the primary rays. This result is in agreement with the view that the energy in the secondary rays is determined by the atoms emitting them. The energy of the secondary rays does not seem to vary much with the nature of the atoms emitting them, for air, hydrogen, and carbon dioxide give the same value, and this is very nearly equal to the value found by Fichtbauer for the secondary rays from metals.

From the potential difference required to stop the secondary rays, the velocity of these is calculated to be 3.7×10^8 cms. per second.

H. M. D.

Positive Electrons. JEAN BECQUEREL (*Compt. rend.*, 1908, 147, 121—124. Compare Abstr., 1907, ii, 421).—In order to justify the

suggestion that several experiments are best explained by assuming the existence of free positive electrons, the author critically examines his results to see whether they are explainable on any other hypothesis.

In the modified Crookes tube previously described, the beam issuing through the hole in the principal cathode appears to be separated by a magnetic field into (1) strongly deviated cathode rays (negative electrons); (2) canal rays (positive ions), which, being presumably attracted by the cathode corpuscles, are slightly deviated in the same direction; (3) rays which are strongly deviated in the opposite direction. The last are supposed to consist of positive electrons.

The positive charges direct themselves towards a second cathode, which is ring-shaped, and having passed through, produce a phosphorescence on a disk of willemite, although they are no longer deviable by a magnetic field. This phosphorescence is not due to the canal rays, which have insufficient penetrating power to reach the willemite. If the willemite disk is brought near to the second cathode, a phosphorescent patch due to canal rays can be seen distinct from that due to positive electrons. The former patch is practically unaffected on bringing a magnet near the second cathode, whereas the latter is notably displaced. The phosphorescent spot due to positive electrons is in respect of position, intensity, and shape independent of the distance of the willemite from the second cathode. The spot due to canal rays, on the other hand, is scarcely perceptible unless the willemite is quite near the second cathode and is negatively charged. Alteration of the electric field by bringing the hand near the tube is sufficient to displace the canal rays, whilst the beam of positive electrons, being apparently not electrified, remains unaffected.

The positive deviable beam cannot consist of ions, because these would be attracted by the cathode stream in the opposite direction to that which the beam in question actually takes. The attraction would, however, be small, and as a matter of fact the canal rays are but slightly deviated along with the cathode stream.

The two images formed on the willemite are not due to canal rays going partly through the ring cathode and partly round it. In one vacuum tube in which this was possible, the canal rays produced a phosphorescent image of the ring cathode on the willemite, but the other, a strong phosphorescent spot, was always present as well.

The deviable ray cannot consist of positive ions of low velocity, since positive ions travelling with the same *E.M.F.* (the canal ions) are already present, and are hardly deviable. The fact that the beam in question, after passing through the second cathode, is apparently no longer electrified, suggests that it is a combination of positive ions with negative electrons. Righi, however, has shown (*Atti R. Accad. Lincei*, 1908, 17, 87) that such systems would, in a magnetic field, be deviated parallel to the lines of force.

Having failed to explain the phenomena by any recognised form of radiation, the author was led to consider the deviable rays as positive electrons liberated by the action of cathode rays on canal rays. The mechanism by which positive electrons are liberated is still obscure.

Perhaps they are grouped at the centres of atoms, and are attracted out by the atmosphere of cathode corpuscles. The negative electrons may act like projectiles against the positive ions which constitute canal rays.

The rapidity with which positive electrons disappear when they emerge from the atmosphere of negative electrons is surprising. The beam beyond the second cathode must be a flux of neutral material formed when the positive electrons disappear. The positive electrons may then have re-combined with the gas in the tube, but if the isolation of two kinds of electrons can be supposed to constitute the complete disintegration of matter, a bolder hypothesis is permissible, namely, that positive electrons combine directly with negative electrons, giving rise, perhaps, to hydrogen, which always appears in a Crookes tube.

R. J. C.

Ionised Gases. A. BLANC (*Compt. rend.*, 1908, 147, 39—42).—The mobilities of positive and negative ions in mixtures of carbon dioxide with hydrogen or air in varying proportions have been measured by a modification of Rutherford's alternating magnetic field method. It is found that the curves representing the inverse of the mobility in terms of the partial pressure of one of the gases in the mixture are in all cases straight lines. An equation is deduced theoretically connecting the mass of an ion with its mobility and the molecular composition of the mixed gases. From this it follows that if the effect of collisions between ions and molecules can be neglected, the mass of an ion must be of the same order as the mass of a molecule.

A positive or negative ion produced in carbon dioxide and travelling into air assumes the ordinary velocity of an ion produced in air.

The author supposes that an ion consists of a cluster of molecules which are constantly interchanged with the molecules of the surrounding gas. A carbon dioxide ion entering air, speedily becomes transformed into an air ion.

R. J. C.

Bose's Phenomenon and the Laws of Contact Electrification. ÉDOUARD GUILLAUME (*Compt. rend.*, 1908, 147, 53—55. Compare Bose, *J. Physique*, 1902, iv, 1, 481).—The production of an *E.M.F.* when a metallic thread immersed in an electrolyte is sharply twisted and the appearance of fatigue in this phenomenon have been further investigated.

If the wire is perfectly clean and the electrolyte is without action on it, no *E.M.F.* can be obtained by twisting the metal. Metals like copper and zinc when immersed in the electrolyte become covered with a thin, grey film. In such cases, twisting the wire produces a potential difference which is independent of the direction, but proportional to the angle of torsion. A number of twists at short intervals produce a gradually diminishing electrification. If a metal which is not superficially attacked by the liquid is covered with a thin, porous film, the same effects can be produced. Thus silver may be coated with its iodide, and platinum with gelatin or a burnt on film of kaolin.

The phenomena can be explained by Perrin's rules of contact electrification (see following abstract), which enable the relative effects of various electrolytes to be calculated with considerable accuracy. R. J. C.

The Bose-Guillaume Phenomenon and Contact Electrification. JEAN PERRIN (*Compt. rend.*, 1908, 147, 55—56).—The following explanation is given of the phenomena observed by Bose and by Guillaume (preceding abstract). When a wire covered with a thin, porous film is immersed in an electrolyte, the spongy sheath is electrified by contact along the whole of its enormous surface. The impregnating solution therefore contains an excess of ions of the opposite sign. When the wire is sharply twisted, the sheath is stretched, and a minute amount of the charged impregnating liquid is squeezed out into the external solution, leaving behind an excess of electricity of the opposite sign, which gives rise to a momentary *E.M.F.*

The extent and sign of the potential difference is determined by the nature of the contact electrification between the material of the film and the electrolyte. H^+ and OH^- ions produce strong positive and negative effects, but are paralysed by multivalent ions of opposite sign.

Electrification by torsion is analogous with electrification by filtration through a porous diaphragm. R. J. C.

Conduction of Electricity by Metals and Amalgams. JENÖ KINSKY (*Zeitsch. Elektrochem.*, 1908, 14, 406—410).—The experiments were intended to test the question whether positively-charged ions take any part in the transport of electricity through metals. Several copper and zinc cylinders with accurately-ground surfaces of contact were placed in contact and 5200 ampere hours passed through them, but no change in weight could be detected; iron and brass gave the same result. With silver and copper plates, no change of weight occurred, and the silver was quite free from copper both before and after the experiment. A large quantity of electricity was also passed through a tube containing homogeneous barium amalgam; after the experiment, the barium was found to be still quite evenly distributed throughout the tube. It appears, therefore, that positive ions take no part in the conduction of the current. T. E.

Relation between Current and Potential Difference in Solutions of Iodine in Potassium Iodide. Experiments with Bright Platinum Electrodes. ERICH BRUNNER (*Zeitsch. physikal. Chem.*, 1908, 63, 487—506. Compare Abstr., 1907, ii, 223).—The experiments have been carried out in the same way as previously described (*loc. cit.*). Except in the neighbourhood of the cathodic limiting current, the values obtained for the polarisation are, as a rule, only a few millivolts greater than those observed at platinised electrodes. The results obtained at the unplatinised electrodes may be expressed by the formula $\epsilon = \epsilon_0 + I(\omega_0 + q.\omega')$ (compare *loc. cit.*), where q varies between 1 and 8, mostly between 2 and 5: during one experi-

ment, and generally also during a series of experiments made successively in different solutions, q is fairly constant.

It is possible that the excess of the polarisation observed at unplatinised electrodes over that found at platinised electrodes is due to a surface resistance caused by cathodic polarisation, a resistance which vanishes as rapidly as it is produced. The excess, as far as can be seen, has nothing to do with chemical polarisation. J. C. P.

Thermodynamic Calculation of Electromotive Forces. FRANZ HALLA (*Zeitsch. Elektrochem.*, 1908, 14, 411—414).—Nernst's theory of the relation between heat development and maximum work in reactions in condensed systems (Abstr., 1907, ii, 153) is tested for the case of the two reactions $2\text{Ag} + \text{PbCl}_2 = \text{Pb} + 2\text{AgCl}$ and $2\text{Ag} + \text{Hg}_2\text{Cl}_2 = 2\text{Hg} + 2\text{AgCl}$, using existing data. Satisfactory agreement is found between the requirements of the theory and the facts. T. E.

Discharge Potentials of the Ions in Solutions of Alkali Alkylloxides. GIACOMO CARRARA and ALDO BRINGHENTI (*Gazzetta*, 1908, 38, i, 698—708).—The anode potential curves of solutions of sodium methoxide in methyl alcohol and sodium ethoxide in ethyl alcohol exhibit characteristic points at 0.32—0.34 volt, referred to the potential of the decinormal calomel electrode as zero. These values, which differ so little in the two cases that they cannot be differentiated, represent the discharge potentials of the ions (OMe) and (OEt). Similar close agreement exists between the heats of formation of the corresponding sodium salts, and it is probable that the tensions of electrolytic decomposition of these salts are also nearly equal in value. Another less sharply marked point is shown by the anode potential curves between 0.60 and 0.65 volt; it is possible that this corresponds with the discharge potential of anions of small quantities of aldehydes or acids formed by the oxidising action of the platinised platinum in presence of air. The corresponding cathode potential curves exhibit a common characteristic point at 1.22 volts, which represents that of the sodium ion. T. H. P.

Stability of the Alternating Arc; a Function of the Atomic Weight of the Metallic Electrodes. CHARLES E. GUYE and A. BRON (*Compt. rend.*, 1908, 147, 49—51).—It was shown in a recent paper (this vol., ii, 561) that the minimum potential required for a stable alternating arc largely depends on the period of extinction of the arc. This theory is now applied to elucidate the results of the authors' earlier researches on short metallic arcs.

Given the same current density, gap between electrodes, period of alternation, and air pressure, the voltage required to establish a stable arc increases regularly with the atomic weight of the electrodes. For example, with arcs 5 mm. long and current density 0.04 ampere per sq. centimetre of electrode, the voltages required are: carbon, 640; magnesium, 700; iron, 850; nickel, 850; copper, 870; silver, 900; cadmium, 725; platinum, 1000; gold, 1070. Cadmium is an exceptional case, as metallic vapour is largely produced, and the arc therefore requires an abnormally low voltage.

The period of alternation being 50, the arc is extinguished and re-lighted 100 times every second. The voltage required to re-light the arc must be the greater the more rapidly the electrodes cool at each extinction. The authors suppose that the cooling of the electrodes is for the most part the result of radiation, which is almost independent of the nature of the metal. Hence, as the specific heat is inversely as the atomic weight (Dulong and Petit), the higher the atomic weight the smaller the heat content of the electrodes, the quicker the cooling, and the higher the voltage required to re-light the arc.

It may also happen that electrons projected from the incandescent cathode have a velocity which is higher the higher the atomic weight. The two explanations are not mutually exclusive. R. J. C.

Chemical Reactions in a Magnetic Field. G. BERNDT (*Physikal. Zeitsch.*, 1908, 9, 512—519).—The influence of a magnetic field on the heat development which accompanies the solution of iron in hydrochloric and sulphuric acids has been examined. The apparatus employed consisted of an electromagnet with square pole-pieces, between which a magnetic field of intensity equal to 3000 Gauss could be established. Two silvered Dewar vessels, packed in cotton-wool, were placed between the pole-pieces, and by means of a nickel-copper thermo-element the difference of temperature between the contents of the two vessels was read off at frequent intervals. One Dewar vessel served for the solution process, and the other acted as a blank to eliminate, as far as possible, temperature changes not due to the passage of iron into solution.

The estimated accuracy of the measurement of the difference between the heat of solution with and without a magnetic field is 1%, and to this extent the experimental data lead to the conclusion that a magnetic field has no influence on the amount of heat developed by the solution of iron in hydrochloric or sulphuric acids. It is shown that the differences previously obtained by Nicholls (*Abstr.*, 1886, 668) are due to secondary disturbances, and that, although it has been shown by Duhem that the development of heat in a magnetic field should theoretically be less than without a field, the difference in question is too small to be experimentally measured.

One difference between the two processes is that the rate of solution in a magnetic field is smaller, and this is attributed to the fact that the iron particles do not respond so readily to the mechanical disturbances resulting from the evolution of gas. The protection of the iron from the action of the acid by the chloride formed may also contribute to the slower rate of solution in the magnetic field.

Experiments with zinc show that the heat change and the rate of solution are not influenced by a magnetic field. H. M. D.

Relation between Magnetic and Chemical Properties of Complex Ferric Salts. P. PASCAL (*Compt. rend.*, 1908, 147, 56—58).—The magnetic susceptibilities of a number of solutions of ferric compounds containing the same weight of iron per litre have been determined by the well-known U-tube method. It is found that as the condition of the iron is more and more removed from

the ordinary (precipitable) ferric state, the solutions become more and more diamagnetic. The gradual addition of acid to ammoniacal ferric pyrophosphate is accompanied by a corresponding increase in paramagnetism, even before the solution has attained to the ordinary ferric colour. Excess of alkali, on the other hand, accentuates the diamagnetism of a ferripyrophosphate.

Ferrimetaphosphates and ferripyrophosphates exhibit the phenomenon of magnetic double refraction. R. J. C.

Orientation of Crystals by the Magnetic Field. Importance of Optical Properties of Mixed Liquids from the Point of View of Crystalline Symmetry. A. COTTON and HENRI MOUTON (*Compt. rend.*, 1908, 147, 51—53. Compare *Abstr.*, 1906, ii, 146; 1907, ii, 727).—The magnetic susceptibility of a crystal in various directions may be represented by an ellipsoid. Electrical and optical properties are also represented by ellipsoids. Although the relation between the ellipsoids cannot be generally stated, the elements of symmetry of the crystal belong to all three. Crystalline fragments suspended in a liquid in a magnetic field will tend to set themselves with the long axis of their magnetic ellipsoid parallel to the lines of force. In an electric field, the long axis of the electric ellipsoid will set itself parallel to the lines of force. Crystals fall into two groups, according as the long axes of their magnetic and electric ellipsoids coincide or not. If, as in the case of the uniaxial system, the two long axes do not coincide, suspended crystals will be completely oriented by the application of electric and magnetic fields at right angles, and the liquid with its suspended crystals will be isotropic in the direction of one of the fields. Some information concerning the crystallographic properties of microscopic crystals can thus be obtained.

The author combats the conclusion of Meslin (*Compt. rend.*, 1908, 146, 1305) that the orientation of a suspended crystal by a magnetic field can alter with variation in the permeability of the suspending liquid. R. J. C.

Glass Thermostats for Higher Temperatures. H. W. FISCHER and O. BOBERTAG (*Zeitsch. Elektrochem.*, 1908, 14, 375—376).—For temperatures above 100°, a large glass beaker containing 10 litres of paraffin oil is used; this is heated by a "cryptol" resistance enclosed in a glass tube. For temperatures below 100°, a glass vessel full of water is used; a stream of hot water, from a reservoir at constant head, flows into the vessel through a copper spiral heated by a gas flame, which is regulated by an ordinary regulator. T. E.

Density and Latent Heat of Fusion of Ice, and the Molecular Depression of the Freezing Point in Aqueous Solutions. W. A. ROTH (*Zeitsch. physikal. Chem.*, 1908, 63, 441—446).—A critical review of the determinations of these constants recorded by various workers. The author considers the following to be the most probable values: for the density of ice at 0°, 0.9168; for the latent heat of fusion, 79.67 cal., the calorie being defined as the heat necessary to raise 1 gram of water from 15° to 16°; for the molecular depression of the freezing point, 1.858°. J. C. P.

Solidification Phenomena Exhibited by Inorganic Salts and Salt Mixtures. WILHELM PLATO (*Zeitsch. physikal. Chem.*, 1908, 63, 447—457. Compare Abstr., 1906, ii, 521; 1907, ii, 239).—Further observations are recorded bearing on the author's method of calculating the latent heat of fusion from the special form of cooling curve described previously (*loc. cit.*). It appears that the formulæ based on the earlier results may be simplified. It is shown, also, that the latent heat of fusion may be deduced from the area enclosed by (1) the actual cooling curve, and (2) the curve that would be traced if no solidification took place. J. C. P.

Specific Heat of Barytes, Witherite, and Fused Lime. LATSCHENKO (*Compt. rend.*, 1908, 147, 58—61).—The amounts of heat required to raise 3 to 7 grams of these substances from the room temperature to upwards of 1050° have been determined by the calorimetric method.

The specific heat of barytes increases regularly from 0.114 at 150° to 0.129 at 500°, remaining practically constant at higher temperatures.

Witherite undergoes a molecular transformation at about 800°, accompanied by a sudden increase of 19 calories per gram in the total heat of warming and a noteworthy change in the specific heat.

Values obtained with fused lime point to the existence of a molecular transformation at 405—410°, accompanied by an absorption of 5 calories per gram. Lime fused in the electric furnace gives good results only on the first occasion that it is plunged into the calorimeter water, as successive wettings and heatings break up the surface. Consistent results were obtained by the use of petroleum in the calorimeter. R. J. C.

Thermochemical Evidence for von Baeyer's Strain Theory. H. STANLEY REDGROVE (*Chem. News*, 1908, 98, 25—27).—A theoretical paper on the thermal behaviour of the hydrocarbons, molecular heats of combustion of which have been determined by Thomsen and Strohmann, considered in the light of Baeyer's strain theory. Values for the thermal equivalent of double and treble linkings are deduced, and the thermal equivalent of strains in polymethylene compounds is found to be proportional to the angle of deviation of the carbon atoms. From thermal data, the conclusion is drawn that the molecular heat of formation found for ethylene oxide and that deduced are quite in accord with the strain theory; the heat equivalent of the molecular strain in this compound is given as 18.0 cal. J. V. E.

Explanation of the Viscosity Curve for Mixtures of Glycerol and Water. JOSÉ R. CARRACIDO (*Anal. Fis. Quim.*, 1908, 6, 320—321).—The viscosity curve obtained by plotting the values given by Martínez-Strong (this vol., i, 307) shows a critical point between the concentrations 60% and 70% of glycerol, beyond which the viscosity increases very rapidly. Examined with the ultra-microscope, solutions containing less than 50% of glycerol do not show luminous points, and present the appearance of true

solutions; solutions containing from 50% to 80% of glycerol show an increasing number of such points, and probably consist of a mixture of a true solution with colloidal glycerol in a state of pseudo-solution. Mixtures containing 90—100% of glycerol do not show points of light, and probably consist of liquid hydrogels which are completely homogeneous. W. A. D.

Osmotic Pressure of Dextrose Solutions at 10°. HARMON N. MORSE and W. W. HOLLAND (*Amer. Chem. J.*, 1908, 40, 1—18. Compare this vol., ii, 671).—At 10°, the osmotic pressures of dextrose solutions are proportional to the concentrations, the maximum, minimum, and mean molecular pressures obtained for individual concentrations being 23·87, 23·70, and 23·80 atmospheres respectively. The excess of osmotic over gas pressure observed in the neighbourhood of 0° (*loc. cit.*) does not disappear at 10°, at which temperature the mean molecular gas pressure is 23·09 atmospheres. The mean value of the ratio of osmotic to gas pressure for 0·1*N* to 1·0*N* dextrose solutions at 10° is 1·031, the limiting values of the ratio being 1·035 and 1·027. The closer approximation of osmotic to gas pressure at 10° than at 0° is due more to the increase in gas pressure between these temperatures than to augmentation of osmotic pressure, the mean increases in molecular gas and osmotic pressures being 0·81 and 0·35 atmosphere respectively.

The following table summarises the results obtained up to the present time:

Temperature.	Mean ratio of osmotic to gas pressure.	Mean molecular osmotic pressure.
21·7—26·9°	0·993	24·01 atmosp:
10·0	1·031	23·80 „
0	1·052	23·45 „

T. H. P.

Explosive Crystallisation. FRANK E. WESTON (*Chem. News*, 1908, 98, 27).—The author finds that when an aqueous solution of the compound formed by the combination of a sulphite with a thiosulphate is evaporated in a partial vacuum, a stage of concentration is reached when crystallisation may be accompanied by explosive violence. It seems probable in the case of the evaporation of some sulphites that crystallisation is suddenly induced on the surface with a consequent sudden increase in the vapour pressure of the surrounding liquid, which under the very low pressure existing causes the liquid to boil violently. J. V. E.

Theory of Dyeing. HUGO FISCHER (*Zeitsch. physikal. Chem.*, 1908, 63, 480—486).—In criticising Freundlich and Losev's theory of adsorption (*Abstr.*, 1907, ii, 534), the author argues against assuming the existence of internal surfaces in colloids. He maintains that the swelling of colloidal substances cannot be explained by reference to any sort of structure. The phenomena of swelling and of dye absorption alike are, in the opinion of the author, essentially solution phenomena. Experiments are quoted which support this view.

J. C. P.

Influence of the Medium on Brownian Motions. VICTOR HENRI (*Compt. rend.*, 1908, 147, 62—65).—Rubber latex is coagulated to a network of fine threads by addition of acids, but is agglutinated by alkalis to a mass of irregular granules without definite structure. Before coagulation sets in, the Brownian motion of the particles in the emulsion is retarded.

The author has made cinematographic photomicrographs of rubber latex diluted to 1 in 500 with water in presence of quantities of hydrochloric acid, acetic acid, sodium carbonate, carbamide, and alcohol too small to bring about coagulation. With alkali, the Brownian movements are twice as slow, and with acid nine times as slow, as in distilled water. Thus the average displacement of a particle in 1/20 second was 0.62μ in water, 0.31μ in $N/10$ sodium carbonate, and 0.07μ in $N/32$ hydrochloric acid. $N/1000$ acetic acid produced the same effect as $N/32$ hydrochloric acid, although the former is a weaker coagulating agent.

The action cannot be attributed to the electrical influence of the ions, because alcohol produces an effect which is as intense as that of acid. On the other hand, carbamide, which does not coagulate the latex, also produces no change in the Brownian movement.

Measurements show that the granules absorb alkali somewhat, and acid very strongly. The author supposes that an adsorption zone containing molecules of the coagulating agent is formed round each granule, and that this surface combination is the cause of the slackening in the Brownian motion of the granules. R. J. C.

Osmotic Pressure and Brownian Motion. JACQUES DUCLAUX (*Compt. rend.*, 1903, 147, 131—134).—Colloidal solutions and very fine suspensions have been shown to possess an osmotic pressure. This has been explained on kinetic grounds, but the osmotic pressures calculated on the kinetic theory are systematically smaller than the experimental values, although of the same order. The recent work of Perrin (*Compt. rend.*, 1908, 146, 967), which leads to an almost absolute agreement between experiment and the kinetic hypothesis, is criticised. The material employed by Perrin (namely, gamboge) is not entirely insoluble, so that in the emulsions which he prepared probably some 23% of the material was in solution. Furthermore, the insoluble particles were not conclusively shown to be of uniform size, and the method of enumerating them was questionable. Thus the kinetic theory does not explain the whole of the osmotic pressures. It is also inferior to the electrification theory of colloidal solutions in explaining many other properties, particularly coagulation.

The author supposes that the osmotic pressure of a colloidal solution is the same as that of an ordinary electrolytic solution containing the same number of electrons in the condition of free ions. It must be assumed that an ion exercises the same osmotic pressure whether free or as part of the layer on an electrified granule.

The charge can be recognised by the conductivity of the granules, that is, the difference in conductivity before and after filtering the colloidal solution through collodion. Knowing the velocity of the granules, their charge, the number of ions surrounding them and the corresponding osmotic pressures can be calculated.

The author has experimented with a true colloid, ferric hydroxide, and results calculated for osmotic pressure from the conductivity are of the same order, but somewhat smaller than the experimental values. The electrical theory gives results which are quite as good as those given by the kinetic theory, and is based on experiments made with a true colloidal solution instead of with a mere suspension, the properties of which in spite of several analogies are not the same. There is nothing incompatible in the two methods of treatment, however, if the kinetic theory is correctly regarded.

R. J. C.

Ammonia Equilibrium. F. JOST (*Zeitsch. Elektrochem.*, 1908, 14, 373—375).—The author points out that the discrepancy between his measurements and those of Haber and Le Rossignol (this vol., ii, 362) is not very great at the lower temperatures. Up to 800° a difference of less than 40° in the measurement of temperature would account for it. The possible error of his own measurements is estimated at about 20° . At higher temperatures, the differences are larger, and it is suggested that in Haber's measurements the equilibrium may have been displaced towards the cooler part of the quartz tube.

T. E.

Experimental and Thermodynamic Researches on Neutral Salt Action. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1908, 63, 421—440. Compare Abstr., 1907, ii, 238).—When carbon dioxide is passed through water containing ultramarine in suspension, hydrogen sulphide is liberated. The presence of neutral salts hinders this reaction, and there appears to be for each salt a concentration which is just sufficient to prevent any discoverable liberation of hydrogen sulphide. The author has determined these limiting concentrations in a number of cases, and regards the reciprocal of this concentration as a measure of the neutral salt action. It is found in this way that sodium salts exert a much stronger neutral salt action than potassium salts. When sodium salts alone are considered, it appears that the neutral salt action increases with the combining weight of the anion; this rule does not apply in the case of the potassium salts. As regards the comparative neutral salt action of sodium chloride and nitrate and potassium chloride and nitrate, the results of this investigation are in harmony with the author's earlier work (*loc. cit.*). There appears to be no immediate connexion between neutral salt action and the influence of the salts on gas solubility. A few experiments made with alcohol show that the general character of neutral salt action is manifest also in alcoholic solutions.

As a practical result of his work, the author advocates a method of testing the quality of a specimen of ultramarine. A sample of the best quality, suspended in a $1.4N$ solution of sodium chloride and exposed to a fairly strong current of carbon dioxide, should not liberate any hydrogen sulphide.

The influence of a neutral salt, such as sodium chloride, on the behaviour of a weak electrolyte, such as carbonic acid, is discussed in general terms on a thermodynamic basis.

J. C. P.

Velocity of the Reaction between Bromine and Benzaldehyde. WALTER HERZ and HERMANN DICK (*Ber.*, 1908, **41**, 2645—2648).—In connexion with experiments on the velocity of the addition of bromine to unsaturated substances in various solvents, the reaction $2\text{PhCHO} + \text{Br}_2 = \text{PhCO}_2\cdot\text{CHPhBr} + \text{HBr}$ has been examined in chloroform, carbon disulphide, and carbon tetrachloride. The value of K , calculated for a bimolecular reaction, is almost the same and independent of the concentration in the first two solvents, but is about one thousand times as great in carbon tetrachloride.

C. S.

Inorganic Chemistry.

Hydrogen Persulphide. RUDOLF SCHENCK and V. FALCKE (*Ber.*, 1908, 41, 2600—2603. Compare Bloch and Höhn, this vol., ii, 579, 580).—The authors have obtained the trisulphide H_2S_3 by distilling the crude polysulphide under diminished pressure. It is essential to blow steam through the glass vessels, and also to boil them in sulphuric acid, in order to remove the alkali from the surface, otherwise the polysulphide decomposes during distillation. It is a colourless, strongly refracting liquid, b. p. $43-50^\circ/4.5$ mm., D^{15}_D 1.496, and n_D over 1.70. Its odour resembles that of camphor, and of the product formed by the slow combustion of sulphur. The substance is extremely volatile, and dissolves in most organic solvents, but these solutions are unstable, with the exception of that in bromoform. Analyses and molecular weight determinations agree with the formula H_2S_3 .
J. J. S.

The Polyiodide Molecule. PIO LAMI (*Boll. chim. farm.*, 1908, 47, 435—441).—A theoretical paper. From the solubility of iodine in potassium iodide solutions of various strengths, and from the electrical conductivity of potassium iodide solutions, it is deduced that undissociated potassium polyiodide has the composition KII_2 , and that it dissociates into the ions K and $\text{I}'\text{I}$.

No reference is made to the work of Jakowkin (*Abstr.*, 1894, ii, 271; 1896, ii, 514; compare also Dawson, *Trans.*, 1908, 93, 1308).
G. B.

So-called Crystalline Boron. HEINRICH BILTZ (*Ber.*, 1908, 41, 2634—2645).—Crystalline silicon can be obtained by Kühne's method (D.R.-P. 147871), but the directions for the preparation of crystalline boron do not give successful results. The author uses the following method. An intimate mixture of boron trioxide (50 grams), sulphur (75 grams), and aluminium (100 grams), or magnesium powder, is fired by a piece of magnesium ribbon. After the reaction, the fused mass is decomposed by water, the globules of aluminium separated, and

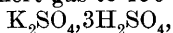
treated with hydrochloric acid. The residual black, crystalline powder is treated successively with concentrated hydrochloric acid, hydrofluoric acid, and dilute hydrochloric acid for many days. When larger quantities of materials are to be used, the proportions must be altered, more aluminium and less sulphur being taken; the yield is smaller and the black crystals are not so large. The preparation is practically an individual substance, has $D_4^{25} 2.554 \pm 0.005$ (by the floating method), and consists of monoclinic crystals [$a:b:c = 0.7130:1:0.7139$]. A complete analysis of the substance proves it to be *aluminium boride*, AlB_{12} (compare Hampe, this Journ., 1877, i, 273). It is identical with the black modification of crystalline boron obtained by Wöhler and Deville (*Annalen*, 1858, 105, 68), the specimens of which, however, contained carbon as an impurity. The yellow, transparent crystals mentioned by these investigators have also been obtained by the preceding aluminothermic method, and will be discussed later. C. S.

Constitution of the Carbon Molecule. JOHN C. THOMLINSON (*Chem. News*, 1908, 98, 37—38. Compare *ibid.*, 1906, 93, 37).—A reply to the criticism (this vol., ii, 177) of Dewar's suggested formula for the constitution of the carbon molecule (*Chem. News*, 1908, 97, 19). J. V. E.

Presence of Rare Gases in the Atmosphere at Different Heights. L. TEISSERENC DE BORT (*Compt. rend.*, 1908, 147, 219—221).—Samples collected at Trappes from the upper regions of the atmosphere have been examined spectroscopically after removal of oxygen, nitrogen, and argon. The latter gas occurred in notable proportions. The samples collected up to a height of 10 kilometres contained both helium and neon, but helium was not detected in a sample obtained at 14 kilometres. W. O. W.

Acid Sulphates of Potassium. L. ARZALIER (*Compt. rend.*, 1908, 147, 129—131).—On evaporation of a dilute solution containing molecular proportions of sulphuric acid and potassium sulphate, there are formed various acid salts, as described by Marignac, and also crystals of the composition $4K_2SO_4, 3H_2SO_4, H_2O$, which, however, from their heat of solution do not appear to be a definite compound.

From concentrated sulphuric acid and normal potassium sulphate, the salts $K_2SO_4, 3H_2SO_4, H_2O$ and $K_2SO_4, 3H_2SO_4, 3H_2O$ were prepared, which, when heated in an inert gas to 150° , yield the salt,



previously obtained by Schultz in an impure state.

G. B.

Thioantimonates of Alkali Metals. I. A. D. DONK (*Chem. Weekblad*, 1908, 5, 529—551).—From aqueous solutions, the following hydrated thioantimonates of sodium, potassium, ammonium, and lithium have been isolated: $Na_3SbS_4, 9H_2O$; $K_3SbS_4, 6H_2O$; $K_3SbS_4, 5H_2O$; $K_3SbS_4, 3H_2O$; $(NH_4)_3SbS_4, 4H_2O$, and $Li_3SbS_4, 10H_2O$. From aqueous-alcoholic solutions, the following have been isolated: $Na_3SbS_4, 9H_2O$; $K_3SbS_4, 5H_2O$; $K_3SbS_4, 3H_2O$; $(NH_4)_3SbS_4, 4H_2O$, and $Li_3SbS_4, 10H_2O$.

A. J. W.

Reaction between Ammonium Persulphate and Sodium Peroxide. R. KEMPF and ED. OEHLER (*Ber.*, 1908, 41, 2576—2580. Compare Abstr., 1906, ii, 19, 25).—The fact that when an aqueous alkaline solution of ammonium persulphate is kept for some time the ammonia formed is quantitatively oxidised to nitric acid, whereas when silver peroxide is present the main oxidation product is nitrogen, is accounted for by the different velocities of the two reactions, the latter being much more rapid than the former. If the first reaction is accelerated by raising the temperature, nitrogen is also formed.

Ammonium persulphate and sodium peroxide react readily. When the dry substances are rubbed together in a mortar, the mixture explodes, producing thick fumes. The same result is obtained by heating the mixture, by passing a stream of carbon dioxide over it, or by the addition of a drop or two of water. The temperature at which the explosion occurs lies between 75° and 140°, and depends on the rate of heating and the amount of moisture present. The gases evolved consist of nitrogen and oxygen, but the proportions vary considerably in different experiments.

The mixture is not explosive when the peroxide is replaced by sodium hydroxide, or the ammonium persulphate replaced by ammonium sulphate, sodium persulphate, or a mixture of the two.

J. J. S.

Hydrates of Baryta and Strontia. ROBERT DE FORCRAND (*Compt. rend.*, 1908, 147, 165—169. Compare this vol., ii, 155, 493).—The hydrate $\text{SrO} \cdot 9\text{H}_2\text{O}$ slowly loses water in a vacuum desiccator at 10° and, after a week, has the composition $\text{SrO} \cdot 2\text{H}_2\text{O}$. When left in a vacuum for a month, this is converted into $\text{SrO} \cdot \text{H}_2\text{O}$. The dihydrate, the existence of which has hitherto been questioned, is also formed by heating $\text{SrO} \cdot 9\text{H}_2\text{O}$ for two hours at 45—50° in a stream of dry hydrogen; if the operation is carried out at 95°, the monohydrate is obtained in the same time, and this does not undergo further dehydration below 540°. At this temperature, however, water is lost until the product has a composition varying between $\text{SrO} \cdot 0.22\text{H}_2\text{O}$ and $\text{SrO} \cdot 0.06\text{H}_2\text{O}$. This has been mistaken by previous authors for anhydrous SrO, but it probably consists of a mixture of condensed hydrates. Anhydrous strontium oxide can only be obtained by heating this mixture to 850° for several hours.

The hydrate $\text{BaO} \cdot 9\text{H}_2\text{O}$ undergoes a somewhat similar series of changes when heated. The dihydrate, however, does not change into the monohydrate below 90—95°. $\text{BaO} \cdot \text{H}_2\text{O}$ has m. p. 325°, and does not lose water below 660°. When maintained at this temperature for several days, it becomes anhydrous; the change, however, is complete in two or three hours at 780°. There is no evidence for the existence of any compound intermediate between the monohydrate (hydroxide) and the oxide.

A table is given showing the heats of formation and heats of solution of the foregoing hydroxides and oxides in water, calculated from their heats of dissolution in dilute aqueous hydrogen chloride. The heat of solution for 1 gram molecule of SrO in 20 litres of water

at 15° is 29.76 Cal., and not 30.8 Cal. as previously stated by the author (*loc. cit.*). From these data, the following conclusions are drawn: (1) The conversion of $\text{SrO}, \text{H}_2\text{O}$ into SrO is more difficult than the conversion of $\text{BaO}, \text{H}_2\text{O}$ into BaO . (2) $\text{SrO}, 9\text{H}_2\text{O}$ and $\text{BaO}, 9\text{H}_2\text{O}$ should dissociate at 142° and 152° respectively, whereas the actual temperatures of dissociation are 102° and 107° . The difference of 40 — 50° is due therefore to an endothermic condensation of the molecule on the formation of the dihydrate. A further endothermic condensation occurs on the conversion of the dihydrate into the monohydrate. (3) The oxides should be represented as $(\text{SrO})_n$ and $(\text{BaO})_n$.
W. O. W.

Action of Hydrochloric Acid on Manganese Dioxide. WILLIS B. HOLMES and E. V. MANUEL (*J. Amer. Chem. Soc.*, 1908, 30, 1192—1193. Compare Abstr., 1907, ii, 873).—The authors cannot as yet confirm the existence of manganese tetrachloride, although they have some evidence of the formation of a compound richer in chlorine than the trichloride.
L. DE K.

Colour and Composition of Guignet's Green. LOTHAR WÖHLER and W. BECKER (*Zeitsch. angew. Chem.*, 1908, 21, 1600—1606).—Scheurer-Kestner's statement is confirmed (*Dingl. Polyt. J.*, 1865, 176, 386), that the boron present in Guignet's green is without influence on the colour, and is present only as a remnant of the chromium borate formed primarily by fusion of potassium dichromate with boric acid. By employing ammonium, instead of potassium, dichromate, Guignet's green is readily obtained free from boron, and has then the composition, $\text{Cr}_4\text{O}_3(\text{OH})_6$, ascribed to it by Scheurer-Kestner. The product obtained on heating potassium dichromate with an excess of boric acid has the composition $\text{Cr}_4\text{O}_3(\text{B}_4\text{O}_7)_8$.

Whilst Guignet's green has a vapour tension of 13 mm. at 75° , 16 mm. at 81° , and 26 mm. at 86° , the greyish-violet chromium hydroxide, which has the same composition, is found to have a vapour tension of only 2 mm., not increasing between 75° and 93.4° . This small vapour tension may result from the presence of moisture. These differences and the difference in colour of the two hydrates are ascribed to isomerism. The greyish-violet hydroxide is converted into its brilliant green isomeride on prolonged heating with water at 250° .

G. Y.

Oxalate Reduction of Alkali Iridiochlorides. MARCEL DELÉPINE (*Compt. rend.*, 1908, 147, 198).—A reply to Vèzes' claim to priority (this vol., ii, 703).
W. O. W.

Mineralogical Chemistry.

Fumaroles of Etna. Boric Acid in the Fumaroles of Vesuvius. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 161—165).—The fumaroles of the recent (1908) eruption of Etna are of the same types as those of Vesuvius, but they are much less active ; this is due

to the short period of the eruption, and to the fact that the magma was poor in volatile materials. The types specially described are : (i) fumaroles depositing alkali chlorides ; (ii) those emitting hydrogen chloride and depositing kremersite, &c., and (iii) those depositing ammonium chloride alone. The crusts of ammonium chloride were found to contain small amounts of fluorine, perhaps present as an alkali silicofluoride.

In one of the fumaroles of the 1906 eruption of Vesuvius, a small amount of sassolite (H_3BO_3) in crystalline scales was detected. This is rare at Vesuvius, but its presence is of importance in connexion with theories of pneumatolytic action.

L. J. S.

Lavas of the Recent Eruption of Etna. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 99—103).—The various products of the 1908 eruption of Etna were examined petrographically and chemically. They closely resemble one another in chemical composition and in the porphyritic crystals (of basic plagioclase, little augite and magnetite, and very little olivine) which they contain. The rock of a lava flow (anal. I) which has cooled more slowly, and has consequently crystallised more completely, contains in its ground-mass microlites of augite and olivine with very little glass ; this rock is a basalt, or, according to the French terminology, a labradorite. In a slightly scoriaceous product (anal. II) of eruptions of the Strombolian type, and in a highly scoriaceous bomb (anal. III) resulting by an explosion of the Hawaiian type, the ground-mass contains more glassy material. Anal. IV is of the ash which fell during the eruption :

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Loss on igni- tion.	Total.
I.	49·75	18·30	2·85	6·28	3·45	9·76	4·96	1·89	2·45	0·03	0·40	100·12
II.	49·71	18·40	1·93	6·96	3·45	9·80	5·13	1·72	2·58	0·02	0·00	99·70
III.	50·40	18·90	2·65	5·82	2·99	9·41	5·20	1·54	2·58	0·03	0·10	99·62
IV.	51·83	18·45	4·97	3·96	2·99	7·55	3·52	1·61	2·45	—	3·00	100·33

L. J. S.

Physiological Chemistry.

Blood-coagulation Time. F. L. GOLLA (*Proc. physiol. Soc.*, 1908, lxi—lxii; *J. Physiol.*, 37).—A modification of Buckmaster's coagulometer is described; it gives very constant results with a given blood. The coagulation time does not exhibit diurnal variation; it is not altered by fasting, or by the internal administration of sodium citrate or calcium salts. Nor is it abnormal in hæmophilia (1 case), purpura (1 case), or urticaria (2 cases). It is markedly prolonged in cases of jaundice, probably because of an alteration in the surface tension of the blood-film.

W. D. H.

Effect of Amyl Nitrite on Red Blood Corpuscles. GR. SLAVU (*Compt. rend.*, 1908, 147, 148—149).—Less than 0·3% of amyl nitrite does not produce a visible spectroscopic change in the blood. Death, after toxic doses have been administered, is not wholly due to want of oxygen, for a considerable quantity of the gas can be extracted from the blood in a vacuum. The oxygen which is set free, both *in vivo* and *in vitro*, is not derived from the plasma, but from the corpuscles.

G. B.

The Behaviour of the Sugar of the Blood after Bleeding. NILS ANDERSSON (*Biochem. Zeitsch.*, 1908, 12, 1—7).—The statement that the amount of sugar in the blood increases after bleeding is confirmed; this occurs in rabbits, especially after a second bleeding. The blood-sugar consists of 75% dextrose, and the remaining 25% is spoken of as residual sugar; it is not fermentable by yeast and gives a positive orcinol reaction, and so is probably a pentose, but this requires confirmation. Both varieties of sugar increase in the same proportion after bleeding; the total amount may be more than doubled.

W. D. H.

The Blood Issuing from the Dog's Suprarenal. F. A. YOUNG and J. E. LEHMANN (*Proc. physiol. Soc.*, 1908, liv; *J. Physiol.*, 37).—The blood issuing from the suprarenal gland, especially if it has been dammed back there for a time by a ligature, produces on injection into the general blood stream a decided rise of pressure, and so presumably contains adrenaline.

W. D. H.

Duration of Effect of Pituitary Extract on Blood Pressure. P. LOCKHART MUMMERY and W. LEGGE SYMES (*Proc. physiol. Soc.*, 1908, lvi; *J. Physiol.*, 37).—In the dog, the elevation of blood pressure produced by injection of pituitary extract may last twenty to thirty minutes; in the pithed cat, it may persist for many hours.

W. D. H.

Influence of Magnesium Sulphate on Metabolism. MATTHEW STEEL (*J. Biol. Chem.*, 1908, 5, 85—124).—Injection of magnesium sulphate into a muscle, or under the skin, does not cause diarrhoea. The total nitrogen eliminated is somewhat increased, but the most marked effect is the rise, relative and absolute, in urinary ammonia.

W. D. H.

Tolerance to Alcohol. JOSEF PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 12, 143—192).—In animals accustomed to alcohol, the same quantity is excreted by lungs, kidneys, and skin as in those unaccustomed to its use. In both classes of animals, the faeces are free from alcohol. In both groups the amount united to glycuronic acid in the urine is the same, but that united to sulphuric acid is slightly higher in the "accustomed" animals. The "accustomed" animals burn off the alcohol more rapidly, that is, in about two-thirds of the time occupied in the burning by the "non-accustomed" group. In acute alcoholic poisoning, the percentage of alcohol in the body is

about 66% more in the "non-accustomed" animals. The seat of combustion is mainly the liver, then comes heart muscle, and the brain is last.

W. D. H.

Temperature-coefficients of Velocities of Various Physiological Actions. CHARLES D. SNYDER (*Amer. J. Physiol.*, 1908, 22, 309—334).—The large number of observations recorded and tabulated show that the temperature-velocities are all of magnitudes similar to those seen in physical and chemical reactions; in cases where it is known that metabolism occurs, the coefficients observed are those of chemical reactions; under this category are included the shortening of muscle, the latent period of smooth muscle, &c. Coefficients lower than these simulate physical actions, for instance, the latent period of striated muscle. In still other cases, the data are insufficient to draw conclusions from, as, for instance, the latent period of cardiac muscle and of vagus stimulation, and the velocity of urinary secretion and of lymph formation.

W. D. H.

Effects of Variations in Inorganic Salts and Reaction on Plants and Animals. BENJAMIN MOORE, HERBERT E. ROAF, and ROBERT E. KNOWLES (*Bio-Chem. J.*, 1908, 3, 279—312).—The range of ionic concentrations compatible with life is a narrow one. Short of the lethal dose, life and growth of plants are stimulated by alkali and not by acid. Potassium is more stimulating than sodium to both rootlets and flowers. The phosphatic anion causes increase in size, but irregularities in the flowers. In amphibia, both acid and alkaline phosphates increase growth. Higher concentrations cause death, which in the case of the alkaline salt is preceded by hyperexcitability. In mammals, alkaline and acid phosphates, in doses of 0.26—0.38 gram per kilo. of body-weight, cause increased metabolism, diminishing body-weight, and finally death. The adipose and muscular tissues waste considerably; other symptoms are polyuria, and with large doses, diarrhoea with ulceration of the alimentary canal, leucocytosis, degeneration of liver cells, and nephritis. The alkalinity of the serum is increased by the alkaline and diminished by the acid salt.

W. D. H.

Chemical Composition of the Herring during the Reproductive Period. THOMAS H. MILROY (*Bio-Chem. J.*, 1908, 3, 366—390).—The herring undoubtedly feeds until spawning time, and so differs from the salmon; the herring is therefore not dependent on its muscle proteins for the growth of its ovaries. In the male, as in the female, the highest fat percentage is found in the muscles just before rapid growth of the reproductive organs occurs; then it falls. The year may be divided into three periods: (1) The restitution or feeding period, three to four months before spawning; the spent fish recovers and accumulates a store of fat. (2) The ripening period, six to seven months. The fish still takes food, but in less amount, and the sexual organs grow as the store of muscle fat lessens. (3) The spawning period, two months; during this time feeding stops, the fat in the muscles falls greatly, and the water increases.

W. D. H.

Glycogen of Frog's Spawn. E. HAENSEL (*Biochem. Zeitsch.*, 1908, 12, 138—142).—Glycogen is present in frog's spawn in amounts varying from 0.016 to 0.052% of the fresh, or from 1.28 to 4.08% of the dry, material. The estimations were made by Pflüger's method. The addition of dextrose, lactose, or sucrose to the spawn causes a rise in the yield of glycogen. W. D. H.

Influence of Strontium on the Growth and Composition of Bone. HELENE STOELTZNER (*Biochem. Zeitsch.*, 1908, 12, 119—137).—The experiments recorded on growing dogs show that if the diet is poor in calcium, or if the calcium is partly replaced by strontium, the bone condition that results differs from that seen in rickets; in the latter condition, the relationship of calcium to fat-free dry substance is lessened, but this was not the case in the experimental puppies. Strontium is laid down in the bone in relatively important amount, but it does not seem able to take the place of calcium in producing healthy bone. W. D. H.

Chemistry of Muscle and Liver of Reptiles. JOHN F. LYMAN (*J. Biol. Chem.*, 1908, 5, 125—127).—Four kilograms of fresh muscle and the livers from two pythons were examined. From the muscle, creatine and sarcosine were separated and identified. The most conspicuous purine derivative is hypoxanthine, as in higher vertebrates.

From the livers, uric acid, guanine, and adenine were obtained. Xanthine and hypoxanthine could not be separated in amounts sufficient for identification. W. D. H.

Contraction of Muscle in Relation to the Presence of Receptive Substances. II. JOHN N. LANGLEY (*J. Physiol.*, 1908, 37, 165—212. Compare this vol., ii, 120).—Further details of the phenomena of nicotine poisoning in frog's muscle, which support the author's previous contention that there exist in the muscle, or its nerve-endings, or both, substances with which the nicotine combines. W. D. H.

Cholesterol in Coelenterata. CHARLES DORÉE (*Proc. physiol. Soc.*, 1908, lviii—lix; *J. Physiol.*, 37).—Cholesterol is generally regarded as a constant constituent of cell protoplasm. It is certainly present in sea-anemones. W. D. H.

Kidney Secretion of Indigo-carmin, Methylene-blue, and Sodium Carminate. GEORGE D. SHAFER (*Amer. J. Physiol.*, 1908, 22, 335—352).—The experiments recorded confirm Heidenhain's views on urinary formation; indigo-carmin, leuco-indigo-carmin, and methylene-blue are secreted at varying rates by the convoluted tubules and the wider limb of Henle's loop. Sodium carminate, on the other hand, passes out by the glomeruli. W. D. H.

[Symptomatic] Significance of Urinary Indoxyl. Detection of Indole in Pus. CHARLES PORCHER (*Compt. rend.*, 1908, 147, 214—217).—Pus, diluted with water and made alkaline, is distilled with steam; the indole is extracted from the distillate by pure

benzene, in which it is detected by the colour reaction with *p*-dimethylaminobenzaldehyde. In less than half the number of specimens examined, indole was present; its formation seems to depend on the presence of particular organisms. G. B.

Renal Calculi. J. SYDNEY ROWLANDS (*Bio-Chem. J.*, 1908, 3, 346—350).—A series of twenty-two calculi from South-west Lancashire and North Wales was examined. The commonest constituent was found to be calcium oxalate. Uric acid was rare, and was absent in nineteen cases. W. D. H.

Concentration of Diphtheria Toxin. P. G. HEINEMANN (*J. Biol. Chem.*, 1908, 5, 27—30).—A high potency diphtheria toxin is advantageous in the production of diphtheria antitoxin. Concentration of the former by precipitating with alcohol or salts of heavy metals is accompanied by loss of potency; this, however, is minimised by the use of neutral salts as the precipitating agent. In the present research, ammonium sulphate was used; the salt was subsequently removed by dialysis through heavy parchment. Phenol was then added to the re-dissolved precipitate as a preservative to the extent of 0.3%; more than this precipitates the toxin. The loss of potency is very slight. W. D. H.

Experimental Glycosuria. II. Glycogenolytic Fibres in the Great Splanchnic Nerve. JOHN J. R. MACLEOD. **III. Influence of Stimulation of the Great Splanchnic Nerve when the Liver is Deprived of its Blood Supply.** JOHN J. R. MACLEOD and H. O. RUH (*Amer. J. Physiol.*, 1908, 22, 397—409).—Stimulation of the great splanchnic nerve in dogs produces marked hyperglycæmia within half an hour, accompanied by diuresis and glycosuria. If the stimulation is continued for hours, these effects reach a maximum in about two hours and then decline. Liberal administration of oxygen lessens, but does not abolish, the effect; atropine, also, does not prevent the effect. Ligature of the hepatic artery or clamping of the portal vein do not in themselves produce hyperglycæmia. The glycogen which disappears from the liver is greater in amount when the nerve is stimulated when the portal blood is diverted into the inferior vena cava than when the stimulation is omitted. This, however, is not conclusive evidence in favour of glycogenolytic secretory fibres, for the stimulation might produce bloodlessness of the liver by constricting the hepatic artery. If, however, the glycogen still disappears during stimulation of the nerve, when the liver is rendered completely anæmic by ligature of the portal vein and hepatic artery, then the existence of such nerve-fibres is definitely proved. In two out of three experiments, the disappearance was greater during a ten minute period of stimulation than in the preceding ten minutes when no stimulation was employed. If no stimulation is used at all, the rate of disappearance during the second ten minutes is the same as, or less than, that occurring during the first period. W. D. H.

Calcium Metabolism in Relation to Rickets. HANS ARON (*Biochem. Zeitsch.*, 1908, 12, 28—77).—A critical and experimental review of calcium metabolism in relation to the ætiology of rickets. The lack of calcium may be due to the small amount in the food, or to its non-absorption, or to its too rapid excretion. The experiments recorded on animals, together with observations on human infants, show the overwhelming importance of the first of these three factors. The effect falls mainly on the skeletal structures, for the amount of calcium may remain normal in other organs. Among the interesting points raised are: (1) the poorness of human milk in calcium, and the suggestion is made that weaning should occur at an earlier date than that usually laid down; and (2) the fact that the milk of mothers of rickety children is poorer in calcium than that of other women in relation to the organic constituents in the milk. Doubtless other factors also step in, especially rapidity of growth in such children.

W. D. H.

Arsenic and Trypanosomes. MARTIN JACOBY and ALBERT SCHÜRZE (*Biochem. Zeitsch.*, 1908, 12, 193—202).—Phagocytosis does not appear to be a factor in the defence of the body against trypanosomes, and the beneficial influence of arsenic is not due to its stimulating leucocytic activity, but rather to its direct influence on the parasites.

W. D. H.

Pharmacological Action of cycloHexane and Some of its Derivatives. A. BRISSEMORET and J. CHEVALIER (*Compt. rend.*, 1908, 147, 217—219).—A comparison of the action of cyclohexane, cyclohexanol, *i*-quercitol, and inositol on the action of the isolated rabbit's heart perfused with Locke's solution. The primary effect (contraction of the heart's muscle) of all four substances is attributed to their having a common carbon skeleton. With cyclohexane, and especially with cyclohexanol, the toxic effect on the nerves of the heart is most prominent.

G. B.

[Physiological] Action of Substances of the Saponin Group. LEONHARD WACKER (*Biochem. Zeitsch.*, 1908, 12, 8—14).—Substances of the saponin group obtained from various plants appear to differ in toxicity; the experiments recorded (on dogs) were performed with a mixture of quillajic acid and sapotoxin. Deleterious effects on the kidney are described. The toxic action on the blood is less if the drug is given by the mouth, and the addition of extracts of the intestinal mucous membrane to solutions outside the body lessens their hæmolytic properties; the gastric mucous membrane is even more powerful in the same direction.

W. D. H.

Absorption of Certain Poisonous Gases by the Respiratory Tract. KARL B. LEHMANN, JOSEPH WIENER, JOHANNES WILLKE, and JIRO YAMADA (*Arch. Hygiene*, 1908, 67, 57—98).—If the air contains from 0·2 to 0·3% of ammonia, from 80 to 90% of this is absorbed, and absorption is mainly brought about by the nasal and buccal mucous membranes. If the mixture is passed directly into the lungs of an

animal, about 56% of the ammonia is absorbed, but it is not possible to say whether the absorption occurs in the bronchial tubes or in the alveoli.

Hydrogen chloride is absorbed by the nose and trachea to the extent of 60—75%. An animal in this way absorbed 252 milligrams of the gas in an hour, sufficient to produce acid poisoning; injury to the mucous membrane is also readily produced. Sulphur dioxide is absorbed by the same channels to the extent of 35—58%. It is relatively more toxic than hydrogen chloride. Acetic acid vapour is less toxic than hydrogen chloride. It produces hyperæmia and acidity of the mucous membrane, but no hæmorrhage. The amount absorbed varies from 62 to 86%. A few experiments on carbon disulphide are also given; the amount absorbed is about 20—22%. Full analytical details are given throughout; the experiments on animals were supplemented throughout by experiments on man. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Heavy Metals on *Bacillus Typhorus*. BENJAMIN MOORE and JAMES LEONARD HAWKES (*Bio-Chem. J.*, 1908, 3, 313—345).—The investigation was undertaken on fresh-water mussels with a view to their purification from the bacillus of typhoid fever. Ferrous sulphate and ferric chloride solutions (1 in 1000) act beneficially on the mussels, and kill all the bacilli in twenty-five hours. Salts of silver, copper, zinc, and lead were found to be useless; they either act detrimentally on the mussels, or do not free them from the bacilli in a reasonable time. W. D. H.

Fermentation of Malic Acid in the Production of Wine. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1908, 147, 150—153. Compare Mestrezat, this vol., ii, 723).—Malic acid is transformed into lactic acid and carbon dioxide by *Micrococcus malolacticus* occurring in the grape; in order to secure proper ripening of the wine, this bacillus should not be allowed to develop rapidly, so that the malic acid disappears slowly. G. B.

Fermentation of Calcium Tartrate. OSKAR EMMERLING (*Centr. Bakt. Par.*, 1908, ii, 21, 317—318).—The experiments were made with a *Spirillum* found in the waste waters from a tannery. When inoculated into a culture solution containing inorganic and organic food substances and solid calcium tartrate, it was found to decompose the latter salt quantitatively, giving rise to calcium carbonate and carbon dioxide. Thus, in one experiment, 5 grams of the tartrate were originally put into the solution, of which 4.3 were decomposed, giving rise to 2.05 grams of calcium carbonate (theor. = 2.2 grams). Decomposition proceeds more rapidly the greater the surface of liquid exposed to the air and the more frequently the liquid is shaken.

In all fermentations of calcium tartrate studied previously, the reaction has been more complex, and has given rise to several fatty acids.
E. J. R.

Influence of the Sterilisation Temperature of Grape Juice and of the Fermentation Temperature on the "Bouquet" of Wine. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1908, 146, 1417—1420).—The best temperature for sterilisation is 50—52°; at 55—60° the bouquet suffers. It is true that at the lower temperature only a partial sterilisation is achieved, but below 26° the surviving yeast cells do not appreciably resume their growth in the first forty-eight hours, so that there is time for the pure culture, with which it is desired to conduct the fermentation, to establish itself. A further reason for conducting the fermentation at a low temperature (20°) is that at a higher temperature the carbon dioxide evolved carries away substances the scent of which makes up the bouquet. The gases given off may be passed into sterile grape juice, to which they communicate the bouquet.
G. B.

De-amidising Ferments of Fungi. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 12, 15—25).—Various fungi, such as yeast and *Aspergillus niger*, have the property of liberating ammonia from nitrogenous substances, especially from amino-acids. This is due to enzymatic action. After treatment with acetone and ether, this property is lost. The de-amidised residue is changed into alcohols, with the evolution of carbon dioxide, by an enzyme contained in yeast, which is also killed by acetone and ether. The theoretical bearing on these facts in relation to the growth of fungi is discussed.
W. D. H.

Influence of the Concentration of Sugar Solutions on Respiration [of Seedlings]. A. MAIGE and G. NICOLAS (*Compt. rend.*, 1908, 147, 139—142).—Bean seedlings placed for fifteen to twenty-two hours in sugar solutions of various concentrations (up to 10%) showed increased intensity of respiration, both normal and intramolecular. With all sugars examined, except lactose, the respiration increases progressively with the concentration.
G. B.

Behaviour of Certain Organic Substances in Plants. I. GIACOMO L. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1908, 38, i, 682—697).—The glucosides amygdalin, salicin, and arbutin are tolerated by maize and French beans to a much greater extent than the aromatic substances present in the glucosides, namely, benzaldehyde, saligenin, and quinol. The plants into which the latter are introduced die within three days, whilst those treated with the glucosides reach complete maturation. In a period of two months, a single plant can be treated with as much as 3 grams of glucoside without injury.

The glucosides introduced into the plants undergo partial hydrolysis, and are apparently utilised by the plants, since extraction of the latter only yields a fraction of the total glucoside introduced.

T. H. P.

Mechanism of the Distribution of Odoriferous Principles in Plants. EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1908, 147, 144—145).—In general, those constituents of an essential oil which are most soluble in water are most readily transported from the leaves to the flowers. Menthol is more soluble than menthone, yet in peppermint plants the flowers contain more menthone than the leaves. This is, however, the result of oxidation of the menthol after it has been transported into the flowers, and therefore a secondary effect.

G. B.

Chemical Changes Consequent on the Wounding of Plants. RUDOLF FRIEDRICH (*Centr. Bakt. Par.*, 1908, ii, 21, 330—347).—The author gives a full résumé of previous work on the subject, dealing especially with (a) the increased evolution of carbon dioxide, (b) the increased production of protein, in wounded potatoes and onions. He finds that the former of these phenomena is also shown by other parts of plants (leaves, fruit, &c.), but not always the latter; thus potatoes and oak leaves respectively gave the following results:

	Total N.	Protein N.	Amide N.	Carbo- hydrate.	Acidity.
Potatoes (tubers), wounded	1·476	1·250	0·123	70·260	24·350
„ „ not wounded	1·301	0·888	0·167	73·820	21·430
Oak leaves, wounded	5·171	3·557	1·230	8·191	59·530
„ „ not wounded	5·392	3·498	1·004	12·436	48·896

The figures refer to percentages on the dry substance.

The fall in carbohydrate is correlated with the increased respiration, but the increase in acidity is not discussed, since the acids actually produced were not investigated. It was found that the protein production in the wounded potato, onion, and pear depended on the presence of the large amount of carbohydrate; the fruits of *Cydonia japonica* and leaves of *Clivia Gardneri*, which behaved like oak leaves, contained only small quantities. This observation lends support to Pfeffer's view that protein is formed from plants by a reaction between carbohydrate and amide material.

E. J. R.

Origin of the Colouring Matter of Red Grapes and of Other Plant Organs. J. LABORDE (*Compt. rend.*, 1908, 146, 1411—1413 *).—By heating the solid parts of young, green grapes with 2% hydrochloric acid to 120° for thirty minutes, a red colouring matter is formed from the tannins. A similar pigment may be formed by boiling with alkali in the presence of air.

G. B.

Oxydase in the Latex of Hevea Brasiliensis. DAVID SPENCE (*Bio-Chem. J.*, 1908, 3, 351—352).—Four samples of this latex (Para rubber) gave marked evidence of the presence of an oxidising enzyme.

W. D. H.

Ripening of Tomatoes (*Lycopersicum esculentum*). F. M. ALBAHARY (*Compt. rend.*, 1908, 147, 146—147).—During ripening, a considerable increase in the amount of organic acids, sugars, starch, and non-protein nitrogenous substances takes place, whilst proteins and cellulose diminish.

G. B.

* and *Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 76—78.

Physiological Action of Dicyanodiamide. OSCAR LOEW (*Chem. Zeit.*, 1908, 32, 676—677).—Whilst under ordinary conditions calcium cyanamide decomposes entirely into calcium and ammonium carbonates, in alkaline soils there is a possibility of a partial production of dicyanodiamide. According to Ulpiani and Perotti (*Abstr.*, 1907, ii, 295), the latter compound is not poisonous to crops, and may even be employed as a source of nitrogen; Kappen showed that it is very slowly converted into ammonia.

Experiments in which young barley plants (14—16 cm. high) were placed in a 0.5% solution of dicyanodiamide showed an injurious action after two days. In the case of small *Lathyrus* plants, no injurious action was observed until several days later, owing, perhaps, to evaporation being less. With 0.05—0.1% solutions, only the points of the leaves were affected; solutions of guanidine hydrochloride of the same strength killed barley plants in a few days.

Further experiments with twigs of *Tradescantia* in 0.1%, and *Elodea* in 0.2%, solutions of dicyanodiamide showed that no injurious effect was produced in either case, and that *Elodea* utilised dicyanodiamide as a source of nitrogen. The poisonous effects observed by Immendorff and Wagner were, perhaps, due to some decomposition product. Threads of *Spirogyra* in 1% solutions of dicyanodiamide remained intact for several days; worms lived for more than four days in 0.5% solutions. Bacteria in broth containing 0.5% were not injured in the least.

As regards the constitution of dicyanodiamide, it is suggested that the imide ring formula (Baumann) best accords with its slightly acid character and with its physiological properties, as compared with dicyanodiamidine and guanidine.

N. H. J. M.

Analytical Chemistry.

Automatic Safety Burette. GUSTAV MÜLLER and O. BERCHEM (*Chem. Zeit.*, 1908, 32, 711).—A modification of the apparatus described previously (this vol., ii, 626). The reservoir has been replaced by a tube connected with a large container. The circulation tube is replaced by an overflow chamber fitted with an open conical lid, which is firmly tied to it by means of glass hooks and strong rubber bands. A float, terminating in a cone, serves as a valve, which closes when, after filling the burette, sufficient liquid has entered the overflow chamber.
L. DE K.

Detection of Fluorine Compounds in Wines. L. VANDAM (*Ann. Chim. anal.*, 1908, 13, 260—262).—A reply to Carles (this vol., ii, 318). The author proves that the amount of fluorine in oenological products is too small to interfere with the use of his process (this vol., ii, 63).
L. DE K.

Apparatus for the Quantitative Distillation of Ammonia. PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1908, 30, 1131—1135).—The author has applied Folin's process to the Kjeldahl nitrogen estimations. The fused mass in the Kjeldahl flask, when sufficiently cooled, is mixed with 40—90 c.c. of water (about 4 vols. of water to 1 vol. of sulphuric acid present), and the flask is connected with two cylinders, one containing an amount of aqueous sodium hydroxide more than sufficient to neutralise all the sulphuric acid, and the other, a standard solution of sulphuric acid to absorb the ammonia given off. By applying suction, the alkali is forced into the flask, and the heat developed is sufficient to expel all the ammonia. When all the alkali has been carried over, the cylinder may be disconnected and replaced by an arrangement for supplying ammonia-free air. The suction is continued until the contents of the flask are perfectly cooled down.
L. DE K.

Folin's Method of Estimating Ammonia in Urine. MATTHEW STEEL and WILLIAM J. GIES (*J. Biol. Chem.*, 1908, 5, 71—84).—Certain urines, collected during metabolism experiments with magnesium sulphate, gave discordant results when the ammonia in them was estimated by Folin's method. This is due to the fact that relatively large quantities of ammonio-magnesium phosphate are eliminated under these conditions, some of it being deposited in crystalline form; this deposit is not thoroughly decomposed by sodium carbonate as used in Folin's process, and so a variable amount of ammonia is lost.

W. D. H.

Limitations of the Copper-Zinc Couple Method in Estimating Nitrates. JOHN E. PURVIS and R. M. COURTAULD (*Proc. Camb. Phil. Soc.*, 1908, 14, 441—446).—The authors have examined the accuracy of the copper-zinc couple method of estimating nitrates and nitrites in waters which contain considerable quantities of organic nitrogen compounds, such as soluble peptones, blood-serum, and soluble albumin. From a comparison of the results with those of blank experiments, it is found that the organic nitrogen is to some extent reduced to ammonia under the influence of the couple. Similar results were obtained with a sample of sewage to which known quantities of potassium nitrate were added. It is suggested that the reduction of the organic nitrogen is not merely due to the hydrogen liberated by the couple, but is influenced by the oxygen liberated simultaneously by the electrolytic action.
H. M. D.

The Nitro-Molybdate Method for the Detection of Phosphorus in Tissues. G. G. NASMITH and E. FIDLAR (*J. Physiol.*, 1908, 37, 278—284).—In agreement with Macallum, but contrary to the view of Scott, the cold nitric acid employed does separate inorganic phosphates from nucleins and nucleic acids. Bensley's view is acquiesced in that the reduction of compounds of molybdenum is the cause of the bluish-green colour which appears in microscopic preparations, and that it is not due to the presence of phosphorus at all.

W. D. H.

Estimation of Phosphoric Acid. NORBERT VON LORENZ (*Chem. Zeit.*, 1908, 32, 707—709).—A defence of the author's method (direct weighing as ammonium phosphomolybdate), which is applicable in all cases, whereas the citrate process gives but indifferent results.

L. DE K.

Microchemical Analysis. III. Arsenic, Antimony, Tin. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1908, 47, 367—389. Compare this vol., ii, 432).—The process is based on the characteristic microscopical appearance of arsenious acid, ammonium calcium arsenate, ammonium magnesium arsenate, and arsenic iodide. Antimony may be isolated as caesium antimony chloride or, preferably, iodide, or as sodium antimonate, whilst tin yields characteristic compounds with caesium and rubidium chlorides, all of which are readily detected microscopically.

Tin and antimony are conveniently separated from arsenic by heating the mixed sulphides obtained in the ordinary course of analysis with 25% hydrochloric acid, which leaves the arsenic practically undissolved. A portion of the filtrate is then tested for tin with rubidium chloride, and another portion for antimony with caesium chloride and potassium iodide. The arsenic is oxidised with nitrohydrochloric acid, and then converted into the magnesium compound.

L. DE K.

Separation of Lithium Chloride from the other Alkali Chlorides and Barium Chloride. LOUIS KAHLENBERG and FRANCIS C. KRAUSKOPF (*J. Amer. Chem. Soc.*, 1908, 30, 1104—1115).—The solution of the mixed chlorides is evaporated just to dryness, and the residue, which should not exceed 2 grams, is boiled for a few minutes with 25 c.c. of pyridine; any large particles are crushed with a stirring rod. The clear liquid is decanted through a small filter, and the insoluble matter washed twice with a little hot pyridine. It is then dissolved in a little water, evaporated to bare dryness, and again extracted with hot pyridine. The pyridine filtrates, which contain all the lithium chloride, are mixed, the bulk of the pyridine is recovered by distillation, and the lithium chloride is converted into sulphate by evaporation with sulphuric acid and weighed as such.

L. DE K.

Assay of Telluride Ores. GEORGE BORROWMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1023—1027).—The irregularities in the assay of high-grade auriferous tellurides are due to lack of homogeneity of the sample, and not, as has been suggested, to the tellurium. In some cases, however, it is advisable to remove the tellurium with nitric acid. Any silver is then precipitated as chloride, and added to the insoluble residue, which is then assayed as usual for gold and silver. The most favourable temperature is about 1200°.

L. DE K.

Evaluation of [Commercial] Red Lead. P. BECK (*Zeitsch. anal. Chem.*, 1908, 74, 465—492).—An exhaustive research as to the most trustworthy methods for the analysis of red lead. The author gives the following summary.

The red lead may be dissolved in dilute nitric acid, and separated from insoluble impurities by the use of such reducing agents as sucrose, oxalic acid, lactic acid, methyl alcohol, formaldehyde, glycerol, phenylhydrazine, salts of hydroxylamine, but best of all by hydrogen peroxide.

When small quantities only are available, Bunsen's process (distillation with hydrochloric acid and estimation of the chlorine liberated) may be used, but in works, Topf's process (titration of iodine liberated from potassium iodide with sodium thiosulphate) should be used, as this allows the use of 5 grams of the sample. L. DE K.

Solubilities of the Oxalates of the Rare Earths. I. Solubility of the Oxalates of Lanthanum, Cerium, and Samarium in dilute Sulphuric and Oxalic Acids or their Mixtures. OTTO HAUSER and FRITZ WIRTH (*Zeitsch. anal. Chem.*, 1908, 47, 389—400).—Tables showing the solubility of the oxalates of the cerium group in dilute sulphuric and oxalic acids, and in a mixture of the two; the strength of the acids varies from 0.05*N* to 4.3*N*.

As a result of this investigation, the following process is recommended. The rare earths are separated from accompanying alkaline earths by precipitation with ammonium chloride and pure ammonia. The washed precipitate is dissolved in hydrochloric acid, and, after expelling the excess by evaporation, the residue is dissolved in about 60 parts of $N/4$ — $N/2$ sulphuric or hydrochloric acid. A saturated solution of oxalic acid is then added in such quantity that the solution will contain about 3% of that acid. If lanthanum is present in large excess, ammonium oxalate should be used. In presence of more acid, the process becomes quite inaccurate for lanthanum, and less accurate for cerium. L. DE K.

Influence of Fine Grinding on the Water and Ferrous Iron Content of Minerals and Rocks. WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1908, 30, 1120—1131).—A series of tabulated experiments on the influence of fine grinding on minerals containing ferrous iron and on the iron and water content. In order to avoid oxidation, it is recommended that the grinding should be effected under alcohol, or, better still, the coarse powder should be treated directly with hydrofluoric acid and the solution titrated for ferrous iron; any undissolved matter is then finely ground under water, and again treated with hydrofluoric and sulphuric acids (for details, compare *Bull.* 305, *U.S. Geol. Survey*, 142). L. DE K.

Volumetric Estimation of Iron and Chromium by means of Titanous Chloride. S. B. JATAR (*J. Soc. Chem. Ind.*, 1908, 27, 673—674).—The principles involved in the method are: (1) hydrogen peroxide oxidises chromium salts in alkaline solutions to chromates, these becoming dichromates on acidifying the solutions; (2) hydrogen peroxide reduces dichromates to chromates in acid solutions, ferric salts being unchanged; (3) on titrating a mixture of a dichromate and a ferric salt, for all practical purposes the dichromate is reduced first,

the colour change marking the reduction and the ferric salt being left in solution. Of these, the first one is involved in bringing the iron and chromium in an ore into solution; on the second and third, the following process depends. A weighed quantity of about 0.5 gram of the finely-powdered ore is fused with a mixture of sodium hydroxide and sodium peroxide, more of the latter being added subsequently. After cooling, the fused mass is extracted with water, the solution is boiled to remove all traces of hydrogen peroxide, then acidified with sulphuric acid, and again boiled and diluted to a volume of 500 c.c. Fifty c.c. of the solution are titrated with standardised titanous chloride solution until a clear violet coloration is obtained, showing that all the dichromate is reduced; a few more drops of titanous chloride are added to make sure that only the ferric salt remains in solution, then a few drops of thiocyanate solution are added as indicator, and the solution is titrated until the colour disappears. The volume of titanous chloride solution used represents the dichromate and iron together. A second 50 c.c. of the solution are treated with hydrogen peroxide to reduce the dichromate, and the mixture is boiled to expel the excess of hydrogen peroxide. When cold, the solution is titrated with titanous chloride solution, a few drops of thiocyanate solution being added as an indicator. In this titration, the volume of titanous chloride used represents the amount of iron only. A sensitive indicator may be prepared by adding a few drops of potassium thiocyanate solution to a dilute ferrous sulphate solution.

W. P. S.

Estimation of Nickel and Chromium in Steel. EDWARD D. CAMPBELL and WALTER ARTHUR (*J. Amer. Chem. Soc.*, 1908, 30, 1116—1120).—A modification of Moore's process. One gram of the sample is converted into sulphate by evaporating with nitric acid and sulphuric acid, and to the solution, measuring about 70 c.c., 13 grams of sodium pyrophosphate dissolved in 70 c.c. of hot water are added. This is preferable to the citric acid usually employed. The precipitate is dissolved by cautious addition of ammonia, and warming towards the end.

Five c.c. of 0.05% silver nitrate and then 5 c.c. of 2% potassium iodide are added, and standardised potassium cyanide is run in until a clear liquid has been obtained. If copper is present, it must be remembered that 1 part of this counts for $\frac{3}{4}$ part of nickel. Copper, however, may be left undissolved by avoiding the use of nitric acid. If chromium is also present, it must be rendered harmless by oxidation with potassium permanganate before adding the pyrophosphate. If chromium only has to be estimated, the chromic acid thus formed is titrated in the usual way with ferrous ammonium sulphate and permanganate.

L. DE K.

Separation of Tungsten from Chromium. Estimation of Tungsten in Steel containing Chromium. GEORG VON KNORRE (*Zeitsch. anal. Chem.*, 1908, 47, 337—366).—1.5—6 Grams of the sample are dissolved in a small quantity of dilute hydrochloric acid. When no further action takes place on boiling, the excess of acid is at

once neutralised with sodium hydroxide, and, when cold, 8—10 c.c. of *N*/10 sulphuric acid are added, and then, without previous filtration, 30—60 c.c. of benzidine reagent (20 grams of benzidine and 25 c.c. of concentrated hydrochloric acid per litre). The precipitate, which contains all the tungsten, also more or less chromium, is washed with the diluted reagent and burnt in a platinum crucible. The ash is then fused with sodium carbonate, and the mass extracted with water. The filtrate is acidified with hydrochloric acid, using methyl-orange as indicator, and then boiled for some time to convert the tungsten into metatungstic acid. When cold, the chromic acid is reduced by a solution of sulphur dioxide, and the tungsten precipitated with excess of the benzidine reagent. Addition of sulphuric acid is, as a rule, unnecessary, as enough is formed owing to the oxidation of the sulphur dioxide. On ignition, pure tungsten trioxide is obtained.

L. DE K.

Volumetric Estimation of Titanium. GINO GALLO (*Gazzetta*, 1908, 38, i, 658—659. Compare Abstr., 1907, ii, 402, and Knecht and Hibbert, Abstr., 1903, ii, 509).—Titanium is usually accompanied by iron, so that the method given by Newton (this vol., ii, 325) for the volumetric estimation of titanium is inapplicable in practice.

T. H. P.

Purity and Volatility of Precipitated Antimony Sulphide. LEWIS A. YOUTZ (*J. Amer. Chem. Soc.*, 1908, 30, 975—979).—Antimony sulphide precipitated from a solution containing free hydrochloric acid is never pure, but is always contaminated with more or less antimony oxychloride, which cannot be removed even by redissolving the precipitate in ammonium sulphide and reprecipitating with acetic acid. In practice, this admixture does not interfere with the accuracy of the analysis if care is taken to heat the precipitate in an atmosphere of carbon dioxide at 250° only just long enough to transform it into the black sulphide; a prolonged heating causes volatilisation of the antimony oxychloride, and consequent loss.

Antimony sulphide precipitated from a solution free from chlorides does not suffer loss on prolonged heating at 250° in a current of carbon dioxide.

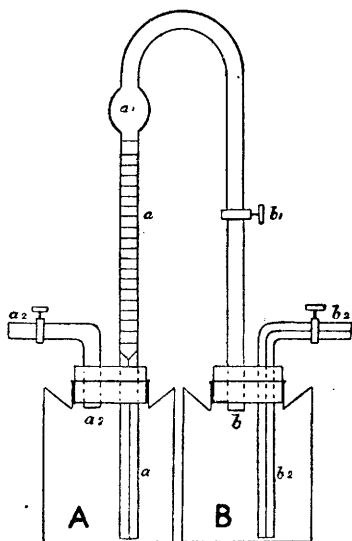
L. DE K.

Electrolytic Estimation of Bismuth. J. PESET (*Zeitsch. anal. Chem.*, 1908, 47, 401).—0.04—0.08 Gram of a bismuth salt is heated with 4—5 c.c. of water and 3 c.c. of sulphuric acid, and, when all is dissolved, the solution is diluted to 140 c.c. and submitted to electrolysis, using a rotating anode. Conditions: 2 volts; 0.002 to 0.01 ampere; temperature, 50°; time, eighteen to twenty hours. When the solution is quite free from bismuth, 0.08—0.15 gram of accurately-weighed cadmium sulphate dissolved in 10 c.c. of water is added, and the electrolysis is continued now under the following conditions: 2.5—3.5 volts; 0.2—0.3 ampere; time, eight hours.

The cadmium thoroughly protects the bismuth from oxidation, and renders it more adhesive.

L. DE K.

Simple Form of Apparatus for Observing the Rate of Absorption of Oxygen by Polluted Waters and by other Fermenting Liquids. WALTER E. ADENEY (*Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 280—287).—It has been shown (Abstr., 1896, ii, 322; 1898, ii, 86; 1902, ii, 221) that the determination of the extent and rate of absorption of oxygen is of fundamental importance in the examination of polluted waters. A simple apparatus for carrying out these determinations has now been devised, and is figured in the accompanying diagram. Flask *B* is charged with the polluted water and *A* with distilled water. The taps a_2 and b_2 being closed, absorption takes place in *B*, but not in *A*, which acts therefore as a standard pressure gauge. The difference of pressure read off on the graduated tube *a*, in which the distilled water rises when b_1 is opened, shows the amount of absorption in *B*. The original should be consulted for details as to the size of the apparatus, the method of use, and the manner of calculating the results.



Detection of Free Acids in Organic Liquids. FERNAND REPITON (*Ann. Chim. anal.*, 1908, 13, 269—270).—Five c.c. of Fehling's solution are boiled in a test-tube, and, if no change takes place, a few drops of the solution to be tested for acidity are added, when a precipitation of copper oxide takes place. One drop of an *N*/10 acid solution will give the test.

L. DE K.

Physico-chemical Analysis of Wines. PAUL DUTOIT and MARCEL DUBOUX (*Compt. rend.*, 1908, 147, 134—137).—A strong solution of baryta is added in small portions to the wine, the conductivity of which is measured after each addition. At first the conductivity falls, and a sharp minimum indicates the point at which all the sulphates have been precipitated. It then rises to a maximum, corresponding with neutrality to litmus. On further addition of baryta, a gelatinous precipitate occurs, and the curve of conductivity shows a shallow dip, the length of which is a measure of the amount of tannins present. After this, the conductivity rises in a straight line. In one operation, three constituents of the wine are thus determined, the sulphates and acids with great accuracy.

G. B.

Origin and Variations of Sulphates in Beer. Interpretation of Analytical Results. ACHILLE MÜNTZ and J. AUGUSTE TRILLAT (*Ann. Chim. anal.*, 1908, 13, 253—260).—An investigation to ascertain whether the presence of more than 2 grams of potassium sulphate per litre in beer should be called adulteration. The authors point out that even more than 2 grams may be fully accounted for by the sulphate derived from the water (Burton water, for instance) and the other materials used in the brewing process. The potassium is derived mainly from the malt, and is often present in sufficient quantity to cover the sulphate fully; the authors, however, doubt whether even then it is really permissible to calculate and report all the SO_3 found as potassium sulphate.

A further quantity of sulphate is due to the sulphuring of the hops or from the use of sulphites; a special test should be made to detect the latter.
L. DE K.

Detection of Thiocyanic Acid by means of Mercurous Chloride. EGIDIO POLLACCI (*Chem. Zentr.*, 1908, i, 1576; from *Arch. Pharmacol. experim.*, 7, 94—96).—To detect thiocyanic acid in saliva, 12—15 c.c. are warmed with 40—42 c.c. of absolute alcohol, the filtrate is concentrated to 6—7 c.c., and the residue again filtered. On adding mercurous chloride, this will be reduced in the cold to metallic mercury, which reaction is characteristic for thiocyanic acid. The process may be applied also to solid animal matter.
L. DE K.

Estimation of Citral in Lemon-grass Oil. ARMAND BLOCH (*Chem. Zentr.*, 1908, i, 1500; from *Bull. Sci. Pharmacol.*, 1908, 15, 72—77).—Ten c.c. of the sample are introduced into a 100 c.c. flask, the neck of which holds fully 10 c.c., and is graduated to 0.1 c.c. Twenty c.c. of a recently-prepared 30% sodium hydrogen sulphite solution are added, and the mass shaken until solidified. After fifteen minutes, the flask is suspended in a water-bath at 85° , and, when with constant shaking the mass has liquefied, the flask is three-fourths filled with the sulphite solution. After four to six minutes, a layer of oil will have formed, and more of the reagent is then added until the flask is filled up to the neck. After eight minutes, more is added so as to fill the graduated neck, and, after keeping the flask in the water-bath for another ten minutes, it is taken out and allowed to cool. The volume of unabsorbed oil is then read off.
L. DE K.

Titration of Chloral Hydrate. JULES GARNIER (*Chem. Zentr.*, 1908, i, 1492; from *Bull. Sci. Pharmacol.*, 1908, 15, 77—82).—In order to prevent a secondary reaction from taking place between the chloroform formed and the alkali, the test should be carried out as follows: 0.1655 gram of the sample is dissolved in 10 c.c. of water, and 12.5 c.c. of $N/10$ potassium hydroxide are added. The temperature should not exceed 15° , and, after fifteen to twenty minutes, the excess of alkali is titrated with $N/10$ sulphuric acid, with phenolphthalein as indicator. Another experiment should then be made, using only the slightest excess of alkali.
L. DE K.

Estimation of Acetone in Urine. T. STUART HART (*J. Biol. Chem.*, 1908, 4, 477—482).—The acetoacetic acid in the urine is first converted into acetone by heating at 100° ; the acetone is then drawn by a current of air into the absorbing cylinder, as in Folin's method (Abstr., 1907, ii, 588). The values for total acetone plus acetoacetic acid closely approximate to those obtained by the more lengthy Messinger-Huppert procedure. W. D. H.

The Estimation of Indole in Fæces by Herter and Foster's Method. E. GORTER and W. C. DE GRAAFF (*Pharm. Weekblad*, 1908, 45, 842—845).—Fæces are distilled with steam in presence of potassium hydroxide, and the distillate again distilled with steam after acidification with sulphuric acid. The indole is estimated in the second distillate by Herter and Foster's colorimetric method, using a standard solution prepared from pure indole. A. J. W.

Direct Application of Kerner's and of Liebig-Hesse's Process to Quinine Disulphate. PIETRO BIGINELLI (*Chem. Zentr.*, 1908, i, 1499—1500; from *Mon. Sci.*, 1908, [iv], 22, 185—187).—The conversion of the quinine disulphate into the normal salt is effected in the cold by lead carbonate (also compare Abstr., 1907, ii, 317). L. DE K.

Estimation of Casein: Determination of its Molecular Weight. GEORG TH. MATTHAIPOULOS (*Zeitsch. anal. Chem.*, 1908, 47, 492—501).—The process is based on the fact that casein forms a definite compound with sodium hydroxide when using phenolphthalein as indicator; in this compound, the casein seems to have a molecular weight of 1131.5, practically agreeing with the molecular weight 1135 attributed to it by Laqueur and Sackur (Abstr., 1903, i, 300).

The analysis is conducted as follows: In two separate beakers are placed 80 c.c. of water and 20 c.c. of milk, *N*/25 sulphuric acid is added to the milk until the casein appears to be completely precipitated, and the same amount is then added to the second beaker; as a rule, some 21 c.c. are required. To the contents of the control beaker is now added 1 c.c. of 1% alcoholic phenolphthalein, and the whole titrated with *N*/10 sodium hydroxide. The contents of the other beaker are filtered until 100 c.c. of a clear filtrate have been obtained. This is then also titrated with *N*/10 soda, and, after making an allowance for the dilution caused by the acid added, the difference in the titrations represents the alkali absorbed by the casein; 1 c.c. of *N*/10 alkali = 0.11315 gram of casein. L. DE K.

Pettenkoffer's Reaction. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1908, [vi], 28, 54—54).—The Pettenkoffer reaction for biliary acids is due to the formation of a trace of furfuraldehyde from the sugar added, and, in fact, a trace of this aldehyde may be substituted for the sugar.

The author now states that if a larger quantity of furfuraldehyde is employed, the colour generated is not purple, but blue. The test may be applied as follows: A small quantity of the biliary salts is dissolved in 1—2 c.c. of alcohol, 5—6 drops of a saturated aqueous solution of

furfuraldehyde are added, and then slowly an equal volume of sulphuric acid, when the blue colour will be developed at once. If an aqueous solution has to be tested, twice the quantity of furfuraldehyde should be employed.

The blue coloration is due entirely to the formation of cholic acid.

L. DE K.

Colour Test for Aल्पine and various other Local Anæsthetics. P. LEMAIRE (*Ann. Chim. anal.*, 1908, 13, 301—303).—The author has successfully applied the sulphonation test for benzoic acid to some local anæsthetics.

Two c.c. of pure sulphuric acid are placed in a test-tube, 0.05 gram of the substance is added, and the mixture heated until white fumes appear. 0.4 Gram of potassium nitrate in fine crystals is then added in small portions, and, when cold, the liquid is poured carefully into a beaker containing 25 c.c. of dilute ammonia (1:1). On adding a drop of ammonium hydrogen sulphide, a reddish-brown coloration appears. The test is successful with aल्पine (benzoyltetramethyldiaminopentanol hydrochloride), stovaine (benzoyldimethylaminopentanol hydrochloride), cocaine hydrochloride, tropacocaine hydrochloride, α -eucaine hydrochloride, and β -eucaine hydrochloride.

With other substances of this class, the test is indistinct, owing to secondary reactions.

L. DE K.

General and Physical Chemistry.

Refraction and Dispersion of Helium. KURT HERRMANN (*Ber. deut. physikal. Ges.*, 1908, 6, 476—482. Compare this vol., ii, 333).—Measurements of the refraction of air, hydrogen, and helium have been made for the cadmium line $\lambda = 0.6438\mu$. The values of the refractive index are for air 1.0002930, hydrogen 1.0001380, helium 1.00003406, at 0° and 760 mm. The values of v in the expression for the relative dispersion $1/v = (n_F - n_C)/(n_D - 1)$, where n_F , n_C , and n_D are the refractive indices for the lines F , C , and D , are for air 98.0, hydrogen 65.9, and helium 39.9. H. M. D.

Index of Refraction of Mixtures of Alcohols and Water. II. ANTONY G. DOROSCHEWSKY and S. V. DVORSCHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 908—931. Compare this vol., ii, 241).—The curves connecting the index of refraction of aqueous alcohol with the proportion of alcohol present for thallium, lithium, and sodium lights are of the same type, all exhibiting maxima at the same concentration; the curves become less convex as the wave-length is increased. Rise of temperature also results in a flattening of the curve, and in a displacement of the position of the maximum towards the water axis.

When water is added to *isopropyl* alcohol, a well-defined maximum refrangibility, corresponding with 93—94% of the alcohol, is observed. With normal propyl alcohol, a less clearly marked maximum exists at about 97%. With butyl and *isobutyl* alcohols, addition of water causes lowering of the index of refraction, no maximum being observed. The rate of change of the index of refraction with temperature, dn/dt , also varies regularly, exhibiting a maximum in the region of the maximum index of refraction. In general, the magnitude of dn/dt for propyl, *isopropyl*, butyl, and *isobutyl* alcohols varies little, but diminishes slightly as the molecular weight of the alcohol increases, and is greater for the *iso*alcohols than for the normal ones.

The value of a in Pulfrich's formula (*Zeitsch. physikal. Chem.*, 1889, 4, 561) $(n - n_v)/n = a(D - D_v)/D$ has been calculated for mixtures of ethyl, propyl, and *isopropyl* alcohols with water, and is found to be a constant independent of the temperature and of the wave-length of the light used. For ethyl alcohol, the mean value of a is 0.975, for propyl alcohol, 0.92, and for *isopropyl* alcohol, 0.95. Knowing the value of a , the indices of refraction of mixtures of alcohol and water, and the specific gravities and indices of refraction of absolute alcohol and water, the compression of the aqueous alcoholic mixtures can be calculated; results obtained in this way for various mixtures of ethyl alcohol and water at 15°, 20°, and 30° agree closely with the experimental numbers. Calculation of the concentration of mixtures of alcohol and water by means of Gladstone's formula, $(n - 1)/d = \text{const.}$,

yields accurate results, which are also given by Pulfrich's (*loc. cit.*) modification of Gladstone's formula.

The expansion of liquids by heat is expressed with great accuracy by the equation $v_t = v_0/(1 - kt)$ (compare Mendeléeff, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 1). The authors find that a similar equation, $n_t = n_0/(1 + kt)$, gives accurately the relation between the index of refraction of a liquid and the temperature; k is termed the modulus of the index of refraction.

T. H. P.

New Law of Series Spectra. W. RITZ (*Physikal. Zeitsch.*, 1908, 9, 521—529).—A formula is given by means of which new series of spectral lines can be deduced from known series. The newly-discovered series of lines in the spectra of the alkali metals are accurately represented by means of the formula, and it is also shown that the series of lines in the spectra of helium, copper, and the alkaline earth metals are in agreement with it.

H. M. D.

Spectrum of the Lighter Constituents of Air. HERBERT E. WATSON (*Proc. Roy. Soc.*, 1908, 81, A, 181—194).—The lighter portions of air were separated by fractional distillation by Coates (*Abstr.*, 1907, ii, 257), and the portion not absorbed by charcoal at -190° was further fractionated. One fraction pumped off charcoal at -205° , and a second fraction at -190° , have now been examined spectroscopically by the author. The spectra of the first order, and, for all lines of wave-length less than 4100, of the second order as well, obtained with a Rowland grating, were photographed. A very long exposure was given in order that faint lines might not be overlooked.

The wave-lengths obtained, along with those of Liveing and Dewar (*Abstr.*, 1901, ii, 213) and Baly (*Abstr.*, 1904, ii, 3) for comparison, are given in tabular form. After allowing for the lines ordinarily ascribed to helium and neon (and also to traces of argon and hydrogen), a considerable number of lines remain unaccounted for. These lines, however, do not appear to show more than accidental coincidences with any of the chief nebular or coronal lines, or with any of the lines of the spectrum of the solar chromosphere. It seems probable, therefore, that the majority are really neon lines which were not observed previously owing to insufficient exposure, and there is no evidence that the fractions contain gases other than those already mentioned.

G. S.

Spectrum of Radium Emanation. ALEXANDER T. CAMERON and SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1908, 81, A, 210—213).—In a previous paper (*Abstr.*, 1904, ii, 529), Ramsay and Collie gave measurements of the spectrum of radium emanation obtained with a direct-vision spectroscope. The spectrum in question has now been photographed. Three successive photographs were taken, but only the first showed the spectrum of the emanation alone, as the effect of the discharge is to drive the emanation towards the negative electrode, where it is largely absorbed, and the tube soon shows only the hydrogen spectrum.

Much better results were obtained with copper electrodes in place of the aluminium electrodes first used. The former electrodes appear not to contain hydrogen, and absorb the emanation much more slowly than aluminium does.

The wave-lengths and intensities of the lines ascribed to the emanation are given in the paper (compare Rutherford and Royds, following abstract). G. S.

Spectrum of Radium Emanation. ERNEST RUTHERFORD and T. ROYDS (*Phil. Mag.*, 1908, [vi], 16, 313—317. Compare Cameron and Ramsay, preceding abstract).—The spectrum of radium emanation purified as well as possible from permanent gases and carbon dioxide was found to consist of entirely characteristic lines. The authors have mapped a spectrum of seventy-four lines between 3612.2 \AA and 6079 \AA , thirty-nine lines being observed visually, and sixty-three photographed. None of these lines has been identified in any stellar spectrum.

The colour of the discharge is bluish, the spectrum being characterised by groups of brilliant green and violet lines.

During the passage of the discharge, the emanation lines grow gradually weaker, and the emanation itself appears to be driven into the walls of the tube, whence it is removed with difficulty by strongly heating the glass. After three days, the glass is much blackened, and the principal lines of helium appear in the spectrum. R. J. C.

Quantitative Indications Furnished by Dissociation Spectra: Silver. ANTOINE DE GRAMONT (*Compt. rend.*, 1908, 147, 307—309. Compare Abstr., 1907, ii, 728; this vol., ii, 645).—The following series of argentiferous materials have been examined spectroscopically, employing the simple or oscillating condensed spark: (1) galena; (2) commercial lead; (3) alloys of lead and silver; (4) alloys of tin and silver, all of known composition. Spectra of the four classes have been photographed on the same plate, and to render the quantitative indications comparable, six spectra of each class, representing six different concentrations of silver, have been recorded by vertical movement of the plate. It is found that the number and intensity of the lines for silver have a direct and constant relation to the concentration of the metal in the sample. A table is given showing the lines which disappear at different concentrations of silver from 1% to 0.0001%.

It is necessary to guard against certain foreign lines which coincide with those of silver, and also against the halo occasioned by bright lines of lead or tin. W. O. W.

Apparatus for Producing Coloured Flames. ROBERT GOLDSCHMIDT (*Bull. Soc. chim. Belg.*, 1908, 22, 255—259).—A description and sketch of a simple arrangement for obtaining a flame permanently and intensely coloured.

The air supply of a Bunsen flame is charged with a spray produced by electrolysis of a suitable solution. W. O. W.

Electro-optical Properties of Liquid Mixtures. J. CHAUDIER (*Ann. Chim. Phys.*, 1908, [viii], 15, 67—140).—The author first gives a résumé of previous work on the changes undergone by light when it traverses a liquid situated in a magnetic field (compare Majorana, *Atti. R. Accad. Lincei*, 1902, 11, i, 374, 463, 531; 11, ii, 90, 139; Meslin, *Abstr.*, 1903, ii, 408, 521, 585).

The laws of electric dichroism are shown, theoretically and experimentally, to be similar to those established by Meslin (*loc. cit.*) for magnetic dichroism. But whilst the sign of electric dichroism is independent of the relative value of the dielectric constants of the media, that of magnetic dichroism can be altered by modifying the relative value of the magnetic constants of the solid and surrounding liquid. The dichroism is proportional to the length of liquid traversed by the light and to the concentration of the liquid, and increases with the intensity of the field to a limiting value.

A mixture of liquids placed in a uniform electric field exhibits marked birefraction, provided that the suspended particles are sufficiently minute.

The field due to gravity is also capable of producing the phenomena of dichroism and even of birefraction. The action of any uniform field is hence manifested in an orientation of the particles of mixed active liquids, which then exhibit the phenomena of dichroism and birefraction; the laws of these phenomena are the same whatever the nature of the field, provided that account is taken of the change of sign due to diamagnetism. If the particles in suspension have a greater magnitude than about 0.3 mm., dichroism alone is observed, and is due to the reflection of light by the crystalline surfaces. If the particles are smaller and uniform in size, dichroism is still the principal phenomenon observed, but birefraction also appears, and the modifications due to diffraction come into play. As the dimensions of the particles diminish, dichroism becomes rarer, and birefraction plays a more important rôle, whilst, when they are infinitely small, as in colloidal solutions, the phenomena of reflection and refraction are no longer produced and the liquids are only birefractive. T. H. P.

Electrochemistry of Light. III. Halogen Carriers. WILDER D. BANCROFT (*J. Physical Chem.*, 1908, 12, 417—447. Compare this vol., ii, 448, 549).—The facts and theories relating to the action of carriers in the chlorination and bromination of hydrocarbons are discussed, and a new theory is put forward which resembles in some respects that advanced by Bruner (this vol., i, 146).

The chief conclusions at which the author arrives are that the action of halogen carriers is not due to the intermediate formation of additive compounds, and that under suitable conditions the carriers react with the hydrocarbons even in the absence of free halogen.

To account for the observed facts of substitution in the side-chain and in the nucleus, it is supposed that the halogens and the carriers give rise to ions, and that substitution takes place in the nucleus when the negative ions are present in excess and in the side-chain when the positive ions predominate. By means of this theory, the catalytic action of ferrie, stannic, and aluminium chlorides, as well as of iodine

monochloride, phosphorus pentachloride, water, and sunlight, can be accounted for. The facts relating to the velocity of the reactions when certain of these carriers are employed can also be explained.

H. M. D.

Photographic Action of Metals and Hydrogen Peroxide (So-called Metallic Radiation). SEM SAELAND (*Ann. Physik*, 1908, [iv], 26, 899—917. Compare Russell, *Abstr.*, 1898, ii, 287; 1899, ii, 720).—An investigation has been made of the conditions under which photographic action is produced by certain metals and by solutions of hydrogen peroxide, and from the results the author concludes that the action of the metals is due to chemical changes and not to the emission of any special type of radiation.

The activity of the metals, measured immediately after polishing the surface, increases with the electropositive character, and the greater the activity of the freshly-polished metal the more rapidly does this activity diminish with time. When the metal is kept in a vacuum, this diminution in the activity does not take place. The photographic activity is also unaltered after the metals have been heated, and exposure to an electrical field has no influence on the photographic effect. The darkening of the plates is greatly increased if the plates are left undeveloped for some time, or if before developing they are gently heated.

In a vacuum containing phosphoric oxide, the photographic action does not take place; conditions under which hydrogen peroxide can be formed appear to be essential. Experiments are also described which indicate that the action does not spread from the active metals in a rectilinear manner, but that, on the other hand, the distribution is such as would be expected if gaseous diffusion were taking place. The photographic action is not observed when certain metals, such as copper, or alloys, like brass, are interposed as diaphragms between the active metals and the photographic plate. It is also inhibited if very thin, non-porous sheets of metals are interposed, or if a sufficiently rapid current of air is passed between the photographic plate and the active metal.

The observations indicate the identity of the action of metals and of hydrogen peroxide solutions. The metals therefore exhibit photographic activity in consequence of the formation of hydrogen peroxide, and are only active when the conditions are such that hydrogen peroxide can be produced.

H. M. D.

Relation of Absorption and Sensitiveness in Photographic Preparations. ERICH LEHMANN (*Zeitsch. physikal. Chem.*, 1908, 64, 89—119).—The question as to the influence of wave-length on the relation of optical absorption to photochemical extinction has not hitherto received a definite answer. The author shows that in the case of silver iodide a solution of the problem is possible. For silver iodide either by itself or in collodion, the maximum of absorption and the maximum of sensitiveness are coincident. In a gelatin emulsion of silver iodide, however, the maximum of sensitiveness is displaced

16.65 μ relatively to the absorption maximum. This may be due to the formation of an organic silver salt.

It is exceedingly probable that similar results would be obtained with silver chloride and bromide if these substances could be subjected to direct observation.

J. C. P.

Photochemical Oxidation of Hydrogen Iodide by Oxygen.

JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1908, 64, 215—228. Compare Abstr., 1907, ii, 212).—The rate of decrease of the oxygen concentration is now found to be proportional to the $2/3$ power of the acid concentration both in the light and in the dark. The fact that in the earlier work different values were found for the exponent of the hydrochloric acid concentration in the light and in the dark was probably due to some catalytic agent, and it is now shown that the presence of copper sulphate is sufficient to cause such a difference.

For the reaction in the dark, the value of K_{T+10}/K_T is now found to be 2.07; for the reaction in the light the value is 1.38.

The author's further experiments show that the photochemical oxidation of hydrogen iodide by oxygen is the sum of two independent changes: (1) the reaction in the dark; (2) the reaction in the light. Hence the velocity may be represented by the formula: $-d(O_2)/dt = [K_d \cdot 10^{aT} + K_l \cdot I \cdot 10^{bT}](HCl)^{\frac{2}{3}}(KI)^{\frac{2}{3}}(O_2)$.

J. C. P.

Method of Carbon Dioxide Assimilation. EMIL BAUR (*Zeitsch.*

physikal. Chem., 1908, 63, 683—710).—A solution of potassium ferric oxalate in diffused daylight evolves carbon dioxide, but the evolution of gas ceases before all the ferric salt is decomposed. When a solution of potassium ferrous oxalate is kept in an atmosphere of carbon dioxide, the gas is gradually absorbed, and ferric salt is produced. These observations may be summed up in the equation: $Fe(C_2O_4)_3K_3 \rightleftharpoons Fe(C_2O_4)_2K_2 + \frac{1}{2}C_2O_4K_2 + CO_2$.

The reversibility of this reaction has led the author to consider the suggestion, that in the original production of organic compounds the reduction of carbon dioxide to oxalic acid was the first stage. In order to make the energy of light available for this reduction, the system ferrous oxalate + ferric oxalate + carbon dioxide must be combined with a system in which oxygen is developed under the influence of light. This latter result is attained, for instance, when silver chloride immersed in water is exposed to light, and the author shows how in a vessel provided with a septum of photochloride and a semipermeable membrane it would be possible, theoretically at least, to effect the conversion of carbon dioxide and water into oxalic acid and oxygen. In endeavouring to find other systems which, like silver chloride in water, would evolve oxygen on exposure to light, the author has studied the way in which the potentials of iron, mercury, uranium, and cerium salts are affected by light. The *P.D.* at a platinum electrode immersed in a solution containing both uranous and uranyl salts is actually less positive when exposed to sunlight than when kept in the dark. The displacement of potential is considerable, and takes place more or less rapidly according to the

nature of the salts employed. The results obtained with iron, mercury, and cerium salts were less noteworthy.

The term "light content" ("Lichtinhalt") is proposed for the quantity of energy which is absorbed by a light-sensitive substance, and which goes to change its chemical potential. The value of this "light content" is deduced from the *E.M.F.* of photoelectric cells and their temperature-coefficients.

J. C. P.

Distribution of the Radiation from Radioactive Substances. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1908, 9, 537—541).—To explain the irregular distribution of the radiation from substances containing uranium, which Greinacher (this vol., ii, 551) found on examination of photographic plates which had been placed in contact with these substances cut into sections of well-defined geometrical forms, it is not necessary to attribute the action to secondary rays. The phenomenon can be referred to the action of the β -rays if it is assumed that the emitted rays follow the cosine law of Lambert. Conversely, the experimental observations indicate the validity of this law in the case of corpuscular radiation.

H. M. D.

Experiments with Radium Emanation. Volume of the Emanation. ERNEST RUTHERFORD (*Phil. Mag.*, 1908, 16, 300—312).—The amount of emanation in equilibrium with one gram of radium is q/λ , where q is the rate of production per second and λ is the radioactive constant of the emanation. The value of λ is about $1/468000$.

Assuming that one atom of radium emits one α -particle and then becomes one atom of emanation, and knowing the number of α -particles emitted per second and the charge on each (Rutherford and Geiger, this vol., ii, 794), the author calculates the volume of the emanation to be 0.57 cub. mm. per gram of radium. Ramsay and Cameron, however (*Trans.*, 1907, 91, 1266), obtained 7.07 cub. mm. of emanation from one gram of radium. The author finds that probably 80% of the gas measured by these authors consisted of matter foreign to the emanation itself.

To obtain pure emanation, radium bromide was either heated in a quartz tube or dissolved in water, the emanation being pumped off with the oxygen and hydrogen formed, and sparked down as described by Ramsay. The emanation was collected over potassium hydroxide, and condensed by cooling in liquid air. After all uncondensed gases had been pumped off, the emanation was allowed to gasify and remain some hours in contact with potassium hydroxide. It was finally liquefied again by liquid pentane at a temperature between 150° and 186° and exhausted by the pump, a portion being volatilised and lost in the process. Difficulty was experienced in obtaining the emanation free from carbon dioxide, although phosphoric oxide was used to lubricate the stopcocks and the emanation frequently stood twenty-four hours over potassium hydroxide. The emanation, as finally measured in a capillary tube, was in such a state of purity that the spectrum of carbon dioxide was hardly seen, but a new spectrum of bright lines certainly due to the emanation itself appeared.

The amount of radium corresponding with the amount of emanation measured was estimated by comparing the γ -ray activity of the emanation with that of a standard sample of radium bromide. When the emanation was well purified, its volume varied from 0.80 to 1.32 cub. mm. per gram of radium, decreasing rapidly and spontaneously to 0.58 to 0.66 cub. mm. The average final volume corrected for temperature and pressure was 0.58 cub. mm. The highly-purified emanation had the usual half-period of 3.75 days, and the author finds it difficult to explain the spontaneous contraction. In one experiment when purified emanation was left eleven days in the capillary, its volume greatly increased again, and a brilliant spectrum was obtained showing all the lines of helium. Passage of electric sparks caused the emanation to condense on the glass walls of the capillary, leaving only carbon dioxide. At the temperature of liquid air, the emanation has a sensible vapour pressure.

R. J. C.

Relative Activity of Emanation and Active Deposit from Thorium and from Actinium. HOWARD L. BRONSON (*Phil. Mag.*, 1908, [vi], 16, 291—299).—It is frequently assumed that each atom of the various radioactive substances gives off either one or no α -particle each time it undergoes transformation. The author's comparisons of the relative activity of emanation and active deposit in the cases of thorium and actinium, making due allowance for the different mean free paths of the α -particles in the various cases, fail to support this view.

A quantity of the volatile radioactive products from thorium or actinium was conveyed to the testing vessel by a current of air, and its total ionising activity was measured. After waiting a short time to allow the emanation to decay, the residual ionising activity due to the active deposit was measured. The activity of the emanation was obtained by difference. Knowing the rates of transformation of all the products, the activity of the deposit when at its maximum value could be calculated.

The ratio of ionisation due to active deposit to that due to emanation was found to vary from 0.34 to 0.40 in the case of thorium, and from 0.28 to 0.41 with actinium, different ratios being obtained with measuring vessels of different sizes.

The active deposit from thorium is supposed to contain thorium *B* and thorium *C*. In all cases with thorium, the calculated ionisation ratio was four times as great as the measured ratio, whilst with actinium the calculated ratio was always twice as great as the measured. The presence of other substances of short transformation periods would serve to explain the results, but there is no evidence for this (compare Hahn, *Abstr.*, 1906, ii, 718). The author prefers to suppose that atoms of thorium *B* and thorium *C* give off the same number of α -particles during transformation, but that an atom of thorium emanation gives off four times as many; also, that a disintegrating atom of actinium emanation gives off twice as many α -particles as an atom of its active deposit. On the other hand, radium emanation, radium *A*, and radium *C* appear to give off the same number of α -particles per atom. The actual number of ejected

α -particles per atom cannot be stated as the determinations are only relative.
R. J. C.

Ozonisation of Air by the Action of Radium Salts and Emanation. RAFFAELLO NASINI and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 46—49).—The authors discuss the formation of ozone by radium salts, which is affirmed by Madame Curie and by Giesel, but denied by Ramsay and by Soddy. The authors' experiments show that, in presence of a large excess of air or oxygen, ozone is formed by the action of radium.

A small bottle containing 0.005 gram of radium bromide dissolved in 30 c.c. of water was placed open in a 5-litre flask containing air. When the flask was closed by a ground-glass stopper, after some hours the air inside gave the reactions of ozone, but if a cork or a rubber stopper was used, the air gave no odour or reactions of ozone, which had been destroyed.

Further experiments indicate that the emanation itself cannot produce ozone, but the results cannot be regarded as absolutely decisive.
T. H. P.

Action of Radium Emanation on Solutions of Copper Salts. MADAME MARIE CURIE and M^{lle}. GLEDITSCH (*Compt. rend.*, 1908, 147, 345—349).—The authors have repeated Cameron and Ramsay's experiments (*Trans.*, 1907, 91, 1593) on the action of radium emanation on copper salts, taking special precautions to employ apparatus and reagents free from traces of lithium. Platinum vessels were used, since it was found that distilled water free from lithium becomes contaminated with traces of this element when allowed to remain in contact with glass for twenty-four hours. The use of quartz vessels, especially of the transparent variety, is inadmissible, since these contain notable amounts of lithium. The water and acids necessary were distilled in platinum retorts, and the reagents were not allowed to come into contact with glass during the experiments. It was found practically impossible to remove the last traces of lithium from copper sulphate. After allowing the emanation to act on the solution, the copper was removed, and, after evaporation of the liquid, the residue, which weighed about 0.0004 gram, was examined spectroscopically. Sodium and potassium were found to be present, but lithium could not be detected. Comparative experiments on sodium sulphate containing known quantities of lithium sulphate indicated that the residue could not have contained more than 0.6×10^{-5} milligram lithium. In order to show that no lithium was lost during the experiment, a control experiment was carried out on a solution containing 0.27 gram of copper and an amount of lithium sulphate equivalent to 1.7×10^{-4} milligram of the chloride. After removal of the copper, lithium was readily detected in the residue.

The authors consider that the formation of sodium and lithium has not been established by Cameron and Ramsay.
W. O. W.

Retardation of α -Rays by Metal Foils, and its Variation with the Speed of the α -Particles. T. SMITH TAYLOR (*Amer. J. Sci.*, 1908, [iv], 26, 169—179).—In the experiments of Bragg and

Kleeman, and also in those of Kučera and Mašek (Abstr., 1907, ii, 4), McClung (Abstr., 1906, ii, 138), Rutherford (Abstr., 1906, ii, 642), and Levin (Abstr., 1906, ii, 595), on the effect produced on the range of α -particles by the interposition of sheets of metals, the air equivalents corresponding with different positions of the screen were obtained by determining the difference of the range with the source of the rays uncovered and with the screen in place. As this method is not very accurate, a new method has been devised, and is described in the present paper.

Polonium was used as the source of the rays, and experiments were made with thin sheets of gold, lead, tin, aluminium, and silver of varying thickness. The results show that the air equivalents of sheets of metal foil decrease with the range, and hence with the speed, of the α -particles. The change is very small for thin foil of the lighter metals when the range of the α -particles is high, but for thicker sheets or a lower range, the change is more considerable. A comparison of the change for sheets of different metals of nearly equal air equivalents shows that the rate of change is in the order of the atomic weights of the metals.

E. G.

Charge and Nature of the α -Particle. ERNEST RUTHERFORD and HANS GEIGER (*Proc. Roy. Soc.*, 1908, 81, A, 162—173. Compare this vol., ii, 555).—The total charge carried by the α -particles expelled per second from a known weight of radium has been determined directly, and from the result and the number of α -particles expelled per second per gram of radium, the charge carried by an α -particle has been calculated as 9.3×10^{-10} E.S. units. In determining the total charge carried by the particles, radium C was used as a source of radiation; the particles passed through aluminium plates into a testing chamber, and the current was measured in the usual way. The methods used to eliminate other rays, and to determine the strength of the radiating source, are fully described.

The charge carried by an α -particle, calculated on the assumption that the heating effect of radium is a measure of the kinetic energy of the α -particles expelled from it, is 9.1×10^{-10} E.S. units, in good agreement with the above value. The charge e carried by a hydrogen atom has been estimated by J. J. Thomson, H. A. Wilson, and others at $3\text{--}4 \times 10^{-10}$ E.S. units, from which it would follow that the charge on the α -particle is between $2e$ and $3e$. Reasons are given for the assumption that the values hitherto found for e are too low. As the α -particle probably carries $2e$, the most probable value for e is 4.65×10^{-10} E.S. units. Support is lent to this view by a new calculation of e from the known period of transformation of radium, the result obtained being 4.1×10^{-10} E.S. units.

As the ratio of the charge on the α -particle to its mass has already been determined, the mass (atomic weight) of the α -particle has now been calculated as 3.84, which supports Rutherford's previous suggestion that the α -particle, after it has lost its positive charge, is a helium atom.

From the data now available, some important radioactive magnitudes, such as the volume of the emanation and the rate of production of helium, have been calculated.

G. S.

Scattering of the α -Particles by Matter. HANS GEIGER (*Proc. Roy. Soc.*, 1908, 81, 4, 174—177).—Radium emanation was employed as a source of α -particles; these were allowed to pass through a narrow slit on their way to a phosphorescent screen, and from a comparison of the area reached by the rays (as determined by observing the scintillations) with the magnitude of the geometrical image of the slit, the amount of scattering could be ascertained.

In a vacuum, scarcely any scintillations were observed outside the image of the slit, but, when air was allowed to enter, the area of scintillation increased. The same effect was produced in a vacuum when the slit was covered with gold leaf, and to a smaller extent when aluminium foil was employed. G. S.

Secondary γ -Rays due to γ -Rays of Radium C. A. S. EVE (*Phil. Mag.*, 1908, [vi], 16, 224—234).—The intensity of secondary cathode radiation from various substances under the impact of Röntgen rays, β -rays, and γ -rays has been shown to be a function of the atomic weight of the secondary radiator, but comparison of Townsend's determinations of secondary radiation, from various substances under the influence of X -rays, with the author's values for the total secondary radiation produced by γ -rays, reveals striking discrepancies. The author has endeavoured to find the origin of these differences, which, if Röntgen rays and γ -rays are fundamentally of the same nature, ought not to arise.

Upwards of 30% of the secondary radiation may consist of secondary γ -rays with a penetrating power equal to that of primary γ -rays from actinium, but greater than that of primary γ -rays from uranium or radium. One or two millimetres of lead or aluminium suffice to absorb completely the secondary cathode rays from lead, iron, or brick radiators, but allow the secondary γ -rays to pass. When comparative experiments are made in such a way that cathode secondary rays are absorbed and only secondary γ -rays reach the electroscope, the secondary effects produced by X -rays and γ -rays of radium are neither in order of the atomic weights nor of the densities of the radiators, and are not in agreement with one another. The secondary rays which reach the electroscope are γ -rays, and not penetrating cathode rays, since their intensity is not affected by a strong magnetic field.

The differences apparently lie more in the velocity than in the nature of the particles. Even cathode secondary radiation, which follows the order of the atomic weights, has a much higher velocity when excited by β - or γ -rays than by X -rays. The similarity of the β - and γ -ray effects in this instance is held to support Bragg's theory that β - and γ -particles are essentially the same, but bear different charges.

The intensity of the secondary γ -rays induced by primary γ -rays from radium depends on the material surrounding the radium. Primary γ -rays traverse steel more readily than lead, but rays which have passed through steel are more readily absorbed by lead than rays which have already passed through lead. Taking the case of radium enclosed in a glass tube, the secondary radiation due to γ -radiation is 7.5% of that due to β - and γ -radiation together. Of this 7.5%, the

larger part is cathode secondary radiation, the proportion of γ -radiation in it being 6.2% from lead, 25% from iron, and 28% from brick.

The coefficient of absorption of primary γ -rays from radium is 0.45—0.57, from uranium 1.4, from actinium 2.7—4.7, whilst the secondary γ -rays excited by radium γ -rays in lead, iron, and brick have a coefficient about 4.6. The author is of the opinion that secondary γ -rays caused by the primary γ -rays of actinium would have a coefficient of absorption even lower than 4.6, and approximating to that of X-rays.

R. J. C.

Polonium Rays. CH. LATTÈS (*Chem. Zentr.*, 1908, i, 2137—2138; from *Le Radium*, 1908, 5, 97—102).—The author has endeavoured to obtain evidence of the production of secondary rays when polonium rays fall upon a metal plate by means of delicate electrical and photographic processes. In this he has been unsuccessful, although it is probable that secondary rays are produced (Logeman, *Abstr.*, 1906, ii, 721), and should be photographically detectable.

J. V. E.

Radioactivity of Certain Goitrogenic Springs. RÉPIN (*Compt. rend.*, 1908, 147, 387—388).—Three samples of spring water from the neighbourhood of St. Jean de Maurienne were found to be distinctly radioactive ($A=0.011$ to 0.031 in Curie-Laborde units). Endemic goitre is known to be prevalent in the districts where these waters are used for drinking purposes, and the author suggests that the well-known disappearance of goitrogenic properties which takes place after the lapse of time is connected with the decay in the radioactivity of the waters.

W. O. W.

Invisible Radiations from the Explosive Discharge in Air. I. SCHINCAGLIA (*Nuovo Cim.*, 1908, [v], 15, 481—491).—An apparatus is described which allows of the very accurate regulation of a spark gap, in order to study the effect of radiations from another spark in causing the spark to pass. The transparency of various liquids to the invisible rays was examined by enclosing them in a quartz or selenite cell and interposing them between the spark gaps.

Whilst water and alcohol are transparent, metallic salts and many organic liquids, such as turpentine, carbon disulphide, and petroleum, are highly opaque, indicating that the radiation from the spark does not contain extreme ultra-violet rays.

C. H. D.

Radiation from Drying Oils. WERNER SCHMIDT (*Zeitsch. physikal. Chem.*, 1908, 64, 243—250).—Gum arabic when kept in the neighbourhood of linseed-oil varnish is found to undergo a slow change and becomes insoluble. If a gum solution contains a little chromate, the gum is rendered insoluble, rapidly when exposed to light, and more slowly when exposed to linseed-oil varnish in a dark room. This analogy between the action of light and the action of the drying oil is borne out by a study of the effect of the latter on a photographic plate. The radiation from the oil affects the plate even through slips

of gelatin or paper, and if a perforated sheet of metal is interposed, an image is obtained. The phenomenon of solarisation has also been observed.

This behaviour of linseed-oil varnish is connected with the oxidation which goes on during drying, and which is possibly accompanied by the formation of ozone or other compounds of a superoxide character. It has been noticed that the bright surface of a metal plate exposed in the neighbourhood of a linseed-oil varnish shows evidence of oxidation.

J. C. P.

Formation of Mists in Presence of Radium Emanation. MADAME MARIE CURIE (*Compt. rend.*, 1908, 147, 379—382. Compare this vol., ii, 7).—The appearance of mists in moist gases induced by radium emanation appears to be due to the formation in the gases of chemical compounds capable of absorbing water vapour. The gases experimented on were contained in sealed glass bulbs illuminated by the electric arc. Air containing pure water vapour and charged with emanation gives a slight mist, persisting for several days; a mist is not produced when the air is replaced by carbon dioxide. If the water contains half its weight of sulphuric acid, an intense mist, lasting for several months, is produced whether the gas employed is air or carbon dioxide.

A permanent mist is also obtained in a bulb containing concentrated sulphuric acid and carbon dioxide; in a blank experiment without emanation, a still more intense mist was produced on warming the bulb, but this disappeared in less than a day. When caoutchouc stoppers are used to close the bulbs, the mists are very dense and persistent, probably through the oxidation of sulphur and organic matter giving rise to products capable of acting as centres of condensation. This is confirmed by the production of a fine, persistent mist in a bulb containing water, air, and emanation, with a fragment of sulphur kept out of contact with the water; at the end of the experiment, sulphuric acid is present in the water. The presence of nitric acid has also been detected when air has been used.

Similar mists are formed in air charged with light petroleum or carbon disulphide, and also in carbon dioxide containing anhydrous ether with emanation. In some instances, mists are formed when solids are employed; in these cases, a deposit is visible on the sides of the vessel. Emanation induces a mist in carbon dioxide containing iodine, or in air containing camphor; in the first instance, the mist subsides in a few days. Actinium causes a mist in moist carbon dioxide.

The drops constituting the mist in the foregoing experiments behave as if they had no electrostatic charge when introduced into an electric field.

W. O. W.

Supersaturation and Nuclear Condensation of Certain Organic Vapours. T. H. LABY (*Phil. Trans.*, 1908, A, 208, 445—474; *Proc. Roy. Soc.*, 1908, 81, A, 219—220).—Dust-free air, saturated with an organic vapour (ester, acid, or alcohol), was subjected to sudden adiabatic expansion in a special apparatus, and the least expansion required to produce condensation of the vapour noted. The

effect of the presence of ionic nuclei, obtained by previous exposure to Röntgen rays, on the conditions of condensation was also noted, as well as the different effects produced according as positive or negative ions were in excess.

The degree of supersaturation, S , existing at the end of the expansion has been calculated for a number of alcohols, esters, and acids; it is greatest for the acids and least for the alcohols. There is good agreement in some cases between the values of S deduced from the expansions and those calculated on the accepted theory of condensation on ionic nuclei.

In the case of certain acids, greater expansion is necessary to produce condensation in the absence of ionic nuclei than when they are present. The positive ions are more efficient condensing agents than the negative for certain organic vapours, but water condenses more easily on negative ions.

Certain organic compounds, including alcohols and esters, become negatively charged when air is bubbled through them, but acetic acid becomes positively charged. G. S.

Influence of Traces of Nitrous Gases on the Condensation of Water Vapour. ERICH PRINGAL (*Ann. Physik*, 1908, [iv], 26, 727—750).—The object of the experiments was to determine whether the condensing action of ordinary ozonised oxygen or air on water vapour is due to the presence of small quantities of nitrous gases. The experimental observations show that this is the case, and that pure ozone has no condensing action. In presence of water vapour, ozone appears to act on nitrogen and yield the condensation agent. Attention is called to the importance of these observations in connexion with the condensation of atmospheric water vapour. H. M. D.

Genesis of Ions by Collision of Positive and Negative Ions in a Gas. Experiments on Argon and Helium. E. W. B. GILL and F. B. PIDDUCK (*Phil. Mag.*, 1908, [vi], 16, 280—290).—Townsend and Hurst (Abstr., 1905, ii, 7), assuming that positive and negative ions produce ionisation of a gas at definite rates, deduced an equation connecting gaseous conductivity and sparking potential with the gap between the electrodes. The authors have determined the minimum voltage required to produce a spark in argon or helium and the conductivity at various pressures in order to test the above theorem.

Each negative ion is supposed to produce α gaseous ions, and each positive ion β gaseous ions, in moving through a centimetre. Experiments were carried out with gaseous pressures of 0.66 mm. to 13 mm. and various distances between the electrodes. The values of the constants α and β at any one pressure could be calculated from three conductivity measurements. The remaining conductivities at this pressure were found to be in satisfactory agreement with Townsend and Hurst's equation. Additional support for the theory is found in the extremely close agreement between the sparking potentials determined directly in argon and helium and the potentials calculated from conductivity measurements at lower potentials. The values of the constants α and β for argon are greater than for air, so that argon is

more readily ionised than air by both positive and negative ions. The helium employed was somewhat impure, but as the theory holds equally well for mixtures, values of α and β could be calculated. Even impure helium is more readily ionised than hydrogen, and, after purification by charcoal cooled in liquid air, the sparking potential of helium was lowered (compare Strutt, *Trans. Roy. Soc.*, 1900, 4, 193, 377). On the other hand, purification of the argon employed did not affect the values obtained with it.

After the passage of one spark, a higher potential was required to pass another immediately. Passing a spark in the reverse direction facilitated recovery. This effect may be due to some kind of polarisation at the zinc electrodes.

R. J. C.

Positive Electrons. A. BESTELMEYER (*Physikal. Zeitsch.*, 1908, 9, 541—542).—It has been found by J. Becquerel (this vol., ii, 751) that canal rays which are caused to pass through a small opening through which cathode rays are also passing are displaced in the immediate neighbourhood of the aperture under the influence of a magnetic field. Becquerel's conclusion, that the canal rays are temporarily transformed into positively-charged carriers as the result of contact with the cathode rays, is refuted by the author. The phenomenon can be satisfactorily explained by the electrostatic charge which the walls of the aperture receives as the result of bombardment by the cathode rays. In consequence of the action of this electrostatic charge, the canal rays are caused to deviate from their rectilinear paths.

H. M. D.

Experimental Investigation of the Stratified Positive Glow. R. HOLM (*Physikal. Zeitsch.*, 1908, 9, 558—562).—Measurements have been made of the potential gradient and the distance between adjacent strata of the positive glow in the discharge through hydrogen, nitrogen, and helium. Curves are plotted which show the dependence of these two factors on the current intensity. Almost identical results are obtained whether the method of Stark or that of H. A. Wilson is employed.

H. M. D.

Cathodic Volatilisation of Metals in Attenuated Gases. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1908, 14, 417—421).—Fischer and Hähnel (this vol., ii, 653) have found that the volatilisation of a metal is the same in argon and hydrogen when the same current is used, whereas Kohlschütter and Goldschmidt (this vol., ii, 457) found large differences.

The author now shows that the results depend on the kind of current used. Two different induction coils are used: (A) a coil with a high resistance primary and low resistance secondary winding, and (B) an ordinary Ruhmkorff coil. Using platinum cathodes in tubes filled with hydrogen and argon respectively and connected in series, he finds that the quantity of platinum volatilised in argon is from four to twenty-two times as much as that volatilised in hydrogen.

The ratio of the quantities volatilised in argon and in hydrogen

is increased by increasing the pressure of the gas and the current strength when one coil is used, but decreased with the other coil. Hence the results obtained appear to depend entirely on the peculiarities of the induction coil employed. T. E.

Volatilisation of Cathodes in Attenuated Gases. FRANZ FISCHER and OTTO HÄHNEL (*Zeitsch. Elektrochem.*, 1908, 14, 433—437; VOLKMAR KOHLSCHÜTTER, *ibid.*, 437—439).—These papers contain the numerical data on which the statements already published (this vol., ii, 653) are founded, and a reply by Kohlschütter (compare preceding abstract). T. E.

Electrical Conductivity of Mixtures of Alcohol and Water. ANTONY G. DOROSCHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 887—908).—After discussing previous work on this subject, the authors give the results of their own measurements.

The values obtained for the conductivities of aqueous-alcoholic solutions of various concentrations at 15° are quite different from those given by Pfeiffer (Abstr., 1885, 1029; 1886, 4, 115), as also is the form of the curve connecting the conductivity with the percentage of alcohol by weight. The curve obtained by the authors not only exhibits no evidence of the existence of definite hydrates of alcohol, but has no singular points. In some respects it resembles the curves connecting the composition of aqueous-alcoholic solutions with other properties, such as the specific gravity and boiling point, the curve falling sharply at both ends and remaining almost horizontal in the middle of its course; there is a slight rise corresponding with about 80% of alcohol.

When the concentration of the alcohol is expressed in grams per 100 c.c. of solution, the electrical conductivity follows the law $K_c \cdot c^{\frac{2}{3}} = \text{constant}$.

The electrical conductivities of aqueous solutions of alcohol are directly proportional to the dielectric constants of the solutions, and inversely proportional to their viscosities. T. H. P.

Electrical Conductivity of Liquid Sulphur. ALBERT WIGAND (*Ber. deut. physikal. Ges.*, 1908, 6, 495—508).—The author has made measurements of the electrical conductivity of liquid sulphur, in order to ascertain whether this is altered under the influence of light. The experiments were suggested by the fact that liquid sulphur, like solid selenium, consists of a mixture of two modifications in equilibrium, and that in the case of selenium, displacement of the equilibrium takes place under the influence of light in the direction of the formation of a larger proportion of the modification which has the greater conductivity. The results are negative, and indicate that the electrical conductivity of the soluble and insoluble forms of sulphur is the same.

Measurements of the conductivity at temperatures ranging from 130° to 446° show that this increases regularly up to 150°, where it reaches a maximum; it then falls, attaining a minimum value between

160° and 170°, above which it increases up to the boiling point. The view is expressed that the measured conductivity is really due to traces of foreign substances which are ionised in the molten sulphur.
H. M. D.

Effect of Concentration on the Temperature of Maximum Electrolytic Conductivity of Weak Electrolytes with Negative Heat of Dissociation. HENRIK WEGELIUS (*Zeitsch. Elektrochem.*, 1908, 14, 514—518).—Solutions of hypophosphorous acid (H_3PO_2) have a maximum conductivity at 72° for 5.75*N.*, 54° for 1.25*N.*, 52° for 0.995*N.*, 70° for 0.328*N.*, 87.5° for 0.12*N.* With weaker solutions, the temperature of maximum conductivity is higher than 100°. Phosphoric acid gave maxima at 77° for 2.715*N.*, 70° for 1.955*N.*, and at 79° for 0.217*N.*; weaker and stronger solutions showed no maximum at temperatures below 93°. An approximate theory showing how the temperature of maximum conductivity depends on the changes of dissociation and of ionic mobility with the temperature is given.
T. E.

A New Primary Voltaic Cell of the Daniell Type. JAMES STRACHAN (*Chem. News*, 1908, 98, 102).—The cell consists of an outer jar in which are placed a number of carbon rods connected by a leaden cover, through which passes a porous pot containing an amalgamated zinc rod immersed in a hydrochloric acid solution of zinc and ammonium chlorides. The outer jar contains an acid solution of lead tetrachloride prepared by dissolving freshly-precipitated lead peroxide in cold concentrated hydrochloric acid, or by adding concentrated hydrochloric acid to a mixture of lead acetate and bleaching powder contained in a pressure bottle and rapidly sealing the latter. Such a solution acts as a rapid depolariser, and is constant in its action; the cell has a higher *E.M.F.*, but a much lower resistance, than a Daniell cell. The disadvantage of the cell due to the escape of chlorine may be overcome by sealing the space between the leaden cover and the porous pot with paraffin wax. The zinc may be replaced by iron, but the *E.M.F.* drops then from 1.5 to 0.95.
P. H.

Gas Electrodes. I. Nitric Oxide. UGO GRASSI (*Nuovo Cim.*, 1908, [v], 15, 467—480).—The potential of a platinised platinum electrode, saturated with nitric oxide, was measured against a normal calomel electrode. In acid solutions, the electrode is stable, and its potential is independent of the rate of passage of the gas; in alkaline solutions the difference of potential changes sign in the first minute, and only attains its final value slowly. This is due to the conversion of the oxide into alkali nitrite and nitrous oxide, which is greatly accelerated by platinum. The first stage of the reaction is the formation of sodium nitrohydroxylamate: $2\text{NO} + \text{Na}_2\text{O} = \text{ON:N(ONa)}_2$, which then decomposes according to the equation $2\text{Na}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{NaNO}_2 + 2\text{NaOH} + \text{N}_2\text{O}$. Quantitative experiments show that the nitric oxide reacts in solution as a double molecule. In acid solutions, the cell $\text{H}-(\text{NO})'_2-\text{NO}$ has an *E.M.F.* of 0.80 volt, nitric oxide being positive to hydrogen.
C. H. D.

Potential of a Hydrogen Electrode in Acid and Alkaline Solutions. C. L. A. SCHMIDT and C. P. FINGER (*J. Physical Chem.*, 1908, 12, 406—416).—The authors have measured the potential of a hydrogen electrode in a series of solutions, each containing 0.25 gram-atom of boron per litre and prepared by mixing solutions of boric acid and borax or sodium hydroxide in different proportions. From the values of the potential difference, the hydrogen-ion concentrations are calculated, and a series of readily reproducible standards for the colorimetric determination of the strengths of acids and bases has been provided.

From the form of the curve, which is obtained by plotting the potential differences against the percentage amount of the hydrogen of the boric acid which is replaced by sodium, the conclusion is drawn that the compound NaH_2BO_3 (or its anhydride, NaBO_2) is the only one formed to any appreciable extent when solutions of boric acid and sodium hydroxide are mixed. This conclusion is in agreement with the results of thermochemical and freezing-point measurements.

H. M. D.

Solid Electrolytes. Their Decomposition by a Current and their Electromotive Properties in Galvanic Chains. FRITZ HABER (*Ann. Physik*, 1908, [iv], 26, 927—973).—Part of this paper represents a summary of work which has been published in detail previously (compare Haber and Tolloczko, *Abstr.*, 1904, ii, 813; Haber and Moser, *Abstr.*, 1905, ii, 667; Haber and Foster, *Abstr.*, 1907, ii, 66; Haber and Fleischmann, *Abstr.*, 1907, ii, 6; Haber, Rieff, and Vogt, this vol., ii, 254).

In the third section [with G. BIRSTEIN], experiments on the electrolytic decomposition of solid salts of the alkali metals are described. Pure potassium chloride yields at the cathode a violet substance which dissolves in water with evolution of hydrogen. It is not acted on by anhydrous ethyl alcohol. The eutectic mixture of potassium and sodium chloride yields a yellowish-brown substance with the same properties. On electrolysing a mixture of sodium chloride and carbonate, carbon separates at the cathode. Potential measurements are recorded which support the view that the coloured substances formed at the cathode are sub-chlorides of the alkali metals.

The last section of the paper [with R. BEUTNER] deals with the potential differences at the surfaces of contact of solid electrolytes and of solid salts and their saturated solutions. Application is made of Nernst's theory of potential differences to the special systems under investigation, and a number of theoretical deductions are made.

H. M. D.

Explanation of Supertension. ERICH MÜLLER (*Zeitsch. Electrochem.*, 1908, 14, 429—433. Compare Kaufler, *Abstr.*, 1907, ii, 924, and this vol., ii, 558).—Polemical.

T. E.

Electrolytic Properties of Dilute Solutions of Sulphuric Acid. W. C. DAMPIER WHETHAM and H. H. PAINE (*Proc. Roy. Soc.*, 1908, 81, A, 58—80. Compare *Abstr.*, 1906, ii, 69).—It has been

shown in a previous paper that the progressive diminution in the equivalent conductivity of dilute sulphuric acid with dilution when the concentration is less than 0.0005—0.001 gram-equivalent per litre is still observed when the solvent is boiled repeatedly under low pressure and the air re-admitted through potash bulbs (to remove carbon dioxide), and it is now shown that the diminution in question persists when the air is re-admitted through bulbs containing dilute sulphuric acid and potassium hydroxide respectively.

The observed diminution in the equivalent conductivity could be accounted for if the H^+ ion travels more slowly in dilute than in concentrated solutions, and to test this point the transport ratio of solutions of different concentration has been determined by a modification of the ordinary method, the changes in concentration round the electrodes due to electrolysis being determined by measuring the conductivity of the solution; in the case of the very dilute solutions, with pairs of electrodes placed in the anode and cathode compartments respectively. Although a change in the expected direction was actually observed, the transport ratio apparently increasing from 0.186 to 0.202 on progressive dilution, it is not considered probable that this is due to a change in the relative migration velocity of the ions, but to some alkaline or saline impurity in the water. As the effect in question is not removed by boiling, the impurity might be ammonium carbonate, but the matter is not regarded as being finally settled.

G. S.

Electrolysis of Copper Solutions. JEAN MEYER (*Bull. Soc. chim. Belg.*, 1908, 22, 259—291).—The author attempts to find a more satisfactory explanation of the anomalous behaviour of the copper voltameter than that provided by the theories of Foerster, Abel, and others. The Foerster-Seidel theory requires that a gram-molecule of cuprous oxide for each 2×96540 coulombs should be formed on electrolysis a hot solution of copper sulphate at a lower potential than that required for the deposition of copper; on repeating these authors' experiments, however, it was found that the weight of the oxide was less than half this. Similar results were obtained when operating in absence of air, hence the deficit cannot be due to oxidation to copper sulphate. When the electrolysis is carried out at 90° , a green basic salt of variable composition is precipitated; this compound, which appears to be identical with that obtained by boiling an aqueous solution of copper sulphate, probably arises from dissolution of the cuprous oxide in the copper sulphate solution. This secondary dissolution of the oxide, which is independent of the current and the concentration of the ions, explains the presence of a cuprous salt, and evidence is adduced to show that it accounts for the formation of cuprous oxide at both electrodes. At the cathode, the following reaction is supposed to occur: $Cu + CuSO_4 + H_2O \rightleftharpoons Cu_2O + H_2SO_4$. The same principle is applied to cover the phenomena observed when solutions of cupric chloride are electrolysed.

It was found possible to estimate the amount of cuprous oxide in the metallic deposits by treating the mixture with a neutral

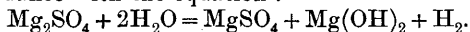
solution of ferric alum, which, after being acidified with sulphuric acid, was titrated by permanganate.

It is pointed out that Bose's phenomenon cannot be due to the partial discharge of cupric ions: $\overset{++}{\text{Cu}} \rightarrow \overset{+}{\text{Cu}}$, as Abel has suggested, since, by electrolysing a hot acid solution of copper sulphate in absence of oxygen and operating with currents of low density, a good yield of pure copper is obtained, the dissolution of copper in copper sulphate solution being accomplished as readily in acid as in neutral solution (compare Heiberg, *Abstr.*, 1903, ii, 263).

In the hope of obtaining a perfect voltametric solution, hydrogen peroxide, instead of sulphuric acid, was added to the copper sulphate in order to prevent the formation of cuprous salts. The results, however, were not satisfactory, probably owing to the formation of persulphates and catalytic decomposition of the hydrogen peroxide at the electrodes.

W. O. W.

Reversed Electrolysis. J. W. TURRENTINE (*J. Physical Chem.*, 1908, 12, 448—467).—A number of apparently anomalous electrolytic phenomena, which are in reality due to secondary reactions, have been examined. When a current is passed through a solution of sodium sulphate between a magnesium anode and a platinum cathode, hydrogen is evolved at the anode, which becomes covered with scales of magnesium hydroxide. It is supposed that the magnesium dissolves at the anode as a univalent metal, a secondary reaction then taking place in accordance with the equation:



In a similar way, hydrogen is evolved at an aluminium anode in the electrolysis of a solution of sodium chloride. It is not possible to determine the effective valence with which solution takes place.

When a solution of potassium permanganate acidified with sulphuric acid is electrolysed between platinum electrodes, the gas evolved at the cathode contains a considerable proportion of oxygen. This has been traced to the decomposition of hydrogen peroxide formed by the electrolytic reduction of manganese dioxide.

H. M. D.

Migration of Ions in Heterogeneous Systems. KARL SPIRO and LAWRENCE J. HENDERSON (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 91—92).—Solutions of phosphates, carbonates, and globulins of the same composition are separated by a membrane, on one side of which a substance such as calcium carbonate, magnesia, or globulin is suspended. When carbon dioxide is passed through the solution which does not contain the suspended matter, its alkalinity to methyl-orange increases; the increase is diminished by passing in oxygen. This arrangement behaves in the same way as blood, and the experiments show that the phenomena are due to simple diffusion, and the assumption of a selective permeability of the walls of the red corpuscles under the influence of carbon dioxide is unnecessary.

T. E.

The Part Played by Ionisation in Certain Chemical Reactions. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1908, 305—306).—The double decomposition between soluble chlorides

and insoluble carbonates in the presence of water is due to the ionisation of the soluble salt; thus in the case of potassium chloride and barium carbonate a small part of the dissociated salt reacts with the barium carbonate to form barium chloride and potassium carbonate.

M. A. W.

Estimation of the Hydration of Ions from Measurements of Electromotive Forces. GILBERT N. LEWIS (*Zeitsch. Elektrochem.*, 1908, 14, 509—510; *J. Amer. Chem. Soc.*, 1908, 30, 1355—1357).—The *E.M.F.* of a concentration cell depends on the ratio of the “activities” of both the electrolyte and the water in the two solutions (this vol., ii, 16), and on the numbers of ions and molecules of water transported by the current. A measurement of the *E.M.F.* of a cell in which the electrolyte has the same concentration in each solution and therefore the same activity, whilst the activity of the water in one solution is altered by the addition of a non-electrolyte, should make it possible to estimate the number of molecules of water carried along with the ions of the electrolyte.

T. E.

Improved Apparatus for the Measurement of Transference Numbers in Solutions of the Halogen Acids and their Salts. EDWARD W. WASHBURN (*Technology Quart.*, 1908, 21, 164—177).—The essentially new features of the author's apparatus are represented by the special form of the silver anode and the silver halide cathode. The anode consists of a silver wire wound into a flat spiral, which is placed at the bottom of a Soxhlet extraction cartridge, this being filled with small crystals of electrolytic silver, which are packed tightly round the silver wire. This arrangement gives an electrode of very large active surface. Using a cartridge 6 cms. long and 1.9 cms. in diameter, an electrode prepared in this way will carry a current of 0.1 ampere for sixteen hours without the formation of the slightest trace of acid or of colloidal silver chloride.

The cathode consists of a silver disk prepared by making it the anode in the electrolysis of a solution of sodium chloride. The disk, which just fits into the apparatus, is covered with a layer of silver chloride, obtained by precipitating a hot solution of silver nitrate with excess of an alkali chloride solution. An electrode, 2.3 cms. in diameter, is able to carry a current of 0.5 ampere without the evolution of hydrogen or the formation of the slightest trace of alkali.

The anode and cathode tubes of the apparatus are provided with stopcocks, and are connected by means of a ground-glass joint.

H. M. D.

Hydrolysis of Salts in Solution: Lecture Experiment. BARTOLO L. VANZETTI (*Gazzetta*, 1908, 38, ii, 98—99).—The following simple experiment renders evident the phenomenon of hydrolysis of salts. A test-tube is filled to about three-fourths of its height with a 5—10% gelatin solution containing faintly alkaline phenolphthalein. When the gelatin has solidified, a 10% ferric chloride solution is

poured on to it. As diffusion into the gelatin proceeds, two strata become more and more distinct, the lower one being colourless, owing to the more rapid diffusion of the acid liberated by hydrolysis, and the less advanced, opaque one consisting of ferric hydroxide. Salts, such as nickel chloride or copper sulphate, containing a coloured ion may also be used.

T. H. P.

Change of Colour of Phenolphthalein. RUDOLF WEGSCHEIDER [with A. SCHUGOWITSCH] (*Zeitsch. Elektrochem.*, 1908, 14, 510—512. Compare Abstr., 1904, ii, 512; this vol., ii, 646).—The concentration of the red ions in dilute alcoholic solutions containing known quantities of phenolphthalein and sodium hydroxide is determined by comparison of the colour with solutions containing an excess of sodium hydroxide. It is found that the expression $[RH][OH']/R'$ (where R' represents the phenolphthalein ion) is only approximately constant when there are more than two molecules of sodium hydroxide for each molecule of phenolphthalein in solution. On the assumption that the red salt contains two atoms of sodium (Abstr., 1905, i, 440), and that it is hydrolysed thus: $R'' + H_2O \rightleftharpoons RH' + OH'$ and $RH' + H_2O \rightleftharpoons RH_2 + OH'$, a satisfactory explanation of the results obtained is possible.

T. E.

New Method for Determining the Specific Heats of Liquids. THEODORE W. RICHARDS and ALLAN WINTER ROWE (*Zeitsch. physikal. Chem.*, 1908, 64, 187—200).—The liquids, the specific heats of which are to be compared (for example, water and a salt solution), are successively put in the calorimeter, and a definite quantity of heat is developed each time by neutralising a given quantity of acid with alkali in a platinum vessel, which is immersed in the liquid of the calorimeter. The calorimeter itself is completely surrounded by a jacket, the temperature of which is constantly adjusted to the changing temperature of the calorimeter (see Richards, Henderson, and Forbes, Abstr., 1905, ii, 677; Richards, Henderson, and Frevert, Abstr., 1907, ii, 604). The rise of temperature, therefore, in the calorimeter takes place adiabatically. The same apparatus may obviously be employed in the determination of heats of dilution.

One or two experiments made with this apparatus are recorded. The specific heat of a hydrochloric acid solution of the composition $HCl + 200H_2O$ has been found to be 0.9809, and the maximum deviation from this figure in four independent experiments was 0.03%. The heat developed when a solution of the composition $NaOH + 5.85H_2O$ is diluted until it has the composition $NaOH + 43.5H_2O$ is 3.79 kilojoules.

J. C. P.

Specific Heats and Heats of Fusion of Isomorphous Substances and their Mixtures. A. BOGOJAWLENSKY and N. WINOGRADOFF (*Zeitsch. physikal. Chem.*, 1904, 64, 251—254).—The authors have determined the specific heats and latent heats of fusion for mixtures of (1) *m*-chloronitrobenzene and *m*-bromonitrobenzene, (2) α -chlorocinnamaldehyde and α -bromocinnamaldehyde, (3) azobenzene and dibenzyl. They find that the specific heats of these

isomorphous mixtures, in both the liquid and the solid state, can be calculated by the mixture rule. In the first two cases, the latent heat of fusion (f) can be calculated by the mixture formula $f = (f_1 p_1 + f_2 p_2) / (p_1 + p_2)$ in fair agreement with the observed values, but in the third case there are marked discrepancies, the observed values being regularly less than the calculated values. It is noted that only in this third case does the freezing-point curve exhibit a minimum, and that the discrepancies referred to are similar to those observed with substances which form a eutectic mixture.

J. C. P.

Specific Heat of Mercury. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 811—813).—The results of a number of measurements show that the mean specific heat of mercury from 0° to 306° is 0.0325—0.0331. This value, together with that previously obtained by the author (*Abstr.*, 1903, ii, 130), and those of other investigators, prove that the specific heat of mercury rises distinctly as the boiling point is approached.

In general, the specific heat of substances, the molecules of which do not change from the melting point to the critical temperature, is represented by a curve approximating to a straight line, and the true specific heat is the minimum between these two temperatures.

T. H. P.

Specific Heat of Alcohol and of its Mixtures with Water. ANTONY G. DOROSCHEWSKY and ADAM W. RAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 860—886).—The authors discuss the various formulæ which have been proposed for expressing the specific heat of alcohol at different temperatures, and come to the conclusion that all these formulæ refer, not to absolute alcohol, but to alcohols containing small, and probably varying, proportions of water. For carefully dehydrated alcohol, the value 0.6597 is obtained as the mean specific heat at 22—99°; this gives the value 0.518 for the specific heat at 20°, taking the value 0.0035 given by Hirn's measurements (*Ann. Chim. Phys.*, 1867, [iv], 10, 32) for the temperature-coefficient between 20° and 100°. For the alcohol used by the authors, D_{15}^{15} 0.79426 and k at 15° is 0.097×10^{-6} ohms.

In general, the changes of specific heat (C) of mixtures of alcohol and water with temperature are irregular. Thus, for 10—40% aqueous alcohol solutions, $C_{0-15^\circ} > C_{0-30^\circ} > C_{0-45^\circ} < C_{0-54^\circ} < C_{0-98^\circ}$, and for 10—20% solutions, $C_{0-15^\circ} > C_{0-98^\circ}$.

For solutions containing 100—50% of alcohol, the specific heat is expressed by the equation: $C = 0.6628 + 0.007945 (100 - p) - 0.000045 (100 - p)^2$, where p represents the % of alcohol by weight in the solution. For 50—20% solutions, $C = 0.9475 + 0.005164 (50 - p) - 0.0000625 (50 - p)^2$, and for 20—0% solutions, $C = 1.0455 - 0.00104 (20.09 - p) - 0.0000482 (20.09 - p)^2$.

The authors' results show that Thomsen's supposition (*Thermochem. Untersuch.*, 1882, vol. i, 74), that at their boiling points the heat effect of the formation of aqueous-alcoholic solutions is zero, is not general, but applies only to one definite solution. The temperature

at which the mixing has a zero heat effect is below the boiling point for strong solutions, and above the boiling point for dilute solutions of alcohol.

T. H. P.

Equation of Condition for Metals: Correction. MAX THIESEN (*Ber. deut. phys. Ges.*, 1908, 6, 604).—According to Grüneisen (this vol., ii, 563), for those metals which have been sufficiently investigated, the relation between the specific heat and the coefficient of expansion is nearly independent of the temperature. In deriving the form of the temperature function of these two magnitudes (this vol., ii, 659), the author assumed that the θ of equation 4 (*loc. cit.*) was a pure temperature function, an assumption which is not justified. The value of θ is given only by a partial differential equation, which leaves the form of the temperature function undetermined. The relations given by the author do not, therefore, follow as consequences of Grüneisen's experimental law, but must be tested by direct experiment, as has been done in the case of platinum.

T. H. P.

Melting-point and Freezing-point Curves of Binary Systems when the Solid Phase is a Mixture (Amorphous Solid Solution or Mixed Crystals) of the Two Components. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1908, 64, 257—297).—A mathematical discussion of the possible forms of curve. In the case of optical isomerides and tautomeric substances, a minimum or eutectic point in the freezing-point curve is impossible (compare Roozeboom, *Abstr.*, 1899, ii, 355, 401). When a racemic compound is formed, two eutectic points are possible. The formation of liquid mixed crystals is also discussed.

In Tammann's method of representing the total heat-content of binary systems (this vol., ii, 660), the heat of mixing may only be neglected in comparison with the heat of fusion so long as only stable systems are dealt with. In the labile region below the eutectic point, the heat of mixing may be considerable.

C. H. D.

Reciprocal Salt-pairs. I. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1908, 64, 305—327. Compare Meyerhoffer, *Abstr.*, 1901, ii, 639).—The conditions occurring in the melting and solidifying of reciprocal pairs of salts, in which there is an equilibrium $M'R' + M''R'' \rightleftharpoons M'R'' + M''R'$, when only one liquid phase is present, are discussed for the two cases: (a) when the only solid phases are the four salts; (b) when only two isomorphous mixtures separate. The equilibrium diagrams for case (a) are completely discussed. In case (b) there are many possibilities. The simplest conditions occur when the melting points of each pair of reciprocal salts have neither a maximum nor a minimum point; the whole system may then be broken up into two ternary systems.

The eutectic curve between the two solid phases may be without any maximum or minimum, or may have either a maximum or a minimum. The last of these cases is illustrated by the system $(K_2, Na_2) - (Cl_2, SO_4)$ (this vol., ii, 841).

C. H. D.

Character of Melting-Point and Clearing-Point Curves for Fluid-Crystalline Substances and their Mixtures. II. ALEX. BOGOJAWLENSKY and N. WINOGRADOFF (*Zeitsch. physikal. Chem.*, 1908, **64**, 229—242. Compare Abstr., 1907, ii, 844).—The method described in the earlier paper has been applied to other binary mixtures, namely, (1) *p*-azophenetole + *p*-azoanisolephenetole, (2) *p*-ethylpropylazophenol + *p*-methylpropylazophenol, (3) *p*-azoanisole + *p*-azoanisolephenetole, (4) *p*-azophenetole + *p*-dipropylazophenol, (5) *p*-azoanisolephenetole + *p*-dipropylazophenol, (6) *p*-azoanisolephenetole + azoxyanisole, (7) *p*-azoxyphenetole + *p*-azoanisolephenetole, (8) *p*-methylpropylazophenol + *p*-azoanisole, (9) *p*-methylpropylazophenol + dipropylazophenol.

The melting-point curves obtained in cases (1) and (2) show that complete series of mixed crystals are formed; the melting-point curves obtained in cases (3) and (4) exhibit a minimum, but it is not certain whether this is an eutectic or not; in cases (5), (6), and (7) the melting-point curves are all marked by eutectics; in cases (8) and (9) the melting-point curves were not traced.

The clearing-point curves show that in all cases the fluid-crystalline phases are completely miscible. The direction of these curves depends exclusively on the clearing points of the two components, and is independent of the course of the melting-point curve. Hence it comes that, as in cases (1) and (2), two substances the clearing points of which lie below their respective melting points form fluid-crystalline mixtures within certain limits of concentration. In cases where the labile clearing point of one component cannot be determined directly, owing to the impossibility of supercooling, it may be ascertained by extrapolating the clearing-point curve, which in the majority of cases is nearly a straight line.

The melting points and clearing points for various azo- and azoxy-compounds are as follows, the melting point being given first in each case: azoanisole 164.1°, 108.0°; azophenetole, 160.2°, 156.1°; *n*-dipropylazophenol, 146.1°, 112.0°; ethyl-*n*-propylazophenol, 144.2°, 139.6°; methylethylazophenol, 134.5°, 132.2°; methyl-*n*-propylazophenol, 113.1°, 110.0°; azoxyphenetole, 136.9°, 167.5°; azoxyanisole, 117.4°, 134.4°; *n*-dipropylazoxyphenol, 116.0°, 122.0°; azoxyanisolephenetole, 93.5°, 149.6°. It will be observed that all the azo-compounds are monotropic, that is, their clearing points lie below their melting points, whilst the azoxy-compounds are enantiotropic. J. C. P.

Inverse Melting Points. J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1908, **64**, 374—377).—The course of the solubility curves for the hydrates of ceric sulphate (Koppel, Abstr., 1904, ii, 819) indicates that two of the hydrates, $\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, are only stable at higher temperatures, passing into the octahydrate and the tetrahydrate at 35° and 100° respectively. Since this would mean the conversion of a solid hydrate into a lower hydrate and an aqueous solution on cooling, the temperatures mentioned may be regarded as inverse melting points. Such fusion on cooling was not directly observed, but is a thermodynamical consequence of the position of the solubility curves.

It is shown on theoretical grounds that inverse melting points can

only occur when, as is the case with ceric sulphate, the solubility of the salt diminishes with increasing temperature. C. H. D.

A Modification of the Cryoscopic Method for Investigating Small Quantities of liquid. TÖSAKU KINOSHITA (*Biochem. Zeitsch.*, 1908, 12, 390—406).—With certain modifications, the Beckmann method can be applied to small quantities of liquid. The chief of these consists in enveloping the thermometer bulb with a thin layer of paraffin, ash-free filter-paper, and sheet-rubber. S. B. S.

Analysis of the Lowering of the Freezing Point in Physiological Fluids. II. Lowering of the Freezing Point of Suspensions. ERNST TEZNER and JOHANN ROSKA (*Zeitsch. physiol. Chem.*, 1908, 56, 495—506).—The depression of the freezing point of water by the addition of a fatty acid is not nearly so marked when solid particles, such as blood-charcoal or casein, are suspended in the solution. This effect is attributed to adsorption, which produces a concentration of the solute around the solid particles, and thus diminishes the concentration of the rest of the solution.

The adsorption depends mainly on the surface tension, and this again on the concentrations of the various dissolved materials, but is not directly proportional to their osmotic concentrations. Hence the lowering of the freezing point of such solutions is not a simple function of the osmotic concentration.

Negative adsorption is not met with. The process of filtration yields a liquid with the same or greater lowering of the freezing point, according as the filtration is more or less complete. J. J. S.

Influence of the Rate of Cooling on the Composition of Saturated Mixed Crystals. W. VON LEPKOWSKI (*Zeitsch. anorg. Chem.*, 1908, 59, 285—292).—Experiments have been made to ascertain whether molten alloys of bismuth and tin and of copper and silver give rise to mixed crystals when rapidly cooled. The supersaturation phenomena requisite for the production of these crystals are found in the case of bismuth-tin alloys, but not in the case of copper-silver alloys.

Alloys containing up to a little more than 1% of tin show no trace of the eutectic mixture when rapidly cooled, but this is found if the percentage of tin exceeds 1.5. The supersaturated mixed crystals, which are formed in the first case, are unaltered by exposure for six hours at 120°.

The difference in behaviour of bismuth compared with copper and silver is attributed to the greater velocity of crystallisation of the supercooled metal in the case of bismuth. H. M. D.

Vaporisation. II. HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1908, 63, 579—618. Compare this vol., ii, 663).—Starting with van der Waals' equation, the author deduces formulæ for the calculation (1) of the internal pressure, $\pi = a/v^2$, due to molecular attraction; (2) of the fraction of the total volume actually occupied by the molecules. The values of these are then deduced for a large number

of substances. It is found that the value of a , in general, increases with the molecular weight, although constitutive influences make themselves felt. From these values of a , the critical constants are calculated, and the expressions $(p_k + \pi_k)/p_k = A$ and $v_i/v_k = B$ [v_i = ideal volume] are evaluated. It is shown that, in general, A increases with B . The question how far these various quantities are affected by molecular association at the critical temperature is also discussed. The term b in van der Waals' equation is regarded as variable with the temperature and internal pressure, possibly also with the attraction of neighbouring molecules.

J. C. P.

Determination of Vapour Pressures of Solutions with the Morley Gauge. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1908, 30, 1219—1228).—The methods most commonly used for determining the vapour pressures of solutions are of two kinds, which may be distinguished as the "differential" and the "dynamic" methods. In the former, the difference between the two vapour pressures, such as that of a given solvent and one of its solutions, is measured by means of a suitable gauge, whilst the latter method is based on the principle that when air, or some other inactive gas, is saturated with the vapour of the liquid or solution, the following relation holds: total volume/volume of the aqueous vapour = total pressure/pressure of the aqueous vapour. Ostwald has simplified this method by allowing the air to bubble first through the solution and then through pure water.

A method has now been studied which is of the "differential" class, and resembles that of Smits, except that his micromanometer is replaced by a mercury gauge, designed by Morley (*Amer. J. Sci.*, 1902, 13, 455) for measuring small differences of pressure. Determinations have been made of the vapour pressures of aqueous solutions of sucrose, potassium iodide, and lithium chloride, and of methyl- and ethyl-alcoholic solutions of tetraethylammonium iodide, potassium iodide, and lithium chloride. The results are tabulated.

It has been found that this method involves several difficulties and sources of error. The readings vary considerably, and it is therefore necessary to make a great many readings and take the average. The time occupied in this way, and also in repairing breaks and overcoming other difficulties, is very great. Moreover, the solutions must always be maintained at a temperature lower than that of the gauge. For these reasons, this "differential" method is regarded as less trustworthy, and subject to more limitations than the "dynamic" or air-bubble method.

E. G.

Osmotic Researches. I. ERNST COHEN and J. W. COMMELIN (*Zeitsch. physikal. Chem.*, 1908, 64, 1—52).—The authors review the attempts which have been made to measure osmotic pressure directly, and criticise in detail Kahlenberg's experimental methods and conclusions (*Abstr.*, 1906, ii, 337). An osmotic apparatus has been devised in which the weaknesses of Kahlenberg's osmometer are remedied, and with which the osmotic pressure of sucrose in pyridine has been determined. As in Kahlenberg's experiments, the semi-permeable membrane was of india-rubber. The authors show that it

is immaterial whether the contents of the osmotic cell are stirred or not. It has not been found possible to get consistent values for the osmotic pressure in parallel experiments, and all the pressures recorded were far below the theoretical values. The authors consider it probable that water is responsible for the irregular results obtained, for it has been found that the presence of water either in the solution or in the pure solvent exerts a very marked influence on the observed pressure. Fresh experiments are therefore planned in which perfectly anhydrous pyridine will be employed.

J. C. P.

[Vapour Pressure of Dry and of Ordinary Sal Ammoniac.] RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1908, 63, 623—624).—A reply to van Laar (this vol., ii, 569).

J. C. P.

The Avogadro-Guldberg Law. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 813—817).—It was shown by Guldberg that the absolute boiling points of different substances represent "corresponding" temperatures, as they are always two-thirds of the absolute critical temperatures. The author finds, however, that this relation is considerably influenced by various factors, and, on the basis of a large number of experimental numbers given by various investigators, he formulates the relationship between boiling point and critical temperature as follows. With all substances having less than five atoms in the molecule, and having, also, low molecular weights, the ratio of boiling point to critical temperature has the mean value 0.666. The ratio varies, however, from 0.580 for the lower members of a homologous series to 0.700 for the highest members investigated.

T. H. P.

Calculation of Thermochemical Constants. V. Calculation of the Thermal Constants of Aromatic Substances. H. STANLEY REDGROVE (*Chem. News*, 1908, 98, 80. Compare this vol., ii, 564).—The author gives in tabular form a comparison of the molecular heats of combustion and formation as determined by Thomsen, and as calculated by himself for toluene, mesitylene, ψ -cumene, chlorobenzene, anisole, and phenol. The method of calculation does not necessitate any assumption concerning the constitution of benzene. The figures show that the various groups exhibit the same thermal behaviour in aromatic as in aliphatic compounds.

P. H.

Free Energy Changes Attending the Formation of Certain Carbonates and Hydroxides. JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1908, 30, 1357—1365. Compare this vol., ii, 358).—The increase of free energy attending the conversion of a hydroxide into the oxide and water vapour, and of a carbonate into the oxide and carbon dioxide, can be expressed by the equation $\Delta F = \Delta H + RT \ln p + IT$ (ΔH being the increase in total energy). Calculations from existing pressure data for the hydroxides and carbonates of magnesium, calcium, lithium, strontium, and barium give, in general, very concordant values for I , the thermodynamically undetermined constant,

The increase in free energy at 25° , accompanying the formation of these substances, and their dissociation pressures at 25° have been calculated. The results show that the stability of the hydroxides and carbonates increases in the order magnesium, calcium, lithium, strontium, barium, sodium.

It is shown that neither Le Chatelier and de Forcrand's rule, $T = \Delta H/30$, nor Nernst's approximate formula for heterogeneous equilibria, $\log p = \Delta H/4.576T + 1.75 \log T + C$, can lead to accurate results, except in special cases. E. G.

Hydrolysis as Illustrated by Heats of Neutralisation. VICTOR H. VELEY (*Trans. Faraday Soc.*, 1908, 4, 19—26. Compare Lundén, this vol., ii, 164).—The paper contains a summary of the available data as to the acid and basic dissociation constants of a number of weak bases and acids and the degree of hydrolysis of their salts, as determined by Bredig, Winkelblech, Walker, Lundén, and the author. The heats of neutralisation determined directly of these weak bases and acids are also given as far as available, as are the values calculated by Lundén and others by means of the van t'Hoff equation connecting heat development and displacement of equilibrium. The data appear to show that the higher the value for the heat of neutralisation the less is the degree of hydrolysis, and conversely.

G. S.

Orthobaric Volumes in Relation to Pressure and Temperature. EDWARD HAIGH (*Phil. Mag.*, 1908, [vi], 16, 201—223); SYDNEY YOUNG (*ibid.*, 222—223).—Haigh puts forward a dual equation to express the relation of the orthobaric volumes of liquid and saturated vapour to vapour pressure and temperature of ebullition. At the critical point, the dual equation reduces to the well-known van der Waals' form. The dual equation affords results which are in excellent accord with the experimental values in the cases of fluorobenzene, isopentane, benzene, and a number of other hydrocarbons. The small deviations observed with methyl and propyl alcohols, carbon tetrachloride, and stannic chloride are explainable as polymerisation effects and experimental errors.

With a liquid far removed from its critical point, a small experimental error in the volume is greatly magnified, and the spheres of action of the molecules may intersect. The theorem may be utilised to test the accepted values of the critical constants of a substance, for on combining them with the data of observations at temperatures below the critical point, the dual equation should hold good.

From the specific volumes of isopentane liquid and vapour at temperatures between 10° and 120° , the critical volume of this substance is calculated to be 4.2686, whereas Young obtained the value 4.266 experimentally.

This agreement does not constitute an independent proof of the validity of the dual equation, since the value of the critical volume (4.266) was assumed for the purposes of the former proof. R. J. C.

Saturated Aqueous Solutions of Sparingly Soluble Salts. II. The Amounts Dissolved and their Alteration with Temperature. FRIEDRICH KOHLRAUSCH (*Zeitsch. physikal. Chem.*, 1908, 64, 129—169. Compare Abstr., 1903, ii, 528).—The experimental material previously collected (*loc. cit.*) has been subjected to recalculation, with the result that some of the values for the solubility already communicated (Abstr., 1905, ii, 152) have undergone alteration. In this extension of the work, special attention has been paid to ascertaining the value of the equivalent conductivity which should be employed in calculating the solubility from the specific conductivity of the saturated solution. It is only in the case of salts with extremely low solubility that λ_{∞} can safely be taken as the equivalent conductivity of the saturated solution. The correct value can, however, be ascertained on the basis of the rule that in dilute solutions λ changes almost proportionally with the square root of the concentration. For details of the way in which this rule is applied to the different salts, the original must be consulted. Another point to which attention has been paid in this extension of the work, is the evaluation of the solubility for temperatures other than 18°.

The following is a list of the salts for the solubility of which an appreciably different value has been found on recalculation; the number given after each salt represents the weight in milligrams present in a litre of the saturated solution at 18°: magnesium fluoride, 87; silver chloride, 1.34; silver iodate, 38.5; lead iodate, 17.8; barium chromate, 3.5; lead chromate, 0.1; barium oxalate ($\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 85.1; barium oxalate ($\text{BaC}_2\text{O}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$), 105. In addition, numbers are given for the following minerals: fluorite, 15.0; barytes, 2.6; celestine, 114.3.

For the values of the solubility at temperatures other than 18°, the original must be consulted. Of the salts examined, magnesium fluoride is the only one the solubility of which diminishes as the temperature rises.

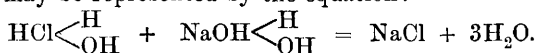
J. C. P.

Studies of the Processes Operative in Solutions. VI. Hydrolysis, Hydrolation, and Hydronation as Determinants of the Properties of Aqueous Solutions. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1908, 81, A, 80—95. Compare Abstr., 1907, ii, 848, 849, 850).—Water is regarded as a complex mixture of active and inactive molecules; the active components are monad *hydrone* (H_2O) molecules and *hydrol-hydrone* (briefly hydronol or hydrol) molecules, $\text{H}_2\text{O} \begin{smallmatrix} \text{H} \\ \diagup \text{O} \diagdown \\ \text{OH} \end{smallmatrix}$; the inactive molecules are a series of polyhydrones (formed by association unaccompanied by rearrangement) of the form $\text{H}_2\text{O}:\text{OH}_2$, $\text{H}_2\text{O} \begin{smallmatrix} \text{OH}_2 \\ \diagup \text{O} \diagdown \\ \text{OH}_2 \end{smallmatrix}$, &c.

When non-electrolytes of the type RX are dissolved in water, interaction takes place with the hydrol molecules present in the solvent, with the ultimate possible production of active complexes, $\text{RX} \begin{smallmatrix} \text{H} \\ \diagup \text{O} \diagdown \\ \text{OH} \end{smallmatrix}$, inactive hydrone complexes, $\text{RX}:\text{OH}_2$, and polymerides of

When, on the other hand, substances which form conducting solutions are dissolved in water, not only does the compound become hydrolyated with formation of complexes of the type $RX \begin{smallmatrix} H \\ < \\ OH \end{smallmatrix}$ (*a*), but its component groups also become distributed (re-arranged), forming complexes of the type $H_2O \begin{smallmatrix} R \\ < \\ X \end{smallmatrix}$ (*b*); the latter process is a kind of hydrolysis, but the groups are only distributed and not set free. The occurrence of electrolysis in such solutions is dependent on influences which the composite molecules (*a* and *b*) exert reciprocally on one another whilst under the influence of the electric strain.

The above considerations are applied to the interpretation of the most various properties of aqueous solutions, such as electrolytic conductivity, hydrolysis, neutralisation of acids by alkalis, hydration, compressibility, and the so-called ionic properties of aqueous solutions. It is considered that the conductivity in concentrated solutions is conditioned mainly by molecules of the hydrolysed solute of type *b*, whilst in dilute solutions it is due mainly to molecules of type *a*. In general, the changes which take place in aqueous solution involve the interaction of the composite molecules above referred to; for example, the neutralisation of hydrochloric acid by sodium hydroxide may be represented by the equation:



The considerable expansion attending such neutralisations cannot be adequately accounted for on the ionic theory, but on the present theory, is a simple consequence of the different modes of combination of the water before and after neutralisation. It is shown that when measurements are made with weight-normal solutions, the change of volume on neutralisation is greater for sodium than for potassium salts.

Hydration may be of two kinds, according as it involves hydrolyation or hydronation. The effect of sugars in reducing the conductivity of electrolytes (compare No. X) is probably connected with the association of their oxygen atoms with hydrol. In hydrones, for example, $NaCl \cdot OH_2$, the salt is rendered comparatively inactive, but, owing to the ethenoid linking, the associated water has probably a greater optical effect than ordinary water, the increase in refractive index which attends solution in water being thus accounted for.

G. S.

Studies of the Processes Operative in Solutions. VII. Relative Efficiencies of Acids as Deduced from their Conductivities and Hydrolytic Activities. HENRY E. ARMSTRONG and E. WHEELER (*Proc. Roy. Soc.*, 1908, 81, A, 95—102).—The electrolytic and hydrolytic activities of hydrochloric, nitric, and sulphuric acids in various dilutions are contrasted, and the conclusion is drawn that the processes are altogether different in character. The hydrolytic activity was determined with sucrose in the usual way, and weight-normal solutions were employed.

When weight-molar solutions of the three acids are compared

nitric acid is least, and sulphuric acid most, active as hydrolyst, and to reduce the other acids to the same activity as nitric acid, 3 mols. of water have to be added to the hydrochloric acid solution and 7 mols. to the sulphuric acid solution. In 1/10 and 1/20 molar solution, hydrochloric and nitric acids are more nearly equal in activity, but sulphuric acid is much stronger than either, its strength not being reduced so much by dilution. The diminution of hydrolytic activity on dilution from molar to 1/10 molar solution for the monobasic acids is not proportional to the dilution, but about 1.5 times as great.

For solutions of the three acids of equal conducting power, the hydrolytic activities at 25° are in the ratio $\text{HNO}_3 : \text{HCl} : \text{H}_2\text{SO}_4 = 100 : 107 : 180$ when the activity of weight-normal nitric acid = 100.

The molecular conductivities of the various solutions are also given in tabular form. G. S.

Studies of the Processes Operative in Solutions. VIII. The Influence of Salts on Hydrolysis and the Determination of Hydration Values. HENRY E. ARMSTRONG and D. CROTHERS (*Proc. Roy. Soc.*, 1908, 81, A, 102—112. Compare Senter, *Trans.*, 1907, 91, 460; *Proc.*, 1908, 24, 89).—It has been shown in a previous paper (No. IV, *loc. cit.*) that the "average degree of hydration" of certain alkali chlorides and nitrates is considerably greater when determined from hydrolysis experiments with sucrose in the presence of the corresponding acids than when methyl acetate is used as hydrolyte, and that the nitrates give lower values than the chlorides, especially with methyl acetate. On the preliminary assumption that the results obtained with sucrose are the true hydration values, and that the smaller values observed with methyl acetate are due to combination of salt and ester, the average amount of each salt combined with the ester is calculated. This explanation of the different effect on the two hydrolytes is not, however, regarded as satisfactory.

In order to obtain further information on this point, the relative influence of nitrates and chlorides on the molecular solution volume of methyl acetate, and on the electrical conductivities of the respective acids in the presence and absence of methyl acetate, has been measured, but in no case is the difference so great as for the influence on the hydrolytic activity. For comparative purposes, the effect of sucrose, dextrose, and raffinose on the conductivity of the salts was also measured.

It is suggested that the differences are best accounted for on the basis of the considerations advanced in communication VI. The "hydration values" will vary from case to case, and the highest values will be obtained by using hydrolytes and hydrolysts which form relatively stable hydrols in solution, as these will be less affected by the introduction of salts. Methyl acetate holds hydrol but weakly, and is therefore easily rendered inactive by salts.

The effect of methyl acetate in diminishing the conductivity of electrolytes is probably mainly mechanical, but the sugars appear to exercise a direct dehydrolating influence as well as a mechanical effect. G. S.

Studies of the Processes Operative in Solution. IX. Determination of Optical Rotatory Power. ROBERT J. CALDWELL and R. WHYMPER (*Proc. Roy. Soc.*, 1908, **81**, *A*, 112—117).—A modified polarimeter provided with a spectroscopic eyepiece is described and figured. A sodium lamp for obtaining a very bright flame is described, but the Bastian mercury lamp was found to possess considerable advantages as a source of illumination, the green line ($546.1 \mu\mu$) being very bright, pure, and of constant intensity. G. S.

Studies of the Processes Operative in Solutions. X. Changes Effected by the Reciprocal Interference of Sucrose and other Substances (Salts and Non-electrolytes). ROBERT J. CALDWELL and R. WHYMPER (*Proc. Roy. Soc.*, 1908, **81**, *A*, 117—140).—The effect on rotatory power, the volume change, and (in the case of salts) the change of conductivity produced by adding sucrose to each of a large number of electrolytes and non-electrolytes in weight-molar solution, have been determined.

The influence of non-electrolytes on the rotatory power is slight; the greatest effect is exerted by acetaldehyde (an increase) and by chloral hydrate (a decrease). Electrolytes all diminish the rotation slightly, and the effect increases in the order nitrates, chlorides, sulphates, alkali hydroxides; it is ascribed mainly to combination between electrolyte and sugar.

The molecular conductivity of the most various salts (in molar solution) is reduced to the extent of 43—51% by the addition of 1 mol. of sucrose. The diminution is partly due to combination between sugar and salt, but mainly to the reduction of the salt to an inactive state, probably by withdrawal of hydrol (compare No. VI). On the basis of certain assumptions, an attempt has been made to ascertain the extent to which sugar enters into combination with certain salts. The order of the effect of salts on the rotatory power is in the main the same as that in which their conductivity is affected by the addition of sugar.

The admixture of sugar with salts in solution is usually attended with considerable expansion, but in the case of non-electrolytes there is very little effect. G. S.

Calculation of the Diffusion Constants of Non-electrolytes in Solution. MAX VON WOGAU (*Ber. deut. physikal. Ges.*, 1908, **6**, 542—545).—By means of the author's formula (*Abstr.*, 1907, ii, 606) for the diffusion constant of a non-dissociated substance in dilute solution, values are obtained for aqueous solutions in approximate agreement with the experimental values. The values for the diffusion constants of bromine and iodine in benzene and carbon disulphide do not agree so well with the observed values, and this is attributed to the relatively larger size of the solvent molecules. H. M. D.

Theory of Capillarity. E. T. WHITTAKER (*Proc. Roy. Soc.*, 1908, **81**, *A*, 21—25).—The surface energy, λ of a liquid is related to the surface tension, γ , by the equation: $\gamma = \lambda + T.d\gamma/dT$, where T denotes absolute temperature. By means of this equation, the surface energy

for a few non-associating liquids has been calculated from the values of the surface tension at different temperatures observed by Ramsay and Shields, and it is then shown that the surface energy of a liquid in contact with its own vapour at any temperature is proportional to the product of the "internal latent heat" and the absolute temperature. The "internal latent heat" is that part of the observed latent heat which is used up in increasing the internal energy of a substance as it passes from the state of liquid to that of vapour.

G. S.

Viscosity of Colloidal Silver Solutions. H. W. WOUDESTRA (*Zeitsch. physikal. Chem.*, 1908, 63, 619—622. Compare this vol., ii, 160).—The viscosity of a given colloidal silver solution gradually diminishes with time. When solutions containing different amounts of silver are compared, it is found that the viscosity increases with the concentration. The viscosity of a colloidal silver solution is lowered by electrolytes, an observation which should be contrasted with the action of electrolytes on gelatin solutions (see, for instance, Levites, this vol., ii, 161).

J. C. P.

The "Negative" Viscosity of Aqueous Solutions. WILLIAM WHITE TAYLOR and T. W. MOORE (*Proc. Roy. Soc. Edin.*, 1908, 27, 461—471. Compare Taylor and Ranken, *Trans. Roy. Soc. Edin.*, 1906, 45, 397; Jones and Veazey, *Abstr.*, 1907, ii, 438; Getman, *ibid.*, ii, 744).—In order to test the theory that the cations, in opposition to undissociated molecules and anions, tend to diminish the viscosity of water, and that the activity of the cations increases in general with the atomic volume, the authors have measured the viscosity of aqueous solutions of tetramethylammonium iodide, tetraethylammonium chloride and bromide, and of tetrapropylammonium chloride and iodide at 25° and 35°.

The viscosity increases with increasing volume of the cation, and in no case is there the slightest approach to "negative" viscosity. The influence of the anion on the viscosity is very small. The values for tetraethylammonium chloride and bromide are much more nearly equal than the viscosities of solutions of hydrochloric and hydrobromic acids, of the potassium salts, or of the ammonium salts. The viscosity of salt solutions cannot therefore be regarded as simply an additive property.

The density of tetrapropylammonium chloride solutions decreases with increasing concentration, the diminution being more marked at 35° than at 25°.

H. M. D.

Theory of Adsorption. T. BRAILSFORD ROBERTSON (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 49—76).—A theoretical paper of a highly controversial character, in which the view is advocated that the phenomena of adsorption are in reality chemical equilibria, in which capillary condensation plays at most a very unimportant part.

T. E.

Adsorption Phenomena of Inorganic Salts. HANS E. WOHLERS (*Zeitsch. anorg. Chem.*, 1908, 59, 203—212).—When barium sulphate is precipitated in a strong solution of potassium permanganate, the precipitate carries down some of the permanganate, as is shown by the fact that after boiling with hydrochloric acid to remove manganese dioxide the precipitate is still rose-red. The amount of permanganate adsorbed is too small to be estimated gravimetrically. The adsorbed permanganate does not react with hydrogen peroxide or sulphurous acid, nor does adsorbed ferric chloride react with potassium ferrocyanide. On heating the precipitates, however, adsorbed substances undergo chemical changes; thus the pink barium sulphate becomes brown on heating, owing to the formation of manganese peroxide, and adsorbed red cobalt sulphate becomes blue on heating.

Strontium sulphate also adsorbs potassium permanganate, but calcium and lead sulphates and silver chloride do not do so to any appreciable extent.

The absence of chemical reactivity on the part of adsorbed substances might be accounted for on physical lines as being due to a great diminution of solubility, but the author considers it more probable that precipitate and adsorbed substance become chemically combined.

G. S.

Dissociation of a Compound in a State of Equilibrium, and a Thermodynamic Relation Necessary to the Validity of the Law of Constant Proportions. RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1908, 64, 357—373).—It has been shown (Abstr., 1907, ii, 433) that a compound AB fusing to a homogeneous liquid, and capable of dissolving both A and B , must be dissociated when in a state of equilibrium. The conditions of such equilibria in the solid, liquid, and gaseous state are now discussed on the basis of the thermodynamic potential. It is shown on theoretical grounds that two solid or two liquid phases must always possess a certain degree of miscibility, although this miscibility may be very small.

C. H. D.

The Unimolecular Course of the Decomposition of Ammonia by the Silent Discharge. ROBERT POHL (*Zeitsch. Elektrochem.*, 1908, 14, 439; MAX LE BLANC, *ibid.*, 507).—A claim for priority against Le Blanc and Davies (this vol., ii, 653) and a reply by Le Blanc, who points out that, whereas Pohl found the decomposition to be unimolecular, he and Davies arrived at the opposite result.

T. E.

Position of the Ammonia Equilibrium. FRITZ HABER and ROBERT LE ROSSIGNOL (*Zeitsch. Elektrochem.*, 1908, 14, 513—514).—In consequence of Jost's criticism (this vol., ii, 761), the authors have made measurements with thermocouples both inside and outside their quartz tube, which show that the difference of temperature is at most 3°. They maintain the accuracy of their results (Abstr., 1907, ii, 454; this vol., ii, 362).

T. E.

Temperature of Dissociation of Ammonia and of Carbon Monoxide. HERMAN C. WOLTERECK (*Compt. rend.*, 1908, 147, 460—461).—Pure dry ammonia was passed through a heated tube of Jena glass. The first signs of dissociation were observed at 620° ; above 630° an explosible mixture of gases was produced. Decomposition occurred at a considerably lower temperature in presence of traces of organic matter or water vapour. When passed over heated iron gauze, dissociation commenced at 320° , whilst in presence of ferric oxide no decomposition took place below 420° .

Carbon monoxide dissociates at 570 — 580° , but in presence of traces of moisture no decomposition occurs even at higher temperatures.

W. O. W.

Theory of Colloids. EDUARD JORDIS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 13—26. Compare this vol., ii, 675).—The suspension theory, the theory of electric charges, the adsorption theory, and the partition theory are criticised, in the sense that none of them is applicable to all colloids, and that they all neglect chemical changes in the colloid itself and reactions between it and substances in solution.

T. E.

Modification of Wolfgang Ostwald's System of Colloids. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 26—27).—In dispersed systems the dispersion may be molecular (as in true solutions of solids or liquids) or the molecules may be aggregated to minute crystals or drops (as in suspensions or emulsions). Between these extremes there are molecular dispersions of compounds of high molecular weight, and then "suspensoids" and "emulsoids" (colloidal solutions in which the colloid is solid or liquid). True solutions are called *dispersions*; colloidal solutions, suspensions, and emulsions are called *dispersoids*. The word colloid is avoided altogether.

T. E.

System of Colloids. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 28—30).—The nature of gelatin and agar-agar solutions is discussed. The author gives reasons for supposing them to contain two liquid phases; the gelatinous precipitates of inorganic salts obtained by von Weimarn (this vol., ii, 90) are regarded as emulsions of two different solutions, which are prevented from mixing by solid membranes of the salt. A high molecular weight is not a necessary condition for the existence of a substance in the gelatinous form, which appears rather to depend on the physical conditions than on the chemical nature of the substance.

T. E.

Classification of Solutions of Colouring Matters. H. FREUNDLICH and W. NEUMANN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 80—83).—The solutions of colouring matters are true solutions, semi-colloidal and colloidal. They are classified by their diffusion through parchment paper and by their ultra-microscopic behaviour. The colloidal solutions belong to two classes, the suspension colloids, the freezing point and surface tension of which are practically the same as those of pure water, and the emulsion colloids, the properties of which differ from those of water.

Measurements of the surface tension of aqueous and alcoholic solutions of several colouring matters are given. They all form true solutions in alcohol, and the surface tension is slightly increased. Among the aqueous solutions, rhodamine (true solution), crystal-violet (semi-colloidal), and night-blue (colloidal) diminish the surface tension, whereas the other colouring matters leave it practically unchanged.

T. E.

Effect of Electrolytes on the Viscosity of Colloids. GOKUN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 84—88).—The effect of ammonium nitrate on the viscosity of solutions of gelatin is studied. The viscosity of a pure gelatin solution (0.28%) increases with time, increasing by one-half in 115 hours. The addition of ammonium nitrate diminishes the rate of increase, so that when the concentration of the salt is from 1.5*N* to 2*N*, the viscosity remains almost constant; with greater concentrations, the viscosity diminishes with the time instead of increasing. The viscosity depends on the mechanical treatment to which the solution has been subjected; repeated passage of the same solution through a capillary tube gives different results; also, the viscosity measured by passing the solution through a narrow tube under high pressure is not the same as that observed with a wider tube and lower pressure. This points to the existence of a structure in the solutions.

T. E.

Nature of Precipitated Colloids. HARRY W. FOOTE (*J. Amer. Chem. Soc.*, 1908, 30, 1388—1394).—Experiments are described which afford evidence that precipitated ferric and aluminium hydroxides may be regarded as solutions of water in the oxides or lower hydroxides, that is, solutions of liquids in solids.

Samples of the precipitated hydroxides were left in the air for several days at the temperature at which the experiments were to be carried out. The composition of the material was then determined by ignition, and a weighed quantity was put into a porcelain crucible, which was placed on a raised triangle in a large weighing bottle containing a little water. The bottle was carefully sealed and left for eighteen to forty-eight hours. The crucible was then quickly removed, and weighed in order to determine the change of weight. The experiments were made at 25° and 45°. The composition of the product at any point could be calculated from the known composition of the original material.

All the moist precipitates lost weight slightly over water, but, after being dried in the air to a certain point, they began to gain weight when placed over water. This was due to the fact that their vapour pressures had fallen below that of the water, showing that the water phase had just disappeared. The composition at the point at which the gain in weight first occurred was approximately that of the saturated hydrate free from mechanically-contained water. The averages of a large number of determinations gave the following as the composition of the saturated solutions of water in the oxides. Ferric hydroxide at 25°: Fe_2O_3 , 47.72—47.79%; at 45°, 54.53—56.74%; aluminium hydroxide at 25°: Al_2O_3 , 49.52—51.17%; at 45°, 52.57—53.82%.

Similar experiments were made with zirconium hydroxide, and the composition of the saturated solutions at 25° were found to be: ZrO_2 , 32.02—32.33%.
E. G.

Coagulation of Colloidal Solutions in Galvanic Cells. WILHELM BILTZ (*Zeitsch. Elektrochem.*, 1908, 14, 567—571).—Two metals are immersed in solutions of colloidal ferric hydroxide, gold, or antimony sulphide, purified by dialysis, and the cell so formed short circuited. In all cases the colloid is coagulated, the precipitate forming partly on one of the metals and partly in the solution near it. The more noble metals alone have no action; the less noble ones have a small action. Ferric hydroxide is precipitated on or near the more noble metal of the couple; gold and antimony sulphide go to the less noble metal. The phenomenon is not due to the current alone; the *E.M.F.* of the zinc copper element, for example, is under 1 volt, and this voltage applied to platinum electrodes in a gold hydrosol produces no precipitate. On the other hand, the quantity of zinc hydroxide which is formed from the zinc electrode is comparable in weight with the quantity of gold precipitated, and it is found almost entirely in the precipitate. The action therefore appears to be mainly due to the action of bivalent ions formed from the metals in the short circuited cells.
T. E.

Agglutination and Coagulation. SVANTE ARRHENIUS (*J. Amer. Chem. Soc.*, 1908, 30, 1382—1388).—The work described was carried out with the object of obtaining evidence as to the nature of agglutination. Two views have been advanced, one, the colloidal theory, according to which the suspended particles (bacteria or blood corpuscles) collect together and subside under the influence of electrolytes or agglutinins, and the other, first proposed by Duclaux, that agglutination depends on the coagulation of some substances in the cells which causes the cells to cling together and subside.

Experiments have been carried out on the precipitation and agglutination of blood corpuscles by means of various salts. Ox-blood corpuscles were suspended in solution of sodium chloride (0.9%) or sucrose (7%), the emulsions containing 4, 1, and 0.25% of corpuscles. To 5 c.c. of such solutions, varying quantities of the salt solutions were added. The minimum quantity of each salt required for precipitation and for agglutination was noted. The results are tabulated, and show that, with certain exceptions, there is a well-marked relation between the precipitating and agglutinating powers of each salt. Salts which give a maximum precipitation at a certain concentration also give a maximum agglutination at a certain concentration, but if a maximum does not appear in the one case, it also fails in the other. It is therefore concluded that, as Duclaux has suggested, agglutination depends on a precipitation, and that this precipitation is due to a chemical reaction between the metal ions and the proteins in the corpuscles. In general, both precipitation and agglutination in sugar solutions require less quantities of the added salt than in sodium chloride solutions.

Many substances cause agglutination as well as hæmolysis of the

blood corpuscles, and among these may be mentioned the nitrates of silver and lead, mercuric chloride, and the acids (compare this vol., ii, 708). The hæmolytic action does not run parallel with the agglutinating action.

The quantity of a salt required to be added for the precipitation of a blood solution is proportional to the concentration of the latter. Since the quantity of the salt required increases more slowly than the concentration, it is evident that there exists a chemical equilibrium between the two salt-like products derived from the blood solution and the ions of the precipitating salt. All the evidence obtained in this investigation is in favour of the physico-chemical theory, according to which the observed phenomena are due to ordinary chemical processes.

E. G.

Permeability of Ultra-filters. HEINRICH BECHHOLD (*Zeitsch. physikal. Chem.*, 1908, 64, 328—343).—The author's gelatin "ultra-filters" (this vol., ii, 24), for the separation of colloids from the solvent, vary in fineness according to the concentration of the gelatin. Some of them are too fine to allow of the determination of the size of their pores by ultra-microscopic examination of the colloids retained by them. By considering the pores as capillary tubes or as slots, their dimensions can be arrived at by measuring the pressure required to force air through them when immersed in water. This method was controlled by tests with a filter-paper which retains ox-blood corpuscles (diam. $7-8\mu$), for which the air-pressure method gave an average value of 1.5μ , and with Chamberland porcelain filters, which retain cocci (diam. 1μ), and where the method gave as a result 0.3μ . The same method provides a test for the uniformity in size of the pores. Ultra-filters may be tested in this way, and by the rate of passage of water.

Tests with ultra-filters indicate that the smallest particles of hæmoglobin have one-sixth the diameter of collargol particles, and that the smallest particles of litmus in alkaline solution, or of soap solution, have less than one-half the diameter of hæmoglobin particles.

C. H. D.

Foam Structure [Cellular Structure] of Sulphur and its Influence on Double Refraction, Dichroism, Electrical Properties and Formation of Crystals. GEORG QUINCKE (*Ann. Physik*, 1908, [iv], 26, 625—711).—A historical account is given of work relating to the different forms which sulphur may assume. The form of the heating and cooling curves of liquid sulphur and the variation of the surface tension with the temperature are also discussed. The micro-structure and the optical properties of the solid products which are obtained by cooling liquid sulphur under different conditions, and also of the products obtained by the condensation of sulphur vapour, have been examined. The conclusions of chief interest are that there are four forms of sulphur, S_a , S_β , S_δ , and S_γ , which are stable respectively between the limits $0-96^\circ$, $96-160^\circ$, $160-300^\circ$, and $300-448^\circ$; further, that liquid sulphur has a jelly-like cellular structure, and represents a mixture of solutions containing these

allotropic modifications in different proportions, the several solutions being separated by limiting surfaces in which surface-tension forces play an important part. At one and the same temperature, liquid sulphur may contain solutions in which these modifications are present in different proportions, this being determined by the previous physical treatment of the sulphur. H. M. D.

Velocity of Reaction. JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1908, 5, 698—705).—A theoretical paper, in which the theory of reaction velocity is criticised, and a new thermodynamic theory put forward. A. J. W.

Temperature-coefficient of the Velocity of Chemical Reactions. I. MAX TRAUTZ and KARL THEODOR VOLKMANN (*Zeitsch. physikal. Chem.*, 1908, 64, 53—88).—The velocity of saponification of eight esters in aqueous solution has been determined over a wide range of temperature. The temperature-coefficient of the velocity rises to a maximum between 10° and 20° in all cases, and thereafter falls off. At 60°, the value of the temperature-coefficient is frequently as low as 1.4, so that the difference in magnitude as compared with the temperature-coefficient of a photochemical reaction is not so marked as has usually been assumed. The existence of a maximum temperature-coefficient between 10° and 20° is probably connected with an irregularity which occurs in the viscosity of water in that region. The observed variation of the temperature-coefficient with the temperature may in fact be reproduced by a formula into which the viscosity of water enters.

The authors' experiments tend to show that the mass action law is strictly applicable to the saponification of esters only when the concentration is less than $N/75$.

The paper contains an extensive list of references to earlier papers on the temperature-coefficient of reaction velocity, and this earlier work is subjected to a critical review. J. C. P.

The Dynamic Theory of a Reversible Chemical Reaction. ERNST COHEN and TH. STRENGERS (*Chem. Weekblad*, 1908, 5, 594—595. Compare Smits and Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 114).—Arguments are adduced to prove that the transformation $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ is not an experimental proof of the truth of the dynamic theory of reversible reactions. A. J. W.

The Dynamic Theory of a Reversible Chemical Reaction. ANDREAS SMITS and J. P. WIBAUT (*Chem. Weekblad*, 1908, 5, 625—626; *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 162—164).—Polemical. A reply to Cohen and Strengers (preceding abstract). A. J. W.

Effect of Ferric Salts on the Rate of Oxidation of Ferrous Salts and on the Catalytic Action of the Latter. W. F. GREEN (*J. Physical Chem.*, 1908, 12, 389—397).—The influence of ferric salts on the rate of oxidation of ferrous salts by chloric acid and by oxygen, and on the rate of oxidation of iodides

by chloric and bromic acids in the presence of ferrous salts, has been investigated. It is found that ferric salts are without influence on the rate of oxidation of ferrous salts by chloric acid and by oxygen. The liberation of iodine from iodides by chloric and bromic acids is accelerated by both ferrous and ferric salts, the rate depending merely on the amount of iron present, and not on its state of oxidation. In solutions containing ferrous and ferric salts, the effects of the two are additive.

H. M. D.

Reaction between Potassium Ferricyanide and Potassium Iodide. GERHARD JUST (*Zeitsch. physikal. Chem.*, 1908, 63, 513—578. Compare Donnan and Le Rossignol, *Trans.*, 1903, 83, 703).—This reaction may be conceived as involving two stages: (1) $\text{FeCy}_6''' + \ominus = \text{FeCy}_6''''$; (2) $\text{I}' + \oplus = \text{I}$. The velocity of the latter process is practically that of an instantaneous reaction, as shown by Brunner (Abstr., 1907, ii, 223). Process (1), however, is not to be regarded as an instantaneous reaction, as shown by a study of the polarisation at an electrode immersed in a solution containing both ferro- and ferri-cyanide. When the electrode consists of platinum, it is practically unpolarisable, but this is not at all the case when the electrode consists of gold or silver. Hence process (1) is not instantaneous; it is very markedly accelerated by platinum, the acceleration being apparently connected with an oxidation and reduction of the metal. The accelerating effect of platinum on the rate of reaction between potassium ferricyanide and iodide can be demonstrated directly. From the fact that process (1) is not instantaneous, the author draws the conclusion that the difference between the FeCy_6''' and FeCy_6'''' groups cannot be one of charge alone; they must have a different constitution.

The results of quantitative experiments made on the rate of reaction between ferricyanide and iodide confirm those recorded by Donnan and Le Rossignol (*loc. cit.*), but the interpretation of the results is different. The application of the Noyes-van't Hoff formula to the author's measurements shows that the reaction is of the first order in regard to the ferricyanide, and of the second order in regard to the iodide. Altogether, therefore, the reaction between potassium ferricyanide and iodide is one of the third order, not of the fifth, as held by Donnan and Le Rossignol.

It appears fairly certain that it is the undissociated ferricyanide which takes part in the reaction, for the velocity is very markedly increased by the addition of indifferent potassium salts. In what form the iodide takes part, whether as ion or as undissociated salt, it is not possible to determine, although it is considered most probable that the ions are actively concerned.

A complete kinetic equation has not been constructed, but attention is drawn to the following observations, which would have to be considered in working out such an equation. The reaction between ferricyanide and iodide is notably retarded by ferrocyanide, but not by iodine; it is accelerated by both cyanide and fluoride ions; it is retarded by hydroxyl ions, but accelerated by hydrogen ions. Indications were also obtained that an intermediate product plays some part in the reaction.

J. C. P.

Are the Stoichiometric Laws Intelligible without the Atomic Hypothesis? OTTO KUHN (*Chem. Zeit.*, 1908, 32, 767—769. Compare Abstr., 1907, ii, 678; this vol., ii, 98).—A further adverse criticism of the papers by Wald (Abstr., 1907, ii, 755; this vol., ii, 367). J. V. E.

Laboratory Apparatus. W. HEBER GREEN (*Chem. News*, 1908, 98, 49—50).—*Determination of Density.*—The maximum error liable to occur in determining the density of water by means of a pear-shaped specific gravity bottle is found to be 0.00002. To obtain this accuracy, the bottle, which can only be used for temperatures above that of the surrounding atmosphere, is filled with the solution and immersed to the neck in a thermostat constant within 0.04° ; after ten to fifteen minutes, the expansion of the solution through the perforated stopper is complete; the bottle is then dried and cooled for fifteen minutes, and finally weighed, the density being calculated from the formula $d = M/W.(1 + 0.0012/d - 0.0012)$, in which W and M are the apparent weights of water and solution respectively required to fill the bottle. The formula is only approximate, and disregards variations of atmospheric pressure which are often sufficient to nullify the correction. The most serious fault of the instrument is the fact that wear on the ground surfaces of the stopper and neck diminishes the capacity of the pycnometer.

A Sensitive Form of Thermo-regulator.—The thermostat is of the ordinary type, and consists of a toluene bulb of about 20 c.c. capacity attached to a U-tube containing mercury, which is connected by a capillary tube to the by-pass, the novelty of which is that the gas inlet-tube is slightly opened out instead of being left square. As soon as the mercury reaches the funnel-shaped opening of this tube, its capillarity tends to force it down again and so admit the gas supply. The temperature was found to remain constant within 0.01° for several weeks, provided the bath was efficiently stirred.

A Sensitive Temperature-compensated Barometer.—A modification of a Huyghens glycerol-mercury barometer in which the former liquid is replaced by paraffin oil, b. p. 230° . The vapour pressure of this oil varies with temperature at such a rate as almost exactly to neutralise the effects of the accompanying expansion of mercury for the particular dimensions of tubes used. The rise and fall of the liquid for a variation of one-hundredth of an inch in the atmospheric pressure is sufficiently large to be seen at some distance. P. H.

Erper's Gas Generating Apparatus. L. GUTMANN (*Zeitsch. angew. Chem.*, 1908, 21, 1798).—The apparatus consists of a pear-shaped funnel for holding marble or iron sulphide, which is fitted into the neck of a bottle containing acid; the lower end of the bottle is connected by a side-tube and a tap, *A*, to a raised reservoir. The top of the funnel is fitted with a tap, *B*, and a delivery tube; near the lower end of the funnel is a side-tube through which the spent acid may be withdrawn after closing the delivery tube and opening the tap *B*. When re-charging with solid, the tap *A* is closed. P. H.

Modified Form of Saint-Claire Deville's Apparatus for Continuous Production of Gases. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1908, [iv], 3, 890—892).—The modification is devised to overcome the disadvantages of the ordinary Saint-Claire Deville apparatus, namely, the difficulty of using up the whole of the acid and the clogging of the rubber tubing by crystals deposited from the saturated solutions formed when the apparatus has been long in action.

For this purpose, the ordinary rubber tube connexion is prolonged upwards at an obtuse angle inside the bottle containing the acid, by a glass tube reaching to a level slightly below that of the liquid, so that it is always the strongest acid which comes into action first, and the denser liquid remains at the bottom of the bottle. Continuity of action can be secured by having the side aperture of the acid bottle halfway up the latter, and making the connexion between the two bottles by two glass tubes parallel to each other and prolonged into the acid bottle at obtuse angles to the horizontal with their arms turned in opposite directions. To permit of this arrangement, the bottle containing the solid is raised on a small block, so that its side aperture is opposite that of the acid bottle. In this way by the action of gravity a continuous flow of acid through the solid to be acted on is maintained.

T. A. H.

Simple Regulator for High Pressure Gas. ROBERT LE ROSSIGNOL (*Chem. Zeit.*, 1908, 32, 820).—By making the cone angle of an ordinary screw-down tap very small (4°), it is possible to obtain gas from a cylinder at any required pressure in a simple manner. A slow, steady current of oxygen, as used for combustion purposes, may be obtained directly from a cylinder of the compressed gas by using such a form of tap.

J. V. E.

New Method for Calibrating Capillary Tubes. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1904, 64, 201—214).—The process and apparatus are practically the same as those employed in the measurement of surface tension. The heights to which water and dilute solutions of isobutyric acid rise in two capillary tubes of about the same bore are accurately measured, and the exact radius of the tubes at various points is thus determined. The application of the method is illustrated by full data for two tubes which the author has examined.

J. C. P.

Improved Pipette. WOITHE (*Chem. Zentr.*, 1908, ii, 1; from *Arbb. Kais. Gesundh.-Amt.*, 1908, 28, 401—404).—This suction arrangement for use with very poisonous or infectious materials consists of a small syringe of about 5 to 7 ccm. capacity, connected to a pipette by a U-tube, and held by a spring-clip.

J. V. E.

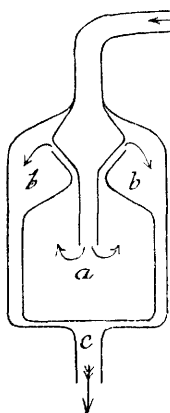
Automatic Syphon Pipette. HERBERT S. BAILEY (*J. Amer. Chem. Soc.*, 1908, 30, 1508—1509).—A description and diagram are given of an apparatus for delivering approximately constant quantities of a reagent, such as the sulphuric acid for the Babcock milk test or

the Kjeldahl nitrogen estimation. For details, the original must be consulted. E. G.

Steam Inlet-tube. H. STOLTZENBERG (*Chem. Zeit.*, 1908, 32, 770).—Instead of the ordinary open inlet-tube used for steam distillation purposes, a tube is described which is closed at the lower end, the steam being allowed to enter the liquid from a number of short, horizontally-curved side-tubes placed near the end. By this means the distillation flask may be used in an upright position; bumping is avoided because the liquid is caused to rotate rapidly by the issuing steam, and the process of distillation is considerably hastened.

J. V. E.

New Safety Valve. H. STOLTZENBERG (*Chem. Zeit.*, 1908, 32, 832).—A safety valve is described for use when gases are to be absorbed in liquids, such as carbon dioxide in potash solution. It will be seen from the figure, that the gas after entering *a*, passes between the open ground-glass joint into the the outer vessel *b*, and then through *c* to the potash solution. Should the absorption be so rapid as to cause the potash solution to flow back, the small inner flask is lifted up and closes the joint connecting *a* with *b*.



J. V. E.

Use of Electrical Heating in Fractional Distillation. THEODORE W. RICHARDS and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1908, 30, 1282—1284; *Zeitsch. physikal. Chem.*, 1908, 64, 120—123).—In determining the latent heat of vaporisation of certain substances by a modification of Kahlenberg's method, it was observed that each organic liquid boiled much more constantly when heated electrically by the platinum

coil immersed in it than when distilled in the ordinary way. A special form of apparatus has therefore been devised for use in fractionating organic liquids.

At the bottom of an ordinary stout distilling flask, a depression is blown of about the same diameter as the neck of the flask, and into this is placed a coil consisting of about 40 cm. of platinum wire with a resistance of about 0.7 ohm. A current of 10—15 amperes is led to the resistance coil from above by heavy copper wires of 2.5—3.0 mm. diameter enclosed in glass tubes, into the ends of which the ends of the platinum wire are sealed, contact being made by a drop of mercury.

Since the bubbles of vapour arise only from the small area of the resistance coil, ebullition proceeds quietly and without any bumping. The method is especially applicable to fractional distillation under reduced pressure; it obviates superheating, and effects a much more rapid and complete separation than the ordinary method of distillation.

E. G.

Receiver for Vacuum Fractional Distillation. J. FREUNDLICH (*Chem. Zeit.*, 1908, 32, 820).—An arrangement is described for collecting fractions in a vacuum without interrupting the process of distillation, the end of the condenser tube communicating by means of taps and short side-arms with two glass cylinders, the upper ends of which communicate with the exhaust tube by means of taps. J. V. E.

Apparatus for the Rapid Distillation of Mercury. FORTUNATO FLORIO (*Nuovo Cim.*, 1908, [v], 16, 93—96).—An apparatus is figured and described, by which 2·5 kilos. of mercury can be distilled per hour. G. B.

Inorganic Chemistry.

A New Method for the Preparation of Pure Hydrogen. MAURICHEAU-BEAUPRÉ (*Compt. rend.*, 1908, 147, 310—311).—Aluminium filings are mixed with a small quantity of mercuric chloride and potassium cyanide in powder. The product, to which the name "hydrogenite" is given, has $D = 1.42$. It can be preserved indefinitely if kept in a dry atmosphere, but when treated with water it becomes oxidised, with development of heat and liberation of pure hydrogen. One kilogram of the powder yields 1300 litres of hydrogen at 15° and 760 mm. To obtain the best yield, the action of the water must be regulated so as to maintain the temperature at about 70° , and a large excess of water should be avoided. W. O. W.

Preparation of Hydrogen Peroxide. C. A. F. KAHLBAUM (D.R.-P. 197023).—Hydrogen peroxide can be prepared from its elements, or from a mixture of steam and these elements, or even from steam alone, when these gases are passed through a source of heat with a velocity of not less than one metre per second. The source of heat may be an electric arc, a spark discharge, or a flame of burning hydrogen, and the gases may be kept stationary while the heating apparatus is rotated. On condensing the steam, the hydrogen peroxide is obtained in the form of an aqueous solution. G. T. M.

Production of Hydrogen Peroxide from Aluminium and Zinc. HOWARD T. BARNES and G. W. SHEARER (*J. Physical Chem.*, 1908, 12, 468).—The statement made previously (this vol., ii, 344), that zinc in contact with water containing air or oxygen does not produce hydrogen peroxide, is contradicted by later observations. The difference between the behaviour of zinc and aluminium is traced to the fact that hydrogen peroxide is decomposed fairly rapidly in contact with zinc, but only slowly, if at all, in contact with aluminium. This is probably due to the difference in the extent to which the covering surface films protect the hydrogen peroxide from the action of the metals.

Copper, platinum, and iron in similar circumstances do not yield hydrogen peroxide. H. M. D.

Preparation of Perhydroxide Bases and their Salts. RICHARD WOLFFENSTEIN (D.R.-P. 196369).—*Sodium perhydroxide*, NaOOH , is precipitated by adding 30% hydrogen peroxide to alcoholic sodium hydroxide or ethoxide; it is a strongly basic substance, and, when saturated with carbon dioxide, forms sodium hydrogen percarbonate, NaHCO_4 . This compound is more stable than the product obtained by Tafel from sodium peroxide and alcohol (Abstr., 1894, ii, 448). G. T. M.

Sulphur Anion and Complex Sulphur Anions. JOSEPH KNOX (*Trans. Faraday Soc.*, 1908, 4, 29—49).—Many of the result given in the present paper have already been published (Abstr., 1906, ii, 608). The predominant complex in the solution of mercuric sulphide in sodium sulphide is Na_2HgS_2 , but, when a solution saturated with both sulphides is concentrated over sulphuric acid, a double sulphide of mercury and sodium, $2\text{Na}_2\text{S} \cdot 5\text{HgS} \cdot 3\text{H}_2\text{O}$, separates in yellow crystals.

The solubility of mercuric sulphide (black and red) in potassium sulphide solutions is somewhat greater than in sodium sulphide; the solubility in equivalent dilute solutions of barium and sodium sulphide is practically equal. The solubility of mercuric sulphide in sodium disulphide, Na_2S_2 , is about half that in the normal sulphide, and in this case, also, the solubility is increased by the addition of sodium hydroxide. From the results of *E.M.F.* measurements, it is probable that the complex anion present in greatest amount is HgS_2^{--} in this case also.

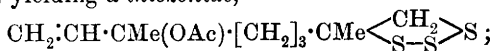
The solubility product $S = [\text{Hg}^{++}][\text{S}^{--}]$ only remains constant for different ionic concentrations when it is assumed that the hydrolysis of sodium sulphide in dilute (0.05 molar) solution is practically complete. Küster and Heberlein (Abstr., 1905, ii, 156), however, found for the same solution a value less than 90% by a method depending on the decomposition of diacetylacetone. The author has repeated these measurements, and finds a greater degree of hydrolysis than Küster, a result which is confirmed by conductivity measurements.

The solubility products of certain sulphides have been determined by *E.M.F.* measurements with rods of the respective metals dipping in a solution of sodium sulphide. The results at 25° are as follows: $[\text{Ag}^+]^2[\text{S}^{--}] = 3.9 \times 10^{-50}$; $[\text{Pb}^{++}][\text{S}^{--}] = 2.6 \times 10^{-15}$, and $[\text{Cu}^{++}][\text{S}^{--}] = 1.2 \times 10^{-42}$. G. S.

Thiozonides. Sulphur and its Cyclic Compounds. HUGO ERDMANN (*Annalen*, 1908, 362, 133—173).—Hoffmann and Rothe have shown (Abstr., 1906, ii, 279) that molten sulphur cooled to 160° separates into two distinct liquid layers. The new modification of sulphur, which according to Smith and Holmes (Abstr., 1902, ii, 650) must be represented by S_x , is shown to be S_8 ; in fact, this highly reactive, labile, dark-coloured form of sulphur is the analogue of

ozone, and is consequently named *thiozone*. As it would be more difficult to isolate thiozone in a pure state than ozone, it is best identified by its action on organic compounds. Ozone acts on unsaturated compounds, yielding ozonides or polyozonides (compare Harries, Abstr., 1906, i, 225); similarly, when unsaturated compounds are heated with sulphur at 160°, thiozonides or polythiozonides are formed: $\text{CR}_1\text{R}_2:\text{CR}_3\text{R}_4 + \text{S}:\text{S}:\text{S} \longrightarrow \begin{array}{c} \text{CR}_1\text{R}_2\cdot\text{S} \\ | \\ \text{CR}_3\text{R}_4\cdot\text{S} \end{array} > \text{S}$.

Terpene Derivatives.—Linalyl acetate is practically unattacked by sulphur at 150°, but at 160° the two substances interact energetically, yielding a *thiozonide*,



the same compound is formed whether the quantity of sulphur employed is very small or greatly in excess of that required to form the monothiozonide; the acetyl group appears to protect the second ethylene linking from the action of thiozone. The thiozonide forms a dark brown, viscid syrup, $D_{23}^{25} 1.133$, and has a characteristic odour. It absorbs oxygen very rapidly, and reacts both as a thio-acid and thio-base; although insoluble in alcohol, it readily dissolves in an alcoholic solution of sodium sulphide, forming a dark brown solution which contains the *sodium* salt, $\text{C}_{12}\text{O}_{20}\text{O}_2\text{S}_4\text{Na}_2$; this could not, however, be isolated. The thiozonide yields characteristic precipitates with the chlorides of antimony, arsenic, bismuth, and mercury. An ethereal solution of the thiozonide and auric chloride liberates hydrogen chloride on evaporation, leaving a brown, tarry residue of a *gold* compound, which, when heated on porcelain, leaves behind a brilliant, coherent coating of gold. The gold compound is also formed by the interaction of the thiozonide dissolved in ethyl acetate with gold sulphide.

Linalool dithiozonide is prepared by heating linalool with sulphur at 160°; hydrogen sulphide is evolved during the reaction, and the brown, viscid mass obtained has the approximate composition $\text{C}_{10}\text{H}_{16}\text{OS}_5$.

With the object of ascertaining whether linalool and linalyl acetate behave in a similar manner towards ozone, equimolecular solutions of the two substances in carbon tetrachloride were added to equal volumes of a solution of ozone in carbonyl chloride at -70° until the blue colour of the ozone had disappeared. It was found that the same quantity of ozone required twice as much linalyl acetate as linalool, so that the former evidently forms a mono-, whilst the latter forms a di-ozonide.

Sulphur Dyes as Derivatives of Thiozone.—This part of the paper is of a somewhat technical nature. Evidence is advanced which shows that the various sulphur dyes first formed by heating many organic compounds with sulphur and sodium sulphide are thiozonides; for example, like thiozonides, they are insoluble in most solvents, soluble in alkali sulphides, and are readily oxidised by the oxygen of the air at the ordinary temperature. The fact that most sulphur dyes are oxidised by atmospheric oxygen with the liberation of sulphuric acid, and yield hydrogen sulphide when reduced, is readily explained on the

assumption that they are thiozonides containing the chromophoric group $\begin{smallmatrix} \text{C}\cdot\text{S} \\ \text{C}\cdot\text{S} \end{smallmatrix} > \text{S}$. Ris's conclusion (Abstr., 1900, i, 419), that the sulphur liberated as hydrogen sulphide is attached to nitrogen, is very improbable.

Theory of Inorganic Polysulphides.—Although sulphur does not readily act on organic substances below 160° , yet, in the presence of sodium sulphide, action takes place at a much lower temperature. It is therefore probable that the polysulphides are closely related to thiozone. The results of work not yet published show that the alkali metals behave towards sulphur like rubidium towards oxygen (compare Erdmann and Köthner, Abstr., 1897, ii, 96); in fact, the yellow disulphide, NaS_2 , corresponds with the brown oxide, RbO_2 . This disulphide may be represented as a thiozonate, $\begin{smallmatrix} \text{NaS} \\ \text{Na} \end{smallmatrix} > \text{S} \leq \text{S}$, that is,

as an additive product of the monosulphide with thiozone. Such thiozonates are among the best characterised polysulphides of the alkali metals; thus, Böttger has shown (Abstr., 1884, 1260) that alkali thiozonates containing varying, yet definite, amounts of water crystallise from solutions of polysulphides containing more or less sulphur; further, the various polysulphides, Na_4S_9 , Na_2S_5 , Na_3S_6 (compare Bloxam, Trans., 1900, 77, 753), when heated at 800° , yield the thiozonate, Na_2S_4 . The fact that pure sulphur dyes are formed by acting on amino-phenols with an alcoholic solution of sodium thiozonate, may be explained by assuming that the thiozonate partly dissociates when its alcoholic solution is warmed, yielding thiozone, $\text{Na}_2\text{S}_4 \rightarrow \text{Na}_2\text{S} + \text{S}_3$, which, in the nascent state, readily unites with the amino-phenol.

Constitution of Ultramarine.—Hoffmann's conclusion (Abstr., 1879, 108), that the sulphur in ultramarine-blue is present in a similar state of combination as in the polysulphide, Na_3S_4 (sodium thiozonate), cannot be correct, since it does not yield silver sulphide with silver nitrate, but is converted into silver ultramarine, in which sodium is replaced by its equivalent of silver (compare Heumann, Abstr., 1880, 217, 367; 1881, 351). Instead, the ultramarines are to be regarded as thiozonides. Hoffmann has shown that white ultramarine, $\text{Na}_{12}\text{Al}_6\text{S}_3\text{Si}_6\text{O}_{24}$, is converted on oxidation into green, and then into blue, ultramarine, both of which also contain the three atoms of sulphur in the molecule. In strict analogy with the ultramarines, sulphur dyes are reduced by powerful reducing agents to leuco-compounds, corresponding with the white ultramarine, which are readily oxidised back to the original dye.

Chemistry of Molten Sulphur.—As has been shown, molten sulphur at 160° contains thiozone; now this substance, like sulphur dioxide, has the character of an acid anhydride, and is consequently able to bring about polymerisation of eight-membered rings (compare Harries, this vol., i, 254). Now ordinary sulphur contains eight atoms in the molecule; consequently, sulphur at 160° probably consists of thiozone, which imparts to the mass its dark colour, together with amorphous sulphur, $(\text{S}_8)_x$, which renders the mass viscid.

Constitution of Polymeric Forms of Oxygen.—Since sulphur exists

as S_8 , it is not improbable that oxygen might also exist in the polymerised form, O_8 . Ladenburg and Lehmann (Abstr., 1906, ii, 509) appear to have obtained evidence of the existence of a highly polymerised form of oxygen, but Warburg and Leithäuser (Abstr., 1907, ii, 342) have thrown doubt on their results. However, it is not improbable that the octa-sulphates described by Weber (Abstr., 1885, 121) contain the eight-membered ring:

$$\begin{array}{c} \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \\ | \quad | \quad | \quad | \\ \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \end{array}$$

Theory of Vulcanised Caoutchouc.—In the vulcanisation of caoutchouc, it is probable that the sulphur liberates thiozone, which forms a thiozonide, and that the viscid, amorphous form of sulphur, $(S_8)_x$, produced simultaneously, forms a semi-solid solution with the caoutchouc, which has a similar constitution to the viscid, amorphous form of sulphur, being a polymerised form of a dimethylcyclooctadiene (compare Harries, *loc. cit.*). Vulcanised caoutchouc is thus a semi-solid solution of polymerised sulphur, $(S_8)_x$, in polymerised dimethylcyclooctadiene, $(C_8H_{10}Me_2)_x$, and its thiozonide. Ebonite is probably a polythiozonide of caoutchouc.

W. H. G.

Selenium and Iodine. GIOVANNI PELLINI and S. PEDRINA (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 78—81).—From a study of the melting-point curve for mixtures of selenium and iodine, the authors conclude that these elements form no compound and no mixed crystals, except within very narrow limits. The eutectic mixture melts at 58° , and corresponds almost exactly with the supposed compound, Se_2I_2 . The identical products obtained in various ways by Schneider (*Pogg. Annalen*, 1866, 129, 627) must be regarded as mixtures of definite composition.

T. H. P.

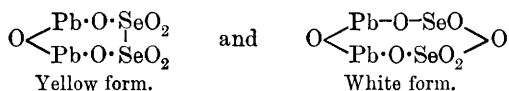
Electrolytic Formation of Selenic Acid from Lead Selenate. FRANK CURRY MATHERS (*J. Amer. Chem. Soc.*, 1908, 30, 1374—1378).—A study has been made of the best conditions for converting lead selenate into lead and selenic acid by electrolysis. The lead selenate is placed in a platinum dish, which serves as the cathode, and a coil of platinum wire is used as the anode. Some reduction products of selenic acid are formed during the process, but these are insoluble and can be removed by filtration. The best efficiency yield, 87%, was obtained at the ordinary temperature, with a low current density at the cathode and a thin layer of lead selenate. The best current yield, 13%, was obtained at 85° , with a low current density and a large amount of lead selenate on the cathode. Selenic acid is only produced in small quantities from lead selenate in contact with the anode.

E. G.

Structural Isomerism. Preparation of Asymmetric Selenites. LUIGI MARINO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 858—866; *Zeitsch. anorg. Chem.*, 1908, 59, 450—460).—If the author's views concerning sulphurous acid (this vol., ii, 106) hold also for selenious acid, it should be possible to obtain asymmetric selenites. To investigate this question, the action of selenious acid on lead peroxide has been studied. In this way, besides ordinary lead selenite,

a salt, $\text{Pb}_2\text{Se}_2\text{O}_7$, has been obtained as a sulphur-yellow, crystalline powder. When treated with potassium carbonate solution, this salt yields 1 mol. of lead peroxide and 1 mol. of lead oxide per mol., whilst the addition of dilute nitric acid to a solution of the salt in 15% sodium hydroxide solution precipitates the sesquioxide, thus: $\text{Pb}_2\text{Se}_2\text{O}_7 = \text{Pb}_2\text{O}_3 + 2\text{SeO}_2$. When heated at 200° , the yellow salt gradually changes into a white isomeride, exhibiting different reactions from the yellow form; for example, it does not yield lead peroxide when boiled with alkali carbonate solutions. When heated at 40 – 50° with dilute sulphuric acid and potassium permanganate, the white isomeride absorbs 1 atom of oxygen per mol.; under the same conditions, the yellow form is stable, but after long heating to 80° it absorbs 2 atoms of oxygen per molecule.

On the basis of these results, the author proposes the constitutions :



The author regards these results as lending further support to the structural formula $\text{Pb} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ for lead peroxide. T. H. P.

Solutions of Metals in Non-metallic Solvents. III. Apparent Molecular Weight of Sodium Dissolved in Liquid Ammonia. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1908, 30, 1197–1219. Compare Abstr., 1907, ii, 935; this vol., ii, 486).—A study of the molecular weight of sodium and potassium in liquid ammonia was made by Joannis (Abstr., 1893, ii, 115; 1906, ii, 161) by determining the change in the vapour pressure of the solvent on addition of a known quantity of the metal. Franklin and Kraus (Abstr., 1899, ii, 202) determined the molecular weight of sodium and lithium in ammonia by the boiling-point method, and obtained results for sodium which were lower than those of Joannis. The results of Franklin and Kraus are regarded as the more trustworthy, as the solutions employed were less concentrated. The present investigation was undertaken with the object of determining the molecular weight of sodium in still more dilute solutions.

A method has been devised for measuring the changes of the vapour pressure of liquid ammonia on the addition of sodium, which gives results of an accuracy within about 1% when the total pressure change is as small as 10 mm. The apparatus employed is described with the aid of a diagram. The determinations were made at about 15° , and the concentration varied from one to ten litres per gram-atom of sodium.

The results show that in dilute solutions the molecular weight of sodium is as low as 23, and in solutions of lower concentration than 0.1*N* is probably even lower. In the more concentrated solutions, the pressure change is smaller than would be expected from Raoult's law. The form of the complete vapour-pressure curve indicates that this deviation is due to a tendency of the solutions to separate into two phases, for which the critical point lies near 3 mols. % of sodium.

It has been shown previously (Abstr., 1907, ii, 936) that separation takes place in this region at lower temperatures. Raoult's law cannot therefore be applied to solutions of greater concentration than 0.1*N*.
E. G.

Solutions of Metals in Non-metallic Solvents. IV. Material Effects accompanying the Passage of an Electric Current through Solutions of Metals in Liquid Ammonia. Migration Experiments. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1908, 30, 1323—1344. Compare Abstr., 1907, ii, 935; this vol., ii, 486, and preceding abstract).—In the first paper of this series, it was suggested that the electrical conductivity of metals is due to ionisation. In this connexion, a study has now been made of the question as to whether the transport of matter accompanies the current through solutions of metals in liquid ammonia, and quantitative migration experiments have been carried out with solutions of sodium. Such solutions are well adapted for the purpose, since they possess a characteristic blue colour, which renders concentration changes visible in solutions as dilute as *N*/40,000. It has been found that the liquid at the surface of the anode becomes colourless, whilst at the cathode the colour becomes more intense. Experiments have also been made with solutions of potassium in potassamide dissolved in liquid ammonia. In this case, it has been found that the blue colour travels towards the anode, whence it might be concluded that the metal in the solution travels in this direction. It has already been shown, however, that the metal travels in the direction of the positive current, and the direction of movement of the colour is not therefore due to a movement of the metal in this direction, but is due to interaction between the negative metal anions and potassamide, whereby free metal is reversibly produced.

From the results of these experiments, it is concluded that the process of conduction in solutions of metals is ionic. The metal constitutes the positive ion, and is identical with the positive ion of a salt of the metal dissolved in ammonia. The negative ion consists of an electron surrounded by molecules of the solvent, and is in equilibrium with ammonia according to the equation: $\epsilon^-(\text{NH}_3)_n = \epsilon^- + n\text{NH}_3$. This electron is also in equilibrium with the metal cation and the neutral metal atoms, thus: $\text{M}^+ + \epsilon^- = \text{M}\epsilon$, where M^+ is the cation and $\text{M}\epsilon$ the neutral atom.
E. G.

Oxidation of the Ammonia in Ammonium Persulphate. MARIO G. LEVI and E. MIGLIORINI (*Gazzetta*, 1908, 38, ii, 10—20. Compare Abstr., 1907, ii, 81).—Experiments made by heating solutions of ammonium persulphate at 100°, 75°, and 50° show that the ammonia of ammonium persulphate may undergo marked oxidation even in solutions which are originally neutral or almost so, and become more and more acid owing to the sulphuric acid liberated; this oxidation is rendered evident by the evolution of nitric oxide. The addition of sodium hydroxide in increasing proportions to the persulphate solution causes

the oxidation first to diminish to a minimum and then to increase indefinitely.

When no alkali is present, there seems to be a true oxidation of the ammonium ions, resulting in the formation of nitric acid in the solution. Corresponding with this oxidation, the amount of oxygen evolved is less than the theoretical quantity. When the decomposition takes place in presence of alkali, the reactions become more complicated; there may then be oxidation in the liquid phase and also in the gaseous phase, especially at the surface of the separation of liquid and gas, where the ammonia may be oxidised directly by part of the oxygen evolved. The courses of these two reactions would depend on the concentrations of the ammonia in the two phases; in general, oxidation takes place more readily and more rapidly in the liquid phase.

The oxidation is diminished in absolute amount by lowering the temperature, and is augmented by increasing the concentration of the persulphate.

T. H. P.

Combination of Nitrogen with Calcium Carbide. GINO POLLACCI (*Zeitsch. Elektrochem.*, 1908, 14, 565—566).—Potassium carbonate accelerates the combination of nitrogen and calcium carbide; the rate of combination is greatest when the mixture contains 4% of potassium carbonate. Increase of pressure also accelerates the reaction, but the acceleration practically reaches a limit at 2 atmospheres, further increase of pressure having little effect. Under the most favourable conditions, the conversion is complete in one hour at 900°.

T. E.

Preparation of Nitrides from Metallic Oxides or Salts with the Aid of Atmospheric Nitrogen. WILHELM BORCHERS and ERICH BECK (D.R.-P. 196323).—A metal capable of combining with nitrogen is used in the form of a fusible salt, or of its oxide mixed with a fusible fluoride. The anode compartment resembles a gas-holder dipping into a layer of some fusible metal capable of forming a fusible alloy with the metal of the salt or oxide. The fused metallic salt or mixture of oxide and fluoride is placed within the inverted anode compartment and above the layer of fused metal. The anodes are composed of some refractory material, whilst the layer of fused metal forms the cathode. On electrolysis, the metal capable of combining with nitrogen is set free at the fusible cathode and alloys with it, and thus passes from under the anode compartment.

Arrived at the outer parts of the cathode vessel, the alloy meets a current of nitrogen, with which the liberated metal combines, forming a nitride which can be removed when necessary.

In preparing magnesium nitride, the cathode vessel contains fused zinc, and the anode liquid consists of a mixture of magnesia and an alkali fluoride.

On passing the current, the liberated magnesium alloys with the zinc, and subsequently combines with the nitrogen blown into the fused metal.

G. T. M.

Preparation of Alloys of Metals which Form Nitrides. ERICH BECK (*Metallurgie*, 1908, 5, 504—521).—The conditions have been studied for the electrolytic preparation of alloys, especially of magnesium, capable of yielding ammonia on treatment with nitrogen and subsequent decomposition of the nitride by steam. Tin or lead may be used as the cathode metal. When the eutectic mixture of sodium and potassium fluorides (m. p. 702°) is used as the flux, magnesium oxide is readily dissolved, an addition of 10% lowering the m. p. to 677° , but, on electrolysis, only alkali metals are set free. A mixture of calcium and magnesium fluorides also dissolves magnesium oxide, and gives good results when the cathode metal is agitated. The eutectic point of calcium and magnesium fluoride lies at 945° and 48% CaF_2 ; mixed crystals are not formed. Barium and strontium fluorides, on the other hand, form only mixed crystals. Mixtures of barium fluoride with the calcium-magnesium fluoride eutectic give a curve having a marked eutectic point at 790° . By the addition of magnesium oxide to this mixture, the melting point is first depressed slightly, further additions raising it considerably. This mixture gives the best results, the magnesium oxide being added gradually, but owing to its high density, a part of the magnesium rises to the surface and is burnt.

If chlorides are used instead of the fluoride-oxide mixture, carnallite gives the best results. C. H. D.

Acid Phosphates. NICOLA PARRAVANO and ALDO MIELI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 33—41).—The authors have prepared the three acid phosphates: $\text{NaH}_2\text{PO}_4, \text{H}_3\text{PO}_4$; $\text{KH}_2\text{PO}_4, \text{H}_3\text{PO}_4$ (compare Staudenmaier, *Abstr.*, 1894, ii, 137), and $(\text{NH}_4)\text{H}_2\text{PO}_4, \text{H}_3\text{PO}_4$, of which they have determined the solubility in phosphoric acid and the behaviour towards water. The phosphoric acid used, m. p. 40.6° , was specially purified and freed from pyrophosphoric acid.

The sodium salt, $\text{NaH}_2\text{PO}_4, \text{H}_3\text{PO}_4$, forms rosettes of long needles or small prisms, m. p. $126-127^{\circ}$. The freezing-point curve of its aqueous solution has three branches, corresponding with the separation of ice, NaH_2PO_4 , and $\text{NaH}_2\text{PO}_4, \text{H}_3\text{PO}_4$ respectively.

The potassium salt, $\text{KH}_2\text{PO}_4, \text{H}_3\text{PO}_4$, for which Staudenmaier (*loc. cit.*) gave m. p. 127° , melts only partly at 127.5° , forming a liquid solution of KH_2PO_4 in H_3PO_4 , whilst part of the KH_2PO_4 remains in the solid state: $x[\text{KH}_2\text{PO}_4, \text{H}_3\text{PO}_4] \rightarrow [x\text{H}_3\text{PO}_4 + y\text{KH}_2\text{PO}_4] + [x-y]\text{KH}_2\text{PO}_4$; at 139° , the whole of the KH_2PO_4 dissolves. The freezing-point curve of its aqueous solutions has two branches, corresponding with the separation of ice and KH_2PO_4 respectively.

The ammonium salt, $(\text{NH}_4)\text{H}_2\text{PO}_4, \text{H}_3\text{PO}_4$, forms shining, deliquescent needles, and, on heating, behaves like the potassium salt; at $77-78^{\circ}$, it undergoes partial fusion, forming a solution of $(\text{NH}_4)\text{H}_2\text{PO}_4$ in H_3PO_4 , together with solid $(\text{NH}_4)\text{H}_2\text{PO}_4$, whilst at 118° perfect solution occurs. Its curve of solubility in phosphoric acid has two branches meeting at 78° , which is the transformation point of the salt; one branch corresponds with the separation of $(\text{NH}_4)\text{H}_2\text{PO}_4, \text{H}_3\text{PO}_4$, and

the other with that of $(\text{NH}_4)\text{H}_2\text{PO}_4$. In contact with water it decomposes rapidly.

T. H. P.

Polyphosphates. NICOLA PARRAVANO and G. CALCAGNI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 731—738).—The various supposed polyphosphates can be considered theoretically as formed by the union of pyrophosphate and metaphosphate in various proportions; thus the salt $\text{Na}_5\text{P}_3\text{O}_{10}$ is $\text{Na}_4\text{P}_2\text{O}_7 + \text{NaPO}_3$, the salt $\text{Na}_6\text{P}_4\text{O}_{13}$ is $\text{Na}_4\text{P}_2\text{O}_7 + 2\text{NaPO}_3$, and so on. The authors have accordingly studied the freezing-point curve of mixtures of sodium pyrophosphate and metaphosphate in various proportions as well as the curve obtained with the corresponding potassium salts. Both curves consist of two continuous branches meeting at a eutectic point; the shape of the curves indicates the non-existence of any compounds of metaphosphate and pyrophosphate, so that the various polyphosphates which have been described are probably mere mixtures of the two salts.

W. A. D.

Action of Phosphoric Acid on Silicic Acid and Silicate Glass. KARL HÜTTNER (*Zeitsch. anorg. Chem.*, 1908, 59, 216—224. Compare Mylius and Meusser, Abstr., 1905, ii, 316).—When finely powdered silica is heated in a quartz vessel with excess of metaphosphoric acid, a clear solution is at first obtained, from which, on continued heating, silicyl phosphate, $\text{SiO}_2\text{P}_2\text{O}_5$, separates in minute crystals (Hautefeuille and Margottet, Abstr., 1883, 782). The same compound is obtained by heating silicon chloride with phosphoric acid.

Silicyl phosphate is not decomposed by boiling water, but on heating strongly, it loses part of the phosphoric oxide and forms amorphous products, which are decomposed by water. The compound itself has also been obtained in an amorphous hydrated form from its solution in metaphosphoric acid, and this modification is being further investigated.

The action of phosphoric acid on the silicates found in glass has been investigated; in most cases, silicyl phosphate and metaphosphates are produced. Orthophosphoric acid scarcely acts on glass at the ordinary temperature, but does so at 100—150°. Phosphoric oxide can be sublimed in glass vessels without affecting them.

G. S.

Silicic Acids obtained by Tschermak. JAKOB M. VAN BEMMELN (*Zeitsch. anorg. Chem.*, 1908, 59, 225—247; *Chem. Weekblad*, 1908, 5, 567—589).—A criticism of the formulæ assigned to the silicic acids obtained by Tschermak (Abstr., 1905, ii, 816) by digesting natural silicates with hydrochloric acid. These formulæ are based on the changes which are observed in the rate of loss of water by the hydrogels when the proportion of water to silica has attained certain values. According to the author, these changes cannot be supposed to differentiate between the chemically-combined and the mechanically-held water, and furnish no basis for the deduction of formulæ for the various preparations of silicic acid. The hydrogels obtained from the silicates are colloidal absorption

compounds of indefinite composition, and the changes in the rate of dehydration are probably due to changes in the mechanical structure of the hydrogels brought about by the gradual removal of water.

H. M. D.

Dissociation of Molten Silicates. II. CORNELIO DOELTER (*Monatsh.*, 1908, 29, 607—644. Compare this vol., ii, 178).—The paper deals with the conductivity and the polarisation of augite, albite, labradorite, and diopside in the molten and in the solid states at high temperatures. In measuring the conductivity of molten salts, a sharper minimum in the telephone is obtained by using electrodes set far apart and placed in a liquid of small cross section. Since the use of capillary vessels is excluded on account of the viscosity of molten silicates, the author employs a conductivity trough of quartz and kaolin of parallelepiped shape, 24—25 mm. long and 1 sq. cm. in area, in which the electrodes are fixed as in his former experiments, not quite at the ends of the vessel. The trough is filled with the powdered silicate, and the conductivity measured at temperatures up to those at which the silicate sinters and fuses. Both direct and alternating currents have been employed, but measurements by the former are only of secondary importance, and do not agree with the values obtained with an alternating current, except in the case of augite.

Experiments, mainly of a qualitative nature to ascertain whether polarisation occurs in the solid as well as in the liquid state, indicate that such a phenomenon is not manifest in crystalline silicates unless the vitreous modification is also present; only in the neighbourhood of the m. p. does slight polarisation occur. For example, with augite, m. p. about 1200°, polarisation is not evident below 1180°, but becomes quite distinct at 1250°; albite, which is especially liable to resolidify in the vitreous state, shows polarisation at 900°, and with strong currents at 1100°, electrolysis occurs, aluminium being deposited on the platinum cathode.

From van't Hoff's equation: $d\log x/dT = -q/RT^2$ is derived the expression: $\log W = v/T + C$, according to which the graphic representation of the relation between the logarithm of the specific resistance, $W (= 1/x)$, and the reciprocal of the absolute temp., T (v and C being constants), is a straight line. The author's experiments show that the formula only holds for temperatures removed from the m. p.

The conductivity of a crystalline silicate first becomes measurable at about 500°, increases with the temperature, and shows a marked augmentation in the neighbourhood of the m. p., causing the conductivity-temperature curve to show a break; a gradual rounding of the curve is exhibited when the molten silicate passes into the vitreous form. In general, the temperature-conductivity curve consists of two parts, one, corresponding with temperatures from 200° below the m. p. up to the m. p., is nearly vertical, and the other, representing the conductivity of the liquid phase, is nearly horizontal. The fact that a crystalline silicate shows a sudden change in conductivity when passing into the liquid or into the amorphous state, is the most important result of the investigation. The paper concludes with theoretical discussions

of the preceding fact and of the relation between crystalline structure and dissociation.

C. S.

Search for Possible New Members of the Inactive Series of Gases. SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1908, 81, A, 178—180. Compare following abstract).—As the periodic system would appear to indicate the existence of two or three elements of the helium group heavier than xenon, the heavier portions of the gas, after the fractional distillation of 120 tons of liquid air, were investigated by Moore (*loc. cit.*); no positive result was obtained, and it is probable that higher members either do not exist in the atmosphere or that they disintegrate during the process of separation.

It is suggested that the emanations from radium, thorium, and actinium may be the missing inactive elements. Some support is lent to this view by the fact that the atomic weight of radium emanation (deduced from diffusion experiments) appears to be about 172, so that it would fit into the vacant space below neon. The most recent experiments, however, indicate that the atomic weight of the emanation may be over 200, which would bring it into the same horizontal period as radium, thorium, and uranium. Nothing very definite is known as to the respective atomic weights of the thorium and actinium emanations.

G. S.

Heavy Constituents of the Atmosphere. RICHARD B. MOORE (*Proc. Roy. Soc.*, 1908, 81, A, 195—209).—The heavy gases from about 120 tons of liquid air have been examined for the presence of gases heavier than xenon, with negative results.

In the first experiment, the heavy residues from 19 tons of liquid air were condensed in liquid oxygen. After most of the oxygen had evaporated, the remainder was removed by means of melted phosphorus, and the nitrogen and other impurities were also removed by means of the appropriate reagents. The residue (about 6 litres of inactive gas) was then fractionated, but the final fraction was not heavier than xenon, and the spectrum afforded no evidence of the presence of a new gas. The water with which the gas had been in contact was boiled, and the gas given off added to the main bulk before fractionation.

In a second experiment, the residues from 100 tons of liquid air were worked up by a modified method, in which the gases did not come into contact with much water, but the results were negative in this case also. The methods of fractionation employed are fully described.

The magnesium and lime used to extract the nitrogen were examined to detect possible reaction products, with negative results.

G. S.

New Reaction for the Production of Sodium Carbonate. D. CRISPO (*Bull. Soc. chim. Belg.*, 1908, 22, 292—295).—The author finds that, contrary to previous statements, sodium carbonate can be rapidly and easily prepared by the interaction, under suitable conditions, of calcium carbonate and sodium silicate. A syrup of

sodium metasilicate is heated with chalk, the mass is then dried at a moderate temperature, and lixiviated with water to remove the sodium carbonate. The polysilicate, $3\text{SiO}_2 \cdot \text{Na}_2\text{O}$, does not react with calcium carbonate.

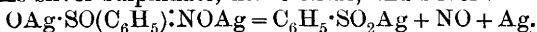
Details are given of an industrial process for preparing the metasilicate from sodium sulphate by heating this salt with charcoal and sand. W. O. W.

The Reciprocal Salt Pair $\text{NaCl-K}_2\text{SO}_4$; $\text{KCl-Na}_2\text{SO}_4$. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1908, 64, 343—356. Compare this vol., ii, 808).—The freezing-point and transformation curves of the four binary systems concerned confirm earlier results ($\text{KCl-K}_2\text{SO}_4$ and $\text{NaCl-Na}_2\text{SO}_4$, Ruff and Plato, *Abstr.*, 1903, ii, 588; NaCl-KCl , Kurnakoff and Schemtschuschny, *Abstr.*, 1906, ii, 443; $\text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$, Nacken, *Abstr.*, 1907, ii, 611). The formation of a compound of sodium and potassium sulphates in the solid state, assumed by Nacken, is not confirmed.

The results are recorded in a space model, the base of which is a square representing the proportions of the four salts present, and the ordinates are the temperatures of solidification. Two classes of mixed crystals are formed, and a minimum freezing point is found at the composition $(\text{Na}_2)_{43}(\text{K}_2)_{57}(\text{Cl}_2)_{46}(\text{SO}_4)_{54}$. C. H. D.

The Silver Hydrogel in Photographic Films. LÜPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 33—36).—Silver nitrate is reduced by pyrogallol and sodium carbonate to a black, finely-divided silver, which is quickly bleached by mercuric chloride, whereas pyrogallol alone gives a light-coloured, coarse-grained precipitate, to which mercuric chloride gives a dark colour. The author has tried many other reducing agents. In general, reduction in presence of a solvent of the silver salts, such as sodium sulphite, thiosulphate, or thiocyanate, or ammonia, tends to give the light-coloured silver, whilst any circumstance which tends to prevent the coalescence of the reduced silver, for example, reduction of an insoluble silver salt or enclosure of the salt in a gelatin film, yields the dark-coloured modification. The silver hydrogel of the photographic film is the dark-coloured form. Collodion does not hinder the coalescence of the silver particles to nearly the same extent as gelatin. T. E.

Decomposition of Certain Salts of Silver. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 695—697).—Whereas the sodium salt of nitrohydroxylamic acid decomposes into sodium nitrite and hyponitrite, thus: $2\text{NaON}:\text{NO}_2\text{Na} = \text{NaO} \cdot \text{N}:\text{N} \cdot \text{ONa} + 2\text{NaNO}_2$, the silver salt gives silver nitrite, nitric oxide, and silver according to the equation: $\text{AgON}:\text{NO}_2\text{Ag} = \text{NO}_2\text{Ag} + \text{NO} + \text{Ag}$. It is possible that the group NOAg is first eliminated and then decomposed; this view is strengthened by the fact that benzene-sulphydroxamic acid, which is decomposed by alkalis into benzene-sulphinic acid and a hyponitrite, gives an unstable silver salt, which readily forms silver sulphinate, nitric oxide, and silver:



Pernitrosocamphor gives a yellow silver derivative, which soon blackens, owing to the formation of silver and a substance, $C_{10}H_{15}O_2N_2$, which melts at 168° ; the change occurring is: $2C_{10}H_{15}O_2N_2Ag = 2C_{10}H_{15}O_2N_2 + Ag_2$.
W. A. D.

Crystallisation of the Alkaline-earth Oxides, especially of Calcium Oxide, from their Nitrates. GOTTFRIED BRÜGELMANN (*Zeitsch. anorg. Chem.*, 1908, 59, 248—270).—When the carefully-purified nitrates of calcium, strontium, and barium are heated to the temperature of decomposition, the corresponding oxides separate out in the form of regular cubes. Calcium and strontium oxides yield well-developed macroscopic crystals. The formation of the calcium oxide crystals is greatly facilitated by the addition of 0.25% to 0.6% of calcium hydroxide to the molten nitrate.

The author's very numerous experiments lead to the conclusion that the usual precautions adopted for the production of well-developed crystals (the use of large quantities of material, slow cooling, and freedom from mechanical disturbance) are not the only important factors of importance. A study of the crystallo-genetic peculiarities is essential.
H. M. D.

Relation of Changes of Solubility of Calcium Sulphate and its Rate of Hydration. PAUL ROHLAND (*Zeitsch. Elektrochem.*, 1908, 14, 421—422).—The effect of twenty-two substances on the rate of hydration of gypsum is tried. Those which increase the solubility of the gypsum in water, also increase its rate of hydration, and vice versa. The same substance may have opposite effects, for example, gypsum is less soluble in dilute solutions of sodium, ammonium, and magnesium sulphates than it is in water, whereas it is more soluble in strong solutions. Hydration is retarded by dilute solutions, and accelerated by strong ones.
T. E.

Preparation of Colloidal Amorphous Forms of Crystalline and Soluble Salts of the Alkaline-earth Metals. P. P. von WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 89—91).—Gelatinous precipitates are obtained in general by rapid separation of a substance from a solution in which it is very sparingly soluble. High viscosity of the solvent is also favourable. The thiocyanate of an alkali or alkaline-earth metal is dissolved in a mixture of amyl alcohol and ether, and mixed with a similar solution of an acid. In this way the following salts have been obtained in the gelatinous form: potassium, sodium, ammonium, calcium, strontium, and barium chlorides, bromides, and nitrates, and the sulphates of potassium, sodium, and ammonium. The sulphates and phosphates of the alkaline-earth metals are obtained in the gelatinous form from solutions in any of the lower aliphatic alcohols.
T. E.

Isomorphism of Calcium and Manganese Bisilicates. A. S. GINSBERG (*Zeitsch. anorg. Chem.*, 1908, 59, 346—363).—A freezing-point curve for the system wollastonite-rhodonite has been obtained by observations on mixtures containing different proportions

of the two silicates. Calcium silicate melts at 1512° ; manganese silicate at 1218° . The temperatures corresponding with the commencement of crystallisation and with complete solidification are given for a series of mixtures. The minimum temperature of 1180° corresponds with a mixture containing 12.8 molecular % of calcium silicate.

From the nature of the freezing-point diagram, the conclusion is drawn that the two silicates form a complete series of mixed crystals, and that wollastonite and rodonite are isomorphous. Since rhodonite is triclinic, the existence of a polymorphic, monoclinic modification must be assumed in order to explain the formation of the monoclinic series of mixed crystals, with which the mineral bustamite is to be identified.

Measurements of the density and hardness of mixtures containing various proportions of the two silicates have been made, which show that these properties vary continuously with the composition. The curve representing the hardness as a function of the composition exhibits a maximum for a mixture containing 15% manganese silicate. The density of wollastonite is 2.919, and that of rhodonite 3.350.

H. M. D.

Action of Soluble on Insoluble Substances. WILLIAM OECHSNER DE CONINCK and L. ARZALIER (*Bull. Acad. roy. Belg.*, 1908, 577—578. Compare *Abstr.*, 1907, ii, 952).—When barium sulphate (1 mol.) is heated at 100° for 620 hours with methylamine hydrochloride (2 mols.) in aqueous solution, a partial double decomposition ensues. A similar result was also obtained in the case of barium sulphate (1 mol.) and an aqueous solution of potassium chloride (2 mols.) at the end of five months, heated at 90 — 95° during two-fifths of the period.

M. A. W.

Action of Soluble on Insoluble Substances. WILLIAM OECHSNER DE CONINCK and L. ARZALIER (*Bull. Acad. roy. Belg.*, 1908, 607—608).—Pure strontium carbonate, shaken with a concentrated solution of potassium chloride gives, in four months, a solution containing strontium chloride.

E. H.

Microscopic Study of Mortar. GINO GALLO (*Gazzetta*, 1908, 38, ii, 142—156. Compare *Stern*, this vol., ii, 589).—Microscopic study of the changes occurring in a mortar shows that the absorption of carbon dioxide by the calcium hydroxide present is intimately related to the presence of water, and, since the calcium carbonate formed is distinctly crystalline, it is concluded that both the lime and the carbon dioxide must be in solution before the reaction takes place. A mortar prepared with a deficit of water lacks solidity and has low resisting properties, owing to the fact that the calcium carbonate formed under these conditions forms a coarse net-work; similar defects are observable in mortar made with coarse sand, the calcium carbonate deposited in the large interstices not adhering to all the neighbouring sand granules.

The injurious effect exercised by the presence of magnesia in a mortar is explained by the slight solubility of the magnesia in the

water present and by the slow absorption of carbon dioxide by the solution formed.

When the water is completely eliminated from a mortar, chemical action ceases, and in the interior of old mortars in which the carbon dioxide could not reach the lime before the water evaporated completely, free lime is found. T. H. P.

Microscopic Study of Mortar and Pozzuolana. GINO GALLO (*Gazzetta*, 1908, 38, ii, 156—204).—The author reviews briefly previous work on pozzuolana and its value as a hydraulic mortar. His own experiments on the setting of mortars prepared from pozzuolana were made with the microscope (see preceding abstract).

All the mortars examined exhibited a distinctly crystalline border of calcite, which forms immediately the mortar is made, and has a thickness of about 0.1 mm.; when good pozzuolana is employed, the thickness of this layer does not change appreciably. This calcitic coating prevents water from finding ready access to the interior of the mortar, and so hinders the solution and removal of the lime.

The first phenomenon observable in the setting of these mortars is the hydration, by means of the lime water, of the silica and alumina, which swell so as to fill the whole space previously occupied by air and water, and yield an impermeable mass bestowing resistance on the mortar. Then follows the formation of soluble calcium aluminate, which, in presence of excess of lime and in supersaturated solution, deposits crystals of the calcium aluminate, $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 10\text{H}_2\text{O}$, which is stable only in presence of calcium hydroxide solution, and is decomposed by water; this crystallisation binds together the various particles which exist as inclusions in the crystals. The limiting surfaces between the flocculent portions and the spaces left by these then become the seat of capillary forces, by means of which the silica attracts the lime into its pores and thus forms nodules in which the lime gradually gives up its water of hydration and crystallises as calcium monohydrate, thus determining complete adhesion of the various parts. The more rapidly the swelling attains its maximum and the greater the latter, the more satisfactory will be the setting of the mortar.

The increases in volume of various specimens of pozzuolana in presence of calcium hydroxide solution have been measured. It is found that this increase is related directly to the amount of lime absorbed, and that it is considerably increased by renewing the calcium hydroxide solution from time to time. The action of calcium hydroxide also causes an increase in the amounts of alumina and silica which can be dissolved by dilute acid.

The value of a pozzuolana for the preparation of hydraulic mortar may be determined by the following measurements: (1) Increase of volume with calcium hydroxide solution. (2) Electrical conductivity (compare Giorgis and Gallo, *Abstr.*, 1906, ii, 447). (3) Amounts of silica and alumina dissolved by treating with 5% sodium hydroxide solution on the water-bath for fifteen minutes. For good pozzuolana, these amounts are almost constant, even where the material has

been previously treated with dilute acid; but for inferior materials, such as ashes from Vesuvius and Bassano, previous disgregation with hydrochloric acid renders increasing amounts of silica and alumina capable of solution in 5% sodium hydroxide solution. T. H. P.

Liquefaction and Sublimation of Certain Sulphides. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1908, 59, 273—284).—The sulphides, contained in porcelain or magnesia tubes through which a current of dry nitrogen was passed, were heated by means of an electrical resistance furnace. The sublimation or liquefaction was observed by means of a telescope, the temperature being registered by a thermo-element or a Wanner pyrometer. The following melting points are recorded: synthetic lead sulphide, 1100° , sublimation commencing at 950° ; galena from Freiberg, $1112^\circ \pm 2^\circ$; ferrous sulphide, $1197^\circ \pm 2^\circ$; nickel sulphide, $797^\circ \pm 2^\circ$; cobalt sulphide, $>1100^\circ$. Zinc, cadmium, and mercuric sulphides sublime without melting. The temperatures at which sublimation begins are as follows: zinc blende from Santander, $1178^\circ \pm 2^\circ$; synthetic zinc sulphide in the form of wurtzite, $1185^\circ \pm 6^\circ$; cadmium sulphide, 980° ; cinnabar and precipitated mercuric sulphide, $446^\circ \pm 10^\circ$.

Stannous sulphide exhibits two melting points. Its behaviour was traced by a study of cooling and heating curves. The lower melting point is about 870° , and, as the temperature is raised from 1000° to 1100° , the viscosity of the liquid increases very quickly, so that at the latter temperature the substance exhibits the properties of a solid. At about 1200° , liquefaction again takes place. The phenomenon has not yet been explained. H. M. D.

Compounds of Lead with Nitrous Acid. ALBERTO CHILESOTTI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 824—834).—The author gives a résumé of the various lead nitrites which have been described, many of which are probably not individual compounds.

By mixing equivalent proportions of solutions of lead chloride and silver nitrite saturated at 25° and concentrating the liquid, first by freezing and then by evaporation over sulphuric acid, he has obtained the hydrate, $\text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$; (compare Lang, *J. pr. Chem.*, 1862, 86, 300), and the anhydrous salt, $\text{Pb}(\text{NO}_2)_2$, mixed with a little lead oxide and lead nitrate. The electrical conductivity of lead nitrite solutions at 25° is as follows:

$v = 16$	32	64	128	256	512	1024
$\Lambda = 59.4$	72.3	85.5	98.9	111.3	122.1	129.7

For the more concentrated solutions, the conductivity of the nitrite is somewhat less than that of the nitrate or chloride, but at greater dilutions the differences are small. The value of $\Lambda_{1024} - \Lambda_{32}$ is 27.6 for the nitrate, 42.1 for the chloride, and 57.4 for the nitrite. It is probable, from their conductivity and from their intense yellow colour, that solutions of lead nitrite contain complex anions of the type $\text{Ag}(\text{NO}_2)_2'$ or $\text{Hg}(\text{NO}_2)_4''$ (compare Abegg and Pick, *Abstr.*, 1906, ii, 833). T. H. P.

Planimetric Analysis of Alloys and the Structure of Phosphor Copper. ALFRED K. HUNTINGTON and CECIL H. DESCH (*Trans. Faraday Soc.*, 1908, 4, 51—58).—The method depends on the measurement, by means of a planimeter, of the relative areas occupied by the different constituents on a polished and etched section of an alloy. It is applicable to alloys for which two solid constituents are visible in the same section, and often also when crystals of a solid constituent are surrounded by a eutectic, but is only to be employed when the alloys are in a known state of equilibrium.

In making an observation, the highly magnified image of the section is projected on a sheet of paper, the outlines of one of the constituents traced with a pencil, and the crystals shaded. A boundary line is drawn to enclose the pattern to be measured, and the shaded area measured with the planimeter. The agreement of planimetric and ordinary analysis for the alloys of copper and aluminium is excellent. The chief recommendation of the method is its rapidity.

When the pattern is very complicated, or made up of many small and detached portions, better results are obtained by dividing the field into squares, estimating the relative shaded areas, and averaging.

Heyn and Bauer, who have investigated the phosphor-copper alloys (Abstr., 1906, ii, 855), observed that the copper areas determined planimetrically were larger than calculation from the composition would indicate. The alloys in question (up to 8% phosphorus) consist mainly of copper crystals and a eutectic copper—copper phosphide, and it is now shown that the difference is due to the fact that the crystals of copper gradually increase in size after solidification by withdrawing copper from the eutectic surrounding them, so that each crystal is surrounded by a clear belt free from copper. The areas of these belts have been determined, and when a corresponding correction is applied to the areas of the copper crystals, the results of the planimetric and direct analysis show excellent agreement.

The paper is illustrated with photomicrographs.

G. S.

Constitution of the Copper-Zinc-Nickel Alloys, and of the Binary Systems Copper-Nickel, Copper-Zinc, and Nickel-Zinc. VICTOR E. TAFEL (*Metallurgie*, 1908, 5, 343—352, 375—383, 413—430).—The study of the copper-nickel equilibrium diagram completely confirms the results of Guertler and Tammann (Abstr., 1907, ii, 174). The results obtained for the copper-zinc series differ somewhat from those of Shepherd (Abstr., 1904, ii, 662). The existence of the compound Cu_2Zn_3 (m. p. 830°) is established, and that of the compound Cu_2Zn , indicated by other methods, is quite consistent with the thermal diagram. The compounds CuZn_6 , CuZn_4 , CuZn_3 , CuZn_2 , and CuZn , described by various authors, certainly do not exist. The alloys, especially in the neighbourhood of 50% Zn, have considerable tendency to liquate.

The nickel-zinc alloys (this vol., ii, 105; compare Voss, *ibid.*, ii, 197) have been more fully investigated. The only compound recognised is NiZn_3 , a highly brittle substance giving a characteristic coloration with dilute nitric acid. Owing to loss of zinc by volatilisa-

tion, it was found necessary to complete the diagram above 50% Ni by extrapolation from the ternary model.

Alloys of copper, nickel, and zinc liquate considerably, the lower portions of the ingots becoming generally richer in nickel. The thermal diagram, constructed as a projection on a triangular base, represents determinations of 92 different alloys. Neither a ternary compound nor a ternary eutectic point was found. The surface of the temperature-concentration model consists of three surfaces, each representing the separation of a series of primary mixed crystals. The third of these, the richest in zinc, is separated from the second by a eutectic line. The observations have also been plotted in the form of vertical sections through the model, the complicated changes taking place in the solid alloys being also represented in this way.

The alloys of technical importance, such as German silver, consist of homogeneous mixed crystals. Alloys containing 15.3–20% Ni, 73–80% Cu, and 7% Zn have a remarkable resemblance to silver, both in their colour when polished and in ductility.

The structure of the alloys, and the transformations undergone during cooling, are illustrated by fifty photomicrographs.

C. H. D.

Cuprous Ammonia Halides. STEWART J. LLOYD (*J. Physical Chem.*, 1908, 12, 398–403).—Evidence of the existence of various cuprous ammonia halides was obtained by saturating the cuprous halides at 0° with dry ammonia, and measuring the vapour pressure at a constant temperature as the ammonia was gradually removed. The curves, obtained by plotting vapour pressures against the ammonia content of the halides, show discontinuities in the vapour pressure corresponding with the following compounds, of which the colour and the approximate melting point are recorded: $\text{Cu}_2\text{I}_2 \cdot 6\text{NH}_3$, light green, 105°; $\text{Cu}_2\text{I}_2 \cdot 3\text{NH}_3$, dark brown, 117°; $\text{Cu}_2\text{Br}_2 \cdot 6\text{NH}_3$, green, 115°; $\text{Cu}_2\text{Br}_2 \cdot 3\text{NH}_3$, brown, 135°; $\text{Cu}_2\text{Cl}_2 \cdot 6\text{NH}_3$, green, 123°; $\text{Cu}_2\text{Cl}_2 \cdot 3\text{NH}_3$, light brown, 144°; $\text{Cu}_2\text{Cl}_2 \cdot \text{NH}_3$, dark brown, 162°. Tables are given which show the vapour pressures of the seven compounds at a series of different temperatures.

H. M. D.

Dissociation Pressures of Certain Oxides of Copper, Cobalt, Nickel, and Antimony. HARRY W. FOOTE and E. K. SMITH (*J. Amer. Chem. Soc.*, 1908, 30, 1344–1350).—The dissociation pressures of cupric oxide, cuprous oxide, cobalto-cobaltic oxide, cobaltous oxide, nickelous oxide, and antimony tetroxide have been measured at temperatures between 800° and 1245°. When possible, the temperature has been determined at which the dissociation pressure equals the pressure of the oxygen in the air. Cupric oxide gives this pressure at about 1025°, cobalto-cobaltic oxide at about 905°, and antimony tetroxide at about 950°. The dissociation pressure of cuprous oxide does not exceed 1 mm. at 1020°. Pure cobaltous oxide does not show a dissociation pressure at 1100°.

The dissociation pressures of cupric oxide and nickelous oxide calculated by Stahl (*Metallurgie*, 1907, 4, 682) from Nernst's formula are much lower than those now obtained by direct measurement.

E. G.

Reduction of Fehling's Solution to Metallic Copper. Deposition of Copper Mirrors on Glass. PUNCHANAN NEOGI (*Zeitsch. anorg. Chem.*, 1908, 59, 213—215).—To obtain a mirror by reduction of Fehling's solution, the copper sulphate solution is poured into a beaker, the tartrate solution added until the precipitate at first formed just disappears, a considerable amount of formaldehyde is then added, the beaker inclined, and heated on one side until the deposition of copper just begins. On rotating the beaker, a mirror forms all over the inner surface. One of the precipitates thus produced contained 98.6% of copper. G. S.

Oxidation by means of Cuprous Oxide in Strongly Alkaline Solution. RICHARD EHRENFELD (*Zeitsch. anorg. Chem.*, 1908, 59, 161—182).—An attempt was made to estimate cupric salts volumetrically by reducing them completely to the cuprous form by the action of an arsenite in strongly alkaline solution, the excess of arsenite being determined by titration with iodine, but the results came out about 6% too high. This result is due to the simultaneous oxidation of part of the arsenite by the oxygen of the air under the catalytic influence of cuprous oxide.

In the absence of a reducing agent, cuprous oxide in the presence of strong alkali undergoes autoxidation, and more than the theoretical amount of oxygen required for the formation of cupric oxide is absorbed. It is probable that the excess of oxygen goes to the formation of hydrogen peroxide, which is, however, immediately used up in oxidising more cuprous oxide. Autoxidation of cuprous oxide also takes place in the presence of concentrated sulphuric acid, excess of oxygen being absorbed and hydrogen peroxide formed.

Strongly alkaline solutions of antimony trichloride behave exactly like arsenite solutions, and the oxidation of alkaline sodium sulphite and stannous chloride solutions is also accelerated by cuprous oxide. In the latter case, however, only the theoretical volume of oxygen is absorbed. On the other hand, cuprous oxide does not accelerate the oxidation of chromic sulphate, potassium nitrite, potassium phosphite, or potassium hypophosphite in alkaline solution. Potassium phosphite and hypophosphite and sodium sulphite are more readily acted on by the oxygen of the air in aqueous than in strongly alkaline solution.

G. S.

Solubility of Precipitated Basic Copper Carbonate in Solutions of Carbon Dioxide. E. E. FREE (*J. Amer. Chem. Soc.*, 1908, 30, 1366—1374).—In connexion with a study of the effect of mine detritus in irrigation waters, it was found necessary to ascertain the solubility of precipitated basic copper carbonate in water containing varying amounts of carbon dioxide, and the influence of certain salts on it. The precipitate obtained on mixing solutions of copper sulphate and sodium carbonate is at first pale bluish-green, but gradually loses carbon dioxide and becomes of a malachite-green colour. The latter product is regarded by Gröger (*Abstr.*, 1900, ii, 542) as the compound $6\text{CuO}, 3\text{CO}_2, 4\text{H}_2\text{O}$. It has now been found that the substance is of variable composition, and is so changed by the

action of carbon dioxide and water that it gradually becomes less soluble in the carbon dioxide solution. On repeatedly treating such precipitates with solution of carbon dioxide of 0.12% strength, they finally reach a constant solubility of about thirty-five parts per million, but the solubility increases with the concentration of the carbon dioxide. The solubilities are but little changed by the addition of small quantities of sodium chloride or sulphate, but are increased by larger amounts of these salts. Sodium and calcium carbonates decrease the solubility greatly, but calcium sulphate does not cause a decided change in either direction.

E. G.

Resolution of Ytterbium into its Components. GEORGES URBAIN (*Chem. Zeit.*, 1908, 32, 730).—The author disputes Welsbach's claim for priority, and states that the decomposition products, neoytterbium and lutetium, which he obtained (*Abstr.*, 1907, ii, 956) are identical with those of Welsbach, called by him aldebaranium and cassiopeium (this vol., ii, 591).

J. V. E.

Interaction of Aluminium Powder and Carbon. FRANK E. WESTON and H. RUSSELL ELLIS (*Trans. Faraday Soc.*, 1908, 4, 60—71. Compare Fichter, *Abstr.*, 1907, ii, 691).—The interaction of finely-powdered aluminium and finely-powdered wood-charcoal, sugar-charcoal, and graphite has been investigated. In all cases, mixtures could be prepared which, when started with a fuse of magnesium and barium peroxide, reacted with vivid incandescence, like the ordinary thermit reaction. Some mixtures, when raised to a dull red heat in a closed crucible, reacted vigorously on exposure to the air.

In all cases the reaction product contained aluminium carbide, nitride, and oxide, as well as the free elements. As the only hydrocarbon obtained by the action of water or hydrochloric acid on the product is methane, it is probable that the only carbide formed is Al_4C_3 .

The authors consider that the air plays a prominent part in the phenomenon, that the first action is the oxidation of the carbon to monoxide and dioxide, the heat given out starts the oxidation of the aluminium, and, finally, the latter reaction raises the temperature sufficiently to bring about combination of the aluminium with carbon and nitrogen. Among other reasons in support of this view, it was found that, when the air was withdrawn from the mixtures by means of a Töpler pump, it was much less easy to initiate combination.

G. S.

Corrosion of Iron by Water and Water Solutions. E. HEYN and O. BAUER (*Chem. Zentr.*, 1908, i, 2063—2065; from *Mitt. K. Mat.-prüf.-Amt, Gross-Lichterfelde*, 1907, 26, 1—104. Compare Friend, this vol., ii, 698).—A. *Influence of Oxygen and Carbon Dioxide on the Corrosion of Iron by Water and by Water Solutions.*—The rusting was estimated by allowing small, weighed wrought-iron plates to rust when suspended in Charlottenburg conductivity water, or aqueous solutions contained

in a glass beaker, and re-weighing them after removing the rust. Air was allowed free access to the iron and water; in some cases, it was drawn through the liquid, and the temperature was that of the ordinary room. The results obtained support the conclusions of Traube (Abstr., 1885, 1105) and Dunstan (Trans., 1905, 87, 1548), that carbon dioxide is not needful, but the presence of free oxygen is a necessary condition for the process of rusting; also, that the iron does not derive oxygen from the water, but from the atmosphere. After discussing the conditions that influence the rate of rusting, the authors cite some experiments which show that the addition of hydrogen peroxide does not increase the rate of rusting so much as does drawing air through the liquid in which the iron is suspended.

B. Rusting Influenced by the Iron being in Contact with other Metals.—Copper when in contact with the iron is found to increase the rusting 25% when suspended in conductivity water and 47% in artificially-prepared sea-water. In contact with nickel, iron rusts 14—19% more than it does by itself, and ingot-iron in contact with cast-iron rusts less readily than when by itself, whilst the cast-iron rusts more readily by about 50%. It is found that iron in contact with a more positive metal, suspended in a liquid causing rusting, rusts less readily, and when in contact with a more negative metal, rusting takes place more readily than when iron is exposed under similar conditions by itself.

C. Comparison of the Rusting of Various Kinds of Iron by Water.—The results show that a content of 0.46 to 3.08% of manganese and 0.072 to 3.38% of phosphorus has very little influence on the rate of rusting.

D. Influence of Various Liquids on the Rusting of Iron at the Ordinary Temperature.—It is found that very dilute solutions of simple electrolytes generally cause iron to rust more slowly than does distilled water alone; with increase of concentration, however, the rusting increases, reaching a maximum and then decreasing slowly. The solutions showing maximum activity are called "critical solutions," and generally cause iron to rust more readily than distilled water. Exceptions to this, however, are solutions of potassium chloride, sodium chloride, potassium sulphate, sodium hydrogen carbonate, sodium sulphate, calcium chloride, and barium chloride, the activity of which is less than that of distilled water. Ammonium nitrate solution and a saturated solution of diammonium hydrogen phosphate cause iron to rust, probably owing to their decomposition, and thus appear to contradict the previous conclusion *A*; the behaviour of the "critical solution" of diammonium hydrogen phosphate is also abnormal.

In the case of certain salt solutions when the concentration is increased beyond the "critical concentration," the rusting is very rapidly decreased, until a concentration is reached where no rusting takes place; such solutions are called "limiting solutions." Diammonium hydrogen phosphate again behaves in a distinctive manner, having a second limiting concentration, and, finally, in still more concentrated solutions, iron is dissolved with liberation of a gas.

E. Electrical Potential between Iron and Various Liquids.—This section not being suitable for abstraction, the original should be consulted.

J. V. E.

Alloys of Iron, Silicon, and Carbon. W. GONTERMANN (*Zeitsch. anorg. Chem.*, 1908, 59, 373—413).—The investigation covers that portion of the iron-carbon-silicon system which includes the components $\text{Fe-Fe}_3\text{C-FeSi}$. Pure iron-carbon alloys were fused with silicon in porcelain tubes in an atmosphere of purified nitrogen. Repeated melting was sometimes necessary to ensure homogeneity.

Iron containing only 0.7% carbon exhibits a transformation point at 1411° , which appears on both the heating and cooling curves, and does not disappear on re-heating, but is absent from alloys containing even a slightly larger proportion of carbon. Owing to undercooling, alloys containing 3—4% C may contain both structurally-free martensite and cementite. A hypothetical equilibrium curve is suggested for the iron-carbon alloys, assuming the existence of two immiscible liquid phases above 3—4% C, one of which readily sets free graphite. The behaviour of white and grey cast-irons may be explained on this assumption. The transformation observed at 800° may be the eutectoid point of β -iron and graphite. Slight modifications are also suggested in the iron-silicon diagram (compare Guertler and Tammann, *Abstr.*, 1906, ii, 32).

The ternary equilibrium is represented by projections on the base of the space-model. The freezing points lie on two surfaces, on one of which an Fe-C-Si solid solution separates (silicon-martensite), and on the other an $\text{Fe}_3\text{C-FeSi}$ solid solution (silicon-cementite), the two intersecting along a eutectic line. At lower temperatures, the stable system consists of silicon-ferrite and graphite, but the reaction is slow and the development of heat very small, so that the exact position of the curve of separation of graphite could not be determined. The only part of the metastable system which could be satisfactorily followed was the eutectoid line between silicon-ferrite and silicon-cementite (silicon-pearlite). Alloys consisting of unsaturated silicon-martensite undergo the metastable change on cooling under the conditions adopted, whilst saturated silicon-martensite, or a mixture of this with silicon-cementite, sets free graphite (stable change) if the silicon-content exceeds 1%. Silicon-cementite containing more than 20% Si does not undergo transformation in the solid state.

C. H. D.

The Thomas Steel Process. F. WUST and L. LAVAL (*Metallurgie*, 1908, 5, 431—462, 471—489).—The relative rate of oxidation of the various elements present in pig-iron during the Thomas basic steel process has been studied experimentally. From 8 to 10% of iron is lost during oxidation, mostly during the last stage of the process, when the last traces of phosphorus are being removed. This increases with rise of temperature, the tendency of iron to oxidise increasing more rapidly with temperature than that of phosphorus. The conditions are not altered by drying or heating the air supply. Curves are given showing the change in composition of metal and slag during the process.

The changes in structure of the alloys are illustrated by photomicrographs. The original phosphoretic iron contains crystals of cementite and martensite and a ternary cementite-martensite-phosphide

eutectic, as well as well-formed crystals of sulphide. With progressive elimination of carbon, the ternary eutectic is replaced by a binary martensite-phosphide eutectic. C. H. D.

Dissociation Pressures of Ferric Oxide. PERCY T. WALDEN (*J. Amer. Chem. Soc.*, 1908, 30, 1350—1355).—Determinations of the dissociation pressures of ferric oxide have been made at temperatures between 1100° and 1400°. At 1350°, the pressure is approximately equal to that of the oxygen in the air. Ferrosoferric oxide does not show any dissociation pressure at 1350°.

By heating cuprous oxide with ferric oxide, Stahl (*Metallurgie*, 1907, 4, 688) obtained a strongly magnetic product, and concluded that the following reaction had occurred: $\text{Cu}_2\text{O} + 3\text{Fe}_2\text{O}_3 = 2\text{CuO} + 2\text{Fe}_3\text{O}_4$. It is now shown that this magnetic substance was probably the compound CuFe_2O_4 described by List (*Abstr.*, 1879, 13). It is probable that there is another magnetic double oxide of iron and copper which has not yet been described, and work on this and similar substances is in progress. E. G.

Ferrinitrososulphides. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1908, [v], 720—724).—A theoretical paper in which facts already abstracted (*Abstr.*, 1907, ii, 960; this vol., ii, 41, 288) are discussed at length with particular reference to the views of Bellucci and Cesaris (*Abstr.*, 1907, ii, 29, 472; this vol., ii, 111, 499, 593).

W. A. D.

Gases Occluded in a Special Nickel Steel. G. BELLOC (*Compt. rend.*, 1908, 147, 244—245. Compare this vol., ii, 108).—The proportion and nature of the gases occluded by a nickel steel containing about 45% of nickel and 0.15% of carbon have been determined by the method described previously. The occluded gases consist of carbon monoxide and dioxide, hydrogen, and nitrogen, the first being completely evolved below 520°, whilst the last only commences to be evolved above this temperature. Different results are obtained according as the steel is in the form of wire or shavings. In the latter case, the total gas evolved is 3.5 times the volume of the alloy; the curve obtained by plotting the variation of the volume of the gas evolved with the temperature (dv/dt) against the temperature (t) is sensibly parallel to the temperature axis, and the proportion of carbon monoxide increases up to 75%, whilst the maximum amount of hydrogen is evolved at 540°, above which the volume of hydrogen produced gradually decreases. With the wire the total volume of gas evolved is ten times that of the metal; the curve (in t , dv/dt) exhibits well-defined maxima at 540° and 830°, and the variations in composition of the gas are no longer gradual; thus at 540° a minimum proportion of carbon monoxide and a maximum of hydrogen are observed, whilst above this temperature the carbon monoxide increases somewhat irregularly. The mean proportion of hydrogen is greater than from the shavings.

This alloy belongs to the type termed by Guillaume "reversible," the limits of its gradual transformation being 350° and 400°. The greater part of the gases is evolved while the iron is in the γ -state and

the nickel in the β -state, from which would be expected a gradual alteration in the composition and volume of the gas evolved. The latter is the case with shavings, and the different behaviour of the wire indicates an alteration in its molecular state. The difference in absolute volumes of the gas evolved from shavings and from wire can be explained either by (1) unequal distribution in the ingot, or (2) large mechanical loss of occluded gas in turning, or (3) absorption of gas during the manufacture of the wire. E. H.

Action of Arsenic Chloride and Arsenic on Cobalt. F. DUCELLIEZ (*Compt. rend.*, 1908, 147, 424—426).—By the action of arsenic chloride, metallic cobalt is transformed into a mixture of chloride and arsenide, the composition of the latter ranging from CoAs_2 to Co_3As_2 according as the temperature of the reaction is increased. When mixtures of arsenic chloride with cobalt or alloys of arsenic and cobalt, or mixtures of arsenic and cobalt (both components being powdered), are heated in an inert atmosphere (hydrogen or carbon monoxide), or when powdered cobalt is heated in a current of hydrogen containing arsenic vapour, the following results are obtained. Between 800° and 1400° , *tricobaltdiarsenide*, Co_3As_2 , is formed, and above 1000° is obtained as brilliant ingots, $D^{20} 7.82$, which lose arsenic about 1400° . From 600° to 800° , cobalt or the arsenide, Co_3As_2 , is converted into *cobalt arsenide*, CoAs , a grey, crystalline powder, $D^{20} 7.62$, which tarnishes slightly in the air, and when heated in a current of hydrogen commences to lose arsenic at 800° without melting. At 400 — 600° , the final product contains 65.6% of arsenic corresponding with the composition Co_2As_3 ; it has $D^{20} 7.35$, and commences to decompose at 600° . Below 400° , the preceding compound is slowly transformed into smaltine, CoAs_2 , which is not directly obtained at these temperatures by the action of arsenic trichloride on cobalt. The product is a grey powder, $D^{20} 6.97$, oxidised by the air, and decomposed slightly above 400° . In the experiments above 600° , a little arsenic is set free, the amount increasing with the temperature. In the first two series of experiments, after the arsenide is formed, continued action of arsenic chloride results in the formation of cobalt chloride and liberation of arsenic, the weight of the compound diminishing. In the last two cases, arsenic is not deposited or cobalt chloride formed after the production of Co_2As_3 or CoAs_2 .

The compound Co_3As_2 can also be prepared by reducing cobalt arsenate or arsenite with hydrogen at 900° ; the heat developed, volatilising part of the arsenic, prevents the formation of cobalt arsenide, CoAs .

The arsenides described are non-magnetic, and their densities are much higher than those found by calculation for mixtures. They are violently attacked by chlorine, oxygen, and sulphur, readily dissolved by nitric acid and aqua regia, and slowly attacked by fused alkalis and alkali carbonates, but hot concentrated hydrochloric acid has very little action, and sulphuric acid still less. E. H.

Alloys of Cobalt with Tin, Antimony, Lead, Bismuth, Thallium, Zinc, Chromium, and Silicon. KURT LEWKONJA (*Zeitsch. anorg. Chem.*, 1908, 59, 293—345).—Freezing-point curves

of mixtures of the metals have been obtained and the micro-structure of the solidified products examined.

Cobalt and tin are miscible in all proportions in the liquid condition. The compounds Co_3Sn , m. p. 1151° , and CoSn , which melts with decomposition at 943° and undergoes a polymorphic change at 526° , are formed. In the solid condition, the maximum amount of tin dissolved by cobalt is 3.5%.

Cobalt and antimony are completely miscible in the liquid state. The compounds CoSb , m. p. 1191° , and CoSb_3 , which melts with decomposition at 879.5° , are formed. In the solid state, antimony is soluble to the extent of 12.5% in cobalt.

Cobalt and lead are partly miscible in the liquid state; molten alloys containing more than 3% or less than 99% of cobalt cannot be obtained. Neither compounds nor mixed crystals are formed in the solid state.

The behaviour of cobalt and bismuth is similar to that of cobalt and lead, the limits of miscibility in the liquid state being represented respectively by 6% and 93% of cobalt.

Cobalt and thallium are only slightly miscible both in the liquid and solid state, and there is no evidence of the formation of definite compounds.

Cobalt and zinc yield mixed crystals when the percentage of cobalt in the fused mass varies from 0.5 to 18.5. The saturated mixed crystals contain 13.4% cobalt. Evidence has also been obtained of the formation of a compound CoZn_4 .

Cobalt and chromium are miscible in all proportions both in the liquid and solid state. The minimum temperature at which crystallisation commences is about 1320° , the composition of the fused mass corresponding with 47% chromium. Alloys containing from 30—100% chromium undergo a change of structure at 1226° . The homogeneous mixed crystals which are primarily formed in the cooling process are transformed at this temperature into two different kinds of crystals, which are readily distinguished after electrolytic etching.

Cobalt and silicon are completely miscible in the liquid condition. In the solid state, the miscibility is confined to alloys containing less than 7.5% or more than 91% silicon. Five compounds are formed: Co_2Si , m. p. 1327° ; CoSi , m. p. 1393° ; CoSi_2 , m. p. 1277° ; CoSi_3 , m. p. 1307° , and Co_3Si_2 , which is formed in the solid state from the compounds Co_2Si and CoSi .

Measurements of the magnetic permeability of the alloys and the temperatures at which the magnetic qualities undergo changes have been made.

The paper concludes with a discussion of the relationships between the metals iron, cobalt, and nickel on the basis of the freezing-point diagrams of their principal alloys. A table is given showing the miscibility in the liquid states and the compounds formed in each case. The data show that in the liquid as well as in the solid state, the miscibility of nickel with other metals is greater than that of cobalt, which in its turn is greater than that of iron. Nickel also yields the greatest number of compounds, and iron the smallest number.

H. M. D.

Cobalt-Tin Alloys. S. F. SCHEMTSCHUSCHNY and S. W. BELYNSKY (*Zeitsch. anorg. Chem.*, 1908, 59, 364—370. Compare Lewkonja, preceding abstract).—The alloys formed by cobalt and tin have been studied by an investigation of the cooling curves of molten mixtures containing different proportions of the two metals, and an examination of the micro-structure of the solidified products. The freezing-point diagram, constructed from the experimental data, shows the existence of five curves. Two compounds, Co_2Sn and CoSn , are indicated. The former corresponds with a maximum freezing temperature of 1171° , the latter being characterised by a transition point at 927° . Above 515° , CoSn separates out in α -crystals, and below in β -crystals. The curves for the compounds are limited by eutectic points at 229° and 1112° . The eutectic alloy corresponding with 229° contains less than 1 atom % of cobalt, and that corresponding with 1112° , 79.5 atom % of cobalt. The two compounds are much harder than either of the components. The compound Co_2Sn is magnetic; CoSn has no magnetic properties either in the α - or the β -modification.

H. M. D.

Phosphorus Compounds of Nickel. N. KONSTANTINOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 742—752).—The freezing-point curve of nickel-phosphorus alloys indicates that, when melted together, nickel and phosphorus form the compounds Ni_5P_2 and Ni_2P , the former of which exists in two modifications; the β -form, which is stable at high temperatures, is transformed into the α -form at 1025° . At lower temperatures there exist also the compound Ni_3P , and another, richer in phosphorus than Ni_2P . With Ni_2P , the β -modification of Ni_5P_2 forms solid solutions, the limiting concentration of which corresponds with about 18% of phosphorus by weight (29.5 atomic %). These solid solutions decompose into the α -form of Ni_5P_2 and Ni_2P at 1000° .

T. H. P.

Action of Arsenic Trichloride on Nickel and the Arsenico-nickels. ÉMILE VIGOUROUX (*Compt. rend.*, 1908, 147, 426—428).—Powdered reduced nickel, when heated in arsenic chloride vapour, is not attacked below 400° . Between 400° and 600° , it is converted into nickel chloride and a compound having a composition corresponding with NiAs . The same compound is formed at 600° to 800° , but at 800° — 1400° the product consists of Ni_3As_2 .

By heating a mixture of powdered nickel and arsenic in an atmosphere of hydrogen, or by heating the metal in arsenic vapour, a series of arsenico-nickels is readily obtained. These contain, when prepared at 300° — 400° , 72% of arsenic; at 400° — 600° , 65% of arsenic; at 600° — 800° , 56% of arsenic; above 800° , 46% of arsenic, whilst an arsenide containing 39% of arsenic is obtained by treating alloys containing 11—38% with dilute sulphuric acid and separating with a magnet. On heating with arsenic chloride vapour, these arsenico-nickels tend to form NiAs at 400° — 800° by absorption or loss of arsenic, whilst at 800° — 1400° the resulting compound is Ni_3As_2 .

The arsenide NiAs , identical with the natural nickeline, has a red

colour, and, according to the temperature of preparation, is obtained as a powder, composed of small crystals with a metallic lustre, or as a slightly fritted mass, D° 7·57.

The arsenide Ni_3As_2 (also obtained by Wöhler, *Ann. Chim. Phys.*, 1832, [ii], 51, 208; by Descamps, *Abstr.*, 1878, 705, and by Granger and Didier, *Abstr.*, 1900, ii, 349) is a grey, pulverulent substance with a metallic lustre, which melts at 1000° , giving a hard, brilliant silver-white ingot, which readily breaks into lamellæ, D° 7·86.

The arsenide NiAs commences to lose arsenic at 100° , being converted into Ni_3As_2 , which is very stable, and is only slightly decomposed at 1400° . Conversely, when heated in an atmosphere of hydrogen at decreasing temperatures in the presence of arsenic, these two compounds absorb the latter, giving, finally, below 400° a grey powder having the composition NiAs_2 , identical with rammelsbergite.

The arsenides are attacked by heated chlorine, oxygen, or sulphur vapour. They are rapidly dissolved by nitric acid and aqua regia, are very slightly attacked by hydrochloric and sulphuric acids, are decomposed by fused potassium chlorate and nitrate, but are only slowly attacked by alkalis or alkali carbonates. E. H.

Some Alloys of Chromium and Manganese. G. HINDRICH (Zeitsch. anorg. Chem., 1908, 59, 414—449).—Aluminothermic chromium and aluminium were used. Chromium is very viscous at its melting point, and requires to be heated more strongly to yield uniform alloys; magnesia crucibles are therefore necessary. When a carbon electric furnace is used, some carbon is always absorbed by the chromium, owing to the passage of gas through the porous magnesia.

The freezing point of chromium (1550°) is lowered by the addition of tin up to 10%, mixed crystals being formed up to 6% Sn. Beyond this, two liquid layers are formed, one of which is practically pure tin.

Chromium and copper are only miscible to a small extent in the liquid state, but the emulsion formed does not separate readily into two layers.

Liquid chromium and silver are also only partly miscible. The addition of 5% Ag lowers the freezing point of chromium by 50° . Solid solutions are not formed.

Molten zinc dissolves chromium to some extent; molten cadmium not at all.

The addition of 27% of lead lowers the freezing point of chromium by 80° ; alloys richer in lead separate into two layers, one of which is pure lead.

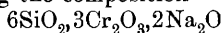
The preparation of alloys of chromium and aluminium is difficult, owing to oxidation and to the action of aluminium on the magnesia crucible at the high temperature necessary. It is better to prepare them by the ignition of a mixture of aluminium, chromium oxide, and potassium dichromate. Between 5% and 55% Cr, the liquid forms two layers, and there appears to be a compound of the formula Cr_3Al , the melting point of which lies much above 1600° .

Manganese and silver form immiscible liquids from 30% to 90% Mn, and do not form solid solutions.

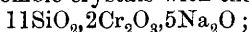
Manganese and aluminium form two compounds, probably Mn_3Al and $MnAl_3$, both of which form mixed crystals. Alloys containing between 57% and 86% Al separate into two liquid layers.

Tammann's rule (Abstr., 1907, ii, 445) is confirmed, that the element with the higher m. p. takes up more of that with the lower m. p. to form mixed crystals than conversely. C. H. D.

Sodium Chromisilicates. ZYGMUNT WEYBERG (*Centr. Min.*, 1908, 519—523).—By fusing a mixture of silica, sodium carbonate, and chromic oxide with a large excess of sodium chloride, a dark green, crystalline powder having the composition



was obtained; the crystals are orthorhombic and strongly pleochroic. A mixture of sodium metasilicate, chromic hydroxide, and excess of sodium chloride gave rhombic crystals with the composition



and a mixture of ammonium dichromate, sodium metasilicate, and sodium chloride gave the product $95SiO_2, 2Cr_2O_3, 3Na_2O$ in tridymite-like crystals.

The compounds obtained when chromium takes the place of aluminium or iron in these experiments are thus of quite a different type (Abstr., 1906, ii, 23, 91, 865). When the sodium salts are replaced by salts of other alkali or alkaline earth metals, no definite results were obtained. With lithium salts, olivine-like crystals of lithium ortho-silicate, Li_4SiO_4 , were formed. L. J. S.

Treatment of Pitchblende Residue. LUDWIG HAITINGER and KARL ULRICH (*Monatsh.*, 1908, 29, 485—496).—The paper deals with the working up of the radioactive residue (10,000 kilograms) from 30,000 kilograms of pitchblende containing 53.4% U_3O_8 . The operations, which occupied two years, are the following: The residue is heated for a working day with half its weight of sodium hydroxide (25% solution). After washing away the greater part of the soluble sulphates, the residue is digested on the water-bath with one and a-half times its weight of hydrochloric acid (1:1), and then washed with water. The hydrochloric acid extract is practically free from radium, but contains the bismuth-polonium and the actinium. The residue is next heated with half its weight of sodium carbonate (25% solution, free from sulphate), whereby a great part of the radium sulphate is converted into the carbonate; the mass is washed until free from soluble sulphates, and treated with pure hydrochloric acid. After three such treatments with sodium carbonate, &c., the final residue is practically free from radium, as also are the sodium carbonate extracts and the aqueous washings. The hydrochloric acid extracts, containing all the radium, are treated with sulphuric acid; the precipitated sulphates of lead, metals of the alkaline earths, and of the rare earths in the form of double sulphates, are heated repeatedly with an excess of concentrated sodium carbonate. The conversion of the sulphates into the carbonates is never complete, and therefore, after extracting

the mass with hydrochloric acid, the residue is boiled with water to remove the lead chloride (which is purified by recrystallisation and utilised for the preparation of radioactive lead) and then added to the next batch of crude sulphates. The hydrochloric acid solution, containing the radium, is freed from lead by hydrogen sulphide, evaporated to dryness, and the greater part of the calcium chloride extracted by concentrated hydrochloric acid. The resulting crude chloride, containing radium and barium, and also strontium, calcium, and small amounts of other substances, weighs 20 kilograms in a moist state; the least soluble constituent is the radium chloride. By repeated fractionation, it is separated into two parts, one (2 kilograms) containing nearly all the radium, and the other (11 kilograms) containing very little. The smaller part is again fractionated until the first crop of crystals is reduced to 9 grams. This crop is dissolved, freed from a little impurity by hydrogen sulphide, and separated in silica vessels into four subsidiary fractions and one "final" fraction, on which a determination of the atomic weight, by Richard's method for barium, gave the value 225, whilst the activity number was 27.2×10^6 . The activity numbers of the four subsidiary fractions are 17.0×10^6 , 6.1×10^6 , 2.5×10^6 , and 3.1×10^6 respectively. The total calculated amount of radium corresponds with 3.236 grams of anhydrous radium chloride of activity 27.2×10^6 .

A portion of the crude barium was converted into the bromide, from which a "final" fraction of radium bromide was obtained. It weighed 0.5 gram, and after a year the weight had decreased to 0.389 gram. It was examined by Brill, who found that it lost 5.4% in weight when heated, gained 17.2% when heated in a current of hydrogen bromide, and contained 0.1792 gram of radium. The fact that radium bromide loses bromine by keeping is not generally known. C. S.

Physicochemical Researches on Tin. VII. ERNST COHEN (*Zeitsch physikal. Chem.*, 1908, 63, 625—634. Compare Abstr., 1900, ii, 83, 212, 408; 1901, ii, 106, 244; 1904, ii, 567; 1905, ii, 168).—Since the publication of the author's earlier papers, numerous cases of the corrosion of coins, organ-pipes, and other articles made of tin, due to partial conversion into the grey modification, have come to light. Photographs of a number of these articles are reproduced.

A large quantity of grey tin having been put at the disposal of the author, the transition temperature has been determined with greater accuracy than heretofore. It is found to lie very close to 18° .

J. C. P.

An Alloy of Thorium and Nickel. ÉDOUARD CHAUVENET (*Bull. Acad. roy. Belg.*, 1908, 684—685).—Moissan and Hönigschmidt (Abstr., 1906, ii, 678), attempting to prepare metallic thorium by reducing potassium thorium chloride or thorium chloride with metallic sodium, obtained a metal containing 10—25% of thoria. The author, using lithium instead of sodium, and heating in a nickel boat, failed to prepare pure thorium, but obtained an alloy of thorium and nickel in the form of either grey lamellæ or a black pyrophoric powder. The analysis of this agrees with the formula Th_2Ni . The alloy in-

variably contains 10% of thorium oxide. The pyrophoric variety inflames spontaneously either when powdered in a mortar or when dried in an oven at 115°. It does not give nickel carbonyl when heated in carbon monoxide at 60°, whilst at 400° the gas is decomposed with depositions of carbon. The alloy is non-magnetic, and is rapidly dissolved by hydrochloric acid. E. H.

Rapid Preparation of Antimony Pentasulphide (Golden Sulphide). ALBERT SARTORIUS (*Chem. Zentr.*, 1908, i, 2130—2131; from *Apoth. Zeit.*, 1908, 23, 342—343).—The usual method of preparing Schlippe's salt is to boil antimony trisulphide and sulphur with sodium hydroxide one and a-half to two hours, when, theoretically, sodium sulphantimonate and sodium meta-antimonate should be formed. If, however, the process is stopped after one-quarter of an hour's boiling, it is found that scarcely any of the antimony trisulphide has been acted on, the reaction that takes place being expressed by $6\text{NaOH} + 4\text{S} = 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$. To avoid this formation of thiosulphate, the author adds the mixture of antimony trisulphide and sulphur to the boiling sodium hydroxide solution, in small portions at a time. Under these conditions, the reaction proceeds according to the following equation: $4(\text{Sb}_2\text{S}_3 + 2\text{S}) + 18\text{NaOH} = 5\text{Na}_3\text{SbS}_4 + 3\text{NaSbO}_3 + 9\text{H}_2\text{O}$, and in a shorter time a larger yield of Schlippe salt of a better quality is obtained. J. V. E.

Thioantimonates of Alkali Metals. II. A. D. DONK (*Chem. Weekblad*, 1908, 5, 629—645. Compare Donk, this vol., ii, 763).—From mixtures of the corresponding alkali thioantimonates with methyl alcohol and water, the following hydrated salts have been isolated: $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ (at 0° and 30°) and $\text{K}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ (at 15°). Similar mixtures of alkali thioantimonates with the corresponding hydroxides and water yielded the following hydrated salts:

$\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$; $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O} + \text{NaOH} \cdot \text{H}_2\text{O}$; $\text{NaOH} \cdot \text{H}_2\text{O}$ (at 30°); $\text{K}_3\text{SbS}_4 \cdot 5\text{H}_2\text{O}$; $\text{K}_3\text{SbS}_4 \cdot 3\text{H}_2\text{O}$; K_3SbS_4 ; $\text{K}_3\text{SbS}_4 + \text{KOH} \cdot \text{H}_2\text{O}$; $\text{KOH} \cdot \text{H}_2\text{O}$ (at 30°); $(\text{NH}_4)_3\text{SbS}_4 \cdot 4\text{H}_2\text{O}$ (at 30°); $\text{LiOH} \cdot \text{H}_2\text{O}$; $\text{Li}_3\text{SbS}_4 \cdot 10\text{H}_2\text{O} + \text{LiOH} \cdot \text{H}_2\text{O}$; $\text{Li}_3\text{SbS}_4 \cdot 10\text{H}_2\text{O}$ (at 30°). A. J. W.

Dissolution of Metallic Gold in Hydrochloric Acid in Presence of Various Organic Substances. N. D. AVERKIEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 840—859).—Metallic gold dissolves in hydrochloric acid in presence of the following compounds, which are arranged in decreasing order of effectiveness: methyl alcohol, amyl alcohol, chloroform, ethyl alcohol, chloral hydrate, phenol, sucrose, glycerol, trioxymethylene, formaldehyde. The dissolution takes place slowly at the ordinary temperature, but much more rapidly on heating, the time of heating having but little effect on the rate of solution. In some cases it was found that the solution of the gold was accelerated by increasing the amounts of acid and organic substance.

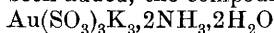
The residues obtained by evaporating these solutions on a water-bath give metallic gold on ignition, the loss on ignition differing from

that observed with $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$ (loss, 51.6%). Thus, with chloroform, this loss is 45.63; with methyl alcohol, 60.3; with phenol, 65.08; with ethyl alcohol, 78.0; with trioxymethylene, 85.1, and with amyl alcohol, 85.01%.

The results obtained indicate the existence of new compounds and reactions of gold, which are being further studied. T. H. P.

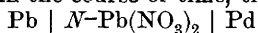
Complex Gold Sulphites. ARTHUR ROSENHEIM, JULIAN HERTZMANN, and MAX PRITZE (*Zeitsch. anorg. Chem.*, 1908, **59**, 198—202).—Two complex sulphites of tervalent gold, $\text{K}_5[\text{Au}(\text{SO}_3)_4] \cdot 5\text{H}_2\text{O}$ and $\text{Na}_5[\text{Au}(\text{SO}_3)_4] \cdot 14\text{H}_2\text{O}$, were obtained in slender, deep yellow needles by the action of the corresponding alkali hydrogen sulphites on a solution of auric chloride in just sufficient alkali to form a clear solution. The compounds are stable in cold alkaline solution, but soon decompose in neutral or acid solution. On heating, the yellow alkaline solutions become colourless, and probably contain univalent gold, but no definite compounds could be isolated.

When a concentrated solution of gold chloride is added drop by drop to a solution of ammonium sulphite containing excess of ammonia, and the solution is gently warmed, it becomes colourless, and the compound, $\text{Au}_3(\text{SO}_3)_2 \cdot 4\text{NH}_3 \cdot 4\text{H}_2\text{O}$, separates in colourless, lustrous leaflets. Similarly, from a solution of potassium sulphite to which excess of ammonia has been added, the compound



is obtained in colourless needles. The constitution of these two compounds has not been established. G. S.

Nature of Palladium-Lead Alloys. NICOLAI A. PUSHIN and N. P. PASHSKY (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 826—829).—The authors have prepared a number of alloys of palladium and lead by melting the metals in a mixture of lithium chloride with either potassium chloride or barium chloride. The potentials of the various alloys were measured by means of a $\text{Pb} \mid \text{N-Pb}(\text{NO}_3)_2 \mid$ alloy element (compare Pushin, Abstr., 1907, ii, 325). All the alloys containing less than 33% (atom.) of palladium have a potential practically identical with that of pure lead, whilst those containing more than 33% (atom.) of palladium give with pure lead a P.D. of more than 600 millivolts. Alloys of the latter class give at first a P.D. of 350—400 millivolts, which, however, increases rapidly at the commencement and more slowly later, approaching asymptotically the value 605—640 millivolts, which value persists for eight to ten hours. The potential of pure palladium also changes in the course of time, the element



having at first a P.D. of 760 millivolts; after two hours, the value 880 millivolts is reached, and after a further three hours, this begins to diminish slowly until 600 millivolts is reached. The above results prove clearly the existence of the compound Pb_2Pd . T. H. P.

Mineralogical Chemistry.

Native Tellurium from Asia Minor. GIUSEPPE CESÀRO (*Bull. Acad. roy. Belg.*, 1908, 255—257).—Amongst a series of specimens from the mines of Balia was a large (2×3 cm.) dendritic crystal of native tellurium intergrown with quartz. A small proportion of gold is the only impurity present in the material. L. J. S.

Action of Potassium Chlorate on Pyrites and on Hauerite. GIORGIO SPEZIA (*Atti. R. Accad. Sci. Torino*, 1908, 43, 728—734).—A mixture of pyrites with sufficient potassium chlorate to oxidise between 1 and 2 atoms of the sulphur of the pyrites explodes when brought into contact with either concentrated sulphuric acid or a flame. Under similar conditions, a mixture of sulphur or stibnite with potassium chlorate undergoes rapid combustion, approaching to explosion. With less or more than the above proportion of chlorate, pyrites gives a mixture which does not explode, but undergoes more or less rapid combustion.

The reaction between pyrites and potassium chlorate in the wet way differs, however, greatly from that between sulphur or stibnite and potassium chlorate. When the former mixture, either in explosive proportions or containing an excess of the chlorate, is heated with water, a vigorous reaction begins at 75° and continues without further heating; a yellow deposit forms, chlorine is evolved, and sulphuric acid is detectable in large proportion in the solution. A reaction also takes place very gradually in the cold, but in this case no evolution of chlorine is observed. With potassium chlorate and sulphur or stibnite, no such reaction occurs, and only after protracted heating at 100° is a trace of sulphuric acid formed.

Marcassite behaves with potassium chlorate, in both the wet and dry ways, in the same manner as pyrites, the vigorous reaction in the presence of water commencing at 70° . Hauerite forms an explosive mixture with potassium chlorate, but does not react with it in the presence of water, even at 100° .

When heated, hauerite begins to lose sulphur at about 170° , and is ultimately converted into manganese monosulphide; pyrites, on the other hand, loses sulphur only at about 350° , and gives a compound corresponding with pyrrhotite as final product, the monosulphide only being obtained from pyrites by heating in a current of hydrogen.

From these results, the author concludes that the sulphur present in combination with iron in pyrites has properties different from those of elementary sulphur. T. H. P.

Natural Ferrous Oxide Hydrate. HART (*Chem. Zeit.*, 1908, 32, 746).—In the clay deposit near Cuxhaven, hard, yellowish-brown lumps have been found among volcanic ash, which crumble when exposed to the air and appear to be ferrous oxide dihydrate, $\text{FeO} \cdot 2\text{H}_2\text{O}$.

Analysis showed 12.55% to be insoluble in hydrochloric acid; the soluble portion had the following composition:

FeO.	Fe ₂ O ₃ .	CaCO ₃ .	MgCO ₃ .	SO ₃ .	Water.	Total.
43.68	0.42	4.5	8.52	0.75	27.71	98.13

The powdered substance had D^{17.5} 3.205.

J. V. E.

Origin of the Boric Acid in the Soffioni of Tuscany. RAFFAELLO NASINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 43—46).—In a paper read before the Sixth International Congress of Applied Chemistry in Rome (1906) on "The Boraciferous Soffioni and the Boric Acid Industry of Tuscany," the author referred to a theory put forward by E. Perrone to explain the formation of these soffioni. This theory regards tourmaline as the source of the boric acid. The original temperature of the vapours of the soffioni cannot be less than 250°, and the depth from which they come must be from 5000 to 8000 metres. At this depth there probably exist granitic rocks containing tourmaline, having the characters of the granite found in Elba and elsewhere. The author's experiments show that when steam at a high temperature is passed over tourmaline extracted from Elba granite and subsequently condensed, the condensed liquid contains boric acid. As, further, this granite exhibits radioactivity, the presence of radioactive gases in the soffioni gases is readily explained.

Objections to this theory raised by D'Achiardi (*Atti Soc. toscana sci. nat. Mem.*, 1907, 23) and Lotti (*Rassegna mineraria dell'indust. chim.*, 1907, 26, No. 14) are discussed.

T. H. P.

The Wide Distribution of Scandium in the Earth. G. EBERHARD (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 851—868).—Although scandium appears to be relatively abundant in the sun and stars, yet it has only rarely been detected in terrestrial materials. Three hundred and sixty-six samples of minerals, rocks, and meteorites of various kinds were examined spectroscopically, and traces of scandium found in a large number of them. It occurs most frequently in zirconium minerals, beryl, titanates, columbates, and titanocolumbates of the rare earths, in micas, and in tin and tungsten ores. Wolframite from Zinnwald, Bohemia, contains 0.2% of scandium oxide (Sc₂O₃).

L. J. S.

Composition of Parisite and Malacon. G. P. TSCHERNIK (*Chem. Zentr.*, 1908, ii, 192; from *Verh. Russ. Min. Ges.*, 1907, 44, 507—545).—The minerals analysed are from a weathered graphic granite from the neighbourhood of Mukden. The prismatic crystals of parisite are of two kinds: I, dark grey and transparent, D 4.396, H 5—6; II, yellowish-grey and opaque, D 4.331, H 4—5:

	Ce ₂ O ₃ .	La ₂ O ₃ .	Y ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	CO ₂ .	H ₂ O.	F.
I.	21.88	33.11	7.86	0.28	3.78	2.28	23.69	2.45	6.37
II.	21.81	32.62	8.76	—	3.69	2.15	22.94	2.93	6.16

The dark grey opaque grains of malacon, with D 4.016 and H over 7, gave the results under III:

III.	SiO ₂ .	SnO ₂ .	ZrO ₂ .	Fe ₂ O ₃ .	MnO.	Y ₂ O ₃ .	CaO.	H ₂ O.
	29.67	0.10	49.04	3.43	0.03	4.55	2.99	9.07

L. J. S.

Existence of a Monoclinic Soda Felspar, Isomorphous with Orthoclase. PHILIPPE BARBIER and A. PROST (*Bull. Soc. chim.*, 1908, [iv], 3, 894—899. Compare this vol., ii, 704).—Analyses of seven samples of orthoclase, briefly described in the original, show that orthoclases exist having the potassium partly or wholly replaced by sodium, the latter occurring as a special silicate (not identical with albite) which can ally itself with the orthoclase molecule without causing a change in crystalline form. If orthoclase is represented by the expression $K_2Al_2Si_6O_{16}$, the sodium compound must be represented as $Na_2Al_2Si_6O_{16}$. T. A. H.

Kaersutite from Linosa and Greenland. HENRY S. WASHINGTON and FRED. EUGENE WRIGHT (*Amer. J. Sci.*, 1908, [iv], 26, 187—211).—Crystals of a black basaltic amphibole were collected from the tuff of a small parasitic cone of Monte Rosso, on the small island of Linosa off the coast of Tunis. They are monoclinic, with a prism cleavage angle of $55^\circ 22'$. Thin sections are brown and strongly pleochroic; the extinction angle is small and in the acute angle β (on the prism plane $c':c = +1.4^\circ$); the optic axial plane lies in the plane of symmetry, and $2V$ is about 80° . Analysis I shows the mineral to be highly titaniferous, and to be very similar to the kaersutite (of Lorenzen, 1884) from Kaersut, in Greenland. A re-examination and a new analysis (II: 0.77% apatite deducted) were made of the original kaersutite:

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	NiO.	MgO.
I.	40.85	8.47	9.89	8.85	3.96	0.12	0.10	12.47
II.	39.52	10.31	11.22	1.22	8.81	0.06	nil	13.31

	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	F.	Total.	Sp. gr.
I.	12.16	2.01	0.63	0.19	0.28	99.98	3.336
II.	10.93	2.95	1.07	0.59	—	100.00	3.137

The presence together of large amounts of titanium and iron oxides (Fe_2O_3 and TiO_2 or FeO and Ti_2O_3) gives rise to uncertainties in the analyses and in the interpretation of the results; the results can, however, be made to conform with the meta-silicate formula of Penfield and Stanley (*Abstr.*, 1907, ii, 102). L. J. S.

Mineralogy of Sardinia. II. A. PELLOUX (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 70—74. Compare *Atti R. Accad. Lincei*, 1904, [v], 13, ii).—The author describes crystals of idocrase found (1) in the Baccu Arroddas Mines in Sarrabus, and (2) in the Rio Planu Castangias Mines in Iglesias.

[CARLO RIMATORI.]—The composition of the crystals from Rio Planu Castangias is as follows:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.	D ²² .
39.17	11.35	13.39	33.31	trace	trace	3.74	100.96	3.358

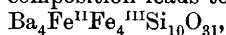
T. H. P.

Taramellite, a New Silicate of Iron and Barium. E. TACCONI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 810—814; *Centr. Min.*, 1908, 506—508).—The author describes a new mineral, *taramellite*, occurring

in radiating, fibrous, acicular aggregates or slender veins in the crystalline, calcareous zone of Candoglia-Ornavasso (Val Toce), where it is found in intimate association with magnetite, pyrites, chalcopyrite, paracelsian, pyroxene, and amphibole. It has a reddish-brown colour, a silky or fatty lustre, a hardness of about 5·5, D^{17} 3·923, n greater than 1·74. The mineral exhibits distinct pleochroism, and has the composition :

SiO ₂ .	Fe ₂ O ₃ .	FeO.	BaO.
36·56	21·54	4·47	87·32

together with traces of titanium, aluminium, manganese, and magnesium. The above composition leads to the formula



and the mineral may be regarded as a basic salt of a polymeride of metasilicic acid, $\text{Ba}_4\text{Fe}^{\text{II}}(\text{Fe}^{\text{III}}\text{O})\text{Fe}_3(\text{SiO}_3)_{10}$. T. H. P.

The Zeolites of Montresta (Sardinia). LUCIANO PELACANI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 66—70).—The zeolites of Montresta include mesolite (anal. I), chabazite (anal. II), heulandite, and stilbite, the first occurring in greatest, and the last in smallest, proportion :

	SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	42·94	25·05	10·87	8·12	trace	13·32	100·30
II.	46·30	21·96	7·78	—	2·27	21·37	99·68

The analyses agree with those of Rimatori (Abstr., 1900, ii, 735). Mesolite is regarded as an isomorphous mixture of scolecite and natrolite, and, from a study of the emission of water on heating, the mesolite of Montresta seems to be more closely allied to scolecite than to natrolite. The amount of water emitted by chabazite when gradually heated to 350° increases more slowly than the temperature rises, whilst with mesolite the reverse is the case. The re-absorption of the water removed by heating to 350° takes place rapidly and completely with chabazite, whilst with mesolite it is slow and only partial. After heating to redness, chabazite absorbs about one-fourth of the total water emitted, whilst mesolite absorbs none at all.

The heulandite has the composition :

SiO ₂ .	Al ₂ O ₃ .	CaO.	SrO & BaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
57·59	15·69	7·62	traces	2·87	trace	15·77	99·54

which approximates to that of the heulandite from Beruflord, analysed by Rammelsberg (*Zeitsch. deut. geol. Ges.*, 1869, 21, 93). The stilbite was found only in small quantity, insufficient for analysis. T. H. P.

New Vein of Nephelitic Basalt containing Noseite (Nosean) in Vincentino. L. MADDALENA (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 802—809).—The author has discovered in Vincentino a nephelitic basalt of microporphyrritic structure, containing pyroxene, biotite, apatite, magnetite, and noseite, the last being scattered irregularly in

crystals and granules, mostly of hexagonal habit. The basalt has the composition :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.
31·39	12·15	5·89	6·41	0·41	16·61	9·82	3·48	1·21
P ₂ O ₅ .	TiO ₂ .	CO ₂ .	H ₂ O at 110°.	H ₂ O at red heat.	Total.			
1·40	1·23	5·31	1·66	3·17	100·14			

which approximates to that of the basalt of Recoaro, the lower proportion of silica in the Vincentino basalt being due to the more advanced condition of alteration of the rock.

T. H. P.

Physiological Chemistry.

Regulation of Respiration. F. H. SCOTT (*J. Physiol.*, 1908, 37, 301—326).—The respiratory mechanism may be stimulated by small amounts of carbon dioxide, or by great diminution of oxygen in the inspired air. These produce increase of both rate and depth of breathing, but if the vagi are divided, the depth increases but not the rate. The alveolar tension of carbon dioxide rises with rise of body temperature; the effect of vagal division on the tension is very variable. Inflation of the lungs even at the height of dyspnoea inhibits inspiration, but if the vagi are divided, it has no effect. The effect of repeated ventilations depends on the washing-out of carbon dioxide from the blood (confirmatory of Haldane). The vagi in reference to respiration are regarded in the same light as the sensory nerves of muscle; without these nerves muscular movements are excessive, and thus resemble those of an ataxic limb. W. D. H.

Heart Perfusion Apparatus. THOMAS G. BRODIE and WINIFRED C. CULLIS (*J. Physiol.*, 1908, 37, 337—340).—A new apparatus for the perfusion of the isolated mammalian heart is described and figured. W. D. H.

Hæmagglutination and Hæmolysis. LEO VON LIEBERMANN (*Centr. Bakt. Par.*, 1908, 47, ii, 372—378).—Polemical and theoretical. Von Eisler (*Centr. Bakt. Par.*, 1908, 46, 353) has attributed to the author the view, that agglutination by ricin is due to the acid nature of this substance, pure and simple. This is a misunderstanding; ricin appears, indeed, to be an acid, but its agglutinant action is a specific property, not shared by other acids, and due to the peculiar physical properties of the ricin-stroma combination (compare Abstr., 1907, ii, 973). In connexion with this, Landsteiner's views are discussed. The inhibitory action of alkali primarily extends to the complement, but also affects the immune substance. G. B.

The Time Relations of Hæmolysis on Exposure to Light of Sensitised Red Blood-corpuscles. O. HARZBECKER and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, 12, 306—313).—Suspensions of red blood-corpuscles were submitted to the action of the sensitising substances eosin and sodium dichloroanthracenedisulphonate in the dark, and then exposed to light. The amount of hæmolysis was ascertained by measuring the volume of blood-corpuscles, and of hæmoglobin in the supernatant liquid, in samples of liquid centrifuged after different intervals of exposure to light. It was found in all cases that hæmolysis was a gradual process, and took place at the same rate whether the fluorescing substance was within or both within and without the cell. S. B. S.

Hæmolysis by Snake Poison. VON DUNGERN and COCA (*Biochem. Zeitsch.*, 1908, 12, 407—421).—The hæmolytic action of cobra poison depends entirely on the existence of a lipolytic enzyme, by means of which hæmolytically-acting scission products, especially deoleo-ecithin and oleic acid, are produced. Compounds of lecithin and cobra toxin do not exist; there are no such substances as either saturated or unsaturated toxolecithides. The preparations of Kyes (Abstr., 1907, ii, 569) are mixtures of ferment with deoleo-ecithin, contaminated with other substances, or their scission products, which are found in commercial lecithin. Cobra poison contains no amboceptors, and the hæmolysis produced by a combination of cobra poison and complement containing serum is due to a complex serum hæmolysin, which acts hæmolytically only under certain conditions, and only when the blood-corpuscles have taken up a certain quantity of lipase.

S. B. S.

Hæmolysis by Soaps, and the Relationship between Soaps and the Complex Hæmolysins of the Blood-serum. MAX FRIEDMANN and FRITZ SACHS (*Biochem. Zeitsch.*, 1908, 12, 259—277).—Noguchi and von Liebermann have shown that soap can be deprived of its hæmolytic properties by admixture with serum, and have expressed the view that this inactivated mixture acts as a complement, the hæmolytic powers of which can be called into play by the addition of an amboceptor. Such an amboceptor, von Liebermann claims to have discovered in oleic acid. The authors have devised experiments to test the above hypotheses. They have confirmed the fact of the combination between serum and the soap, which is rendered more stable by heating to 70°. They have, however, been unable to confirm the hypotheses as to the complement nature of this combination, or of the amboceptor-nature of oleic acid. The activation of the amboceptor by the addition of the soap-serum mixture, they ascribed to the action of a true serum complement contained in the sera, which had not been entirely destroyed by heating to 50°. The supposed amboceptor action of oleic acid they ascribed to the additive action of the acid and of the soap-serum mixture, each of which was, by itself, unable to produce hæmolysis. S. B. S.

Hæmolysis by Soaps. FRITZ SACHS (*Biochem. Zeitsch.*, 1908, 12, 278—289).—Although soaps can be deprived of their hæmolytic power

by previous admixture with serum, the latter can accelerate their action if the soaps be added first to the suspension of corpuscles. Serum can also accelerate in a like manner, the hæmolytic action of oleic acid, which fact, amongst others, led von Liebermann to ascribe amboceptor functions to this acid. The author has attempted to determine the nature of the substance in serum which accelerates hæmolysis by soaps. Serum-albumin is inactive; alkalis markedly accelerate the action. It is not to the alkali, however, that serum owes the accelerating property, for neutralised or dialysed serum still possesses it; furthermore, serum which has been deprived of its proteins loses this property. Serum which has been extracted with ether, gains in the hæmolysis-accelerating power. The experiments with alkali render it probable that the concentration of hydroxyl ions influences the hæmolysis, and the extraction of serum by ether, in removing the fatty acids from the soaps contained therein, may increase the alkalinity of the serum. The experiments, however, lead to no definite conclusions as to the nature of the hæmolysis-accelerating substances in serum.

S. B. S.

The Point of Attack of Photodynamic Substances in Paramœcia. HERMANN VON TAPPEINER [with F. OSTHELDER and E. ERHARDT] (*Biochem. Zeitsch.*, 1908, 12, 290—305).—*Paramœcia*, which have been treated with eosin in the dark, are no more strongly sensitised than those which have been exposed immediately to the light. The eosin does not appear to possess the property of penetrating the cell; its action in sensitising is entirely at the periphery. Dichloro-anthracenedisulphonic acid and methylene-blue, on the other hand, are taken up in active form by the cell in the dark; their point of attack is intracellular; there is evidence, however, in the case of these two substances of a peripheral, in addition to the intracellular, action. As to the nature of the peripheral action, nothing definite can be stated.

S. B. S.

Action of Fluorescent Substances on Red Corpuscles. HERMANN VON TAPPEINER (*Biochem. Zeitsch.*, 1908, 13, 1—23).—Eosin and sodium dichloroanthracenedisulphonate produce in the dark at the room temperature no noteworthy destruction of red corpuscles, and, after removal from the solution, they undergo hæmolysis at 59° at the same rate as untreated corpuscles. In the light, however, rapid hæmolysis occurs. These substances are therefore taken up by the corpuscles in a form in which they are not sensibilised. This hæmolysis is more rapid if the light acts before than after washing of the corpuscles from the fluorescent solution. Whether the action occurs in the interior or on the surface of the corpuscles is discussed; phenosafranine shows both kinds of action; methylene-blue only a surface action.

W. D. H.

Action in the Dark of Fluorescent Substances on Proteins, Toxins, and Ferments, and its Reversibility. T. KUDO and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, 13, 24—43).—Many fluorescent substances act in the dark on the alexin of serum and on tetanolsin, inhibiting their specific actions. This is not the case with

all fluorescent substances, and the concentration necessary to produce the effect in the dark is relatively high in comparison with that of those which act photodynamically. Those which act in the dark are considered to be adsorbed, and the action is reversible; the presence of alkali is favourable, whilst that of invertase, inhibits. W. D. H.

Nucleoli of *Hydra fusca*. C. E. WALKER and ALICE L. EMBLETON (*Quart J. Exp. Physiol.*, 1908, 1, 287—290).—The observations relate to the movements of the nucleoli of the cells of the hydra from the nucleus into the surrounding cell protoplasm. The phenomenon is not related to cell division, but is connected with or dependent on metabolic changes, especially with digestion, since it is seen principally in endoderm cells. A marked change takes place in the staining reactions of the extruded nucleolus, which suggests that it undergoes an important chemical or physical change. W. D. H.

The Death of Leucocytes. The Vacuolation of Leucocytes. H. C. ROSS (*J. Physiol.*, 1908, 37, 327—332, 333—336).—Methylene-blue kills cells; it is not until death occurs that the nucleus is stained; this is hastened by heat and alkalis, and delayed by neutral salts. After death, the cytoplasm liquefies, and the granules show Brownian movements; this may be brought about by the absorption of fluid. During life the cytoplasm is a jelly.

Certain spots in leucocytes described by previous observers as centrosomes are droplets of fluid absorbed by the cells, which are suspended in the jelly-like cytoplasm. With the liquefaction of the latter which occurs on death, these droplets disappear. W. D. H.

The Production in vivo and in vitro of Precipitins for Ovalbumin by means of Antigens of a Chemically definite Nature. ANDRÉ MAYER and GEORGES SCHÆFFER (*Compt. rend.*, 1908, 147, 311—313).—The precipitating serum for egg-albumin, usually produced from the rabbits by repeated injection of egg-albumin into the animal, can also be obtained if the animal is starved for five or six days, and the serum collected when it has lost about one-third of its weight and the urine is markedly acid. The precipitating property also appears after chloroform intoxication, and after the formation of aseptic peritoneal abscesses by turpentine. In every case the serum loses its precipitating property after warming to 60°. It was assumed that precipitating sera were produced by the presence therein of products of tissue degradation. Amongst such products are the fatty acids, and attempts were made to produce precipitating sera by injection of these acids. It was found that the sera of animals which had received repeated injections of propionic, butyric, valeric, hexoic, and oleic acids produced marked precipitins with solutions of egg-white. No precipitants were produced by the injections of octoic, stearic, palmitic, hydrochloric, lactic, or succinic acids.

The precipitate produced is specific for egg-albumin, and the precipitate is soluble in excess of either of the reacting substances; the serum also loses its precipitating properties on warming to 60°.

Soaps and ethyl esters on injection also produce precipitating sera, but the action is not so marked as in the case of the free acids.

Precipitating sera have also been obtained by adding directly to sera (without injection into animals) fatty acids, soaps, and ethyl esters. In the first case, which yields the most marked results, the precipitating property is only destroyed with difficulty by heating.

S. B. S.

Chemico-physical Studies of Animal Fluids. Ia. Viscosity of Blood-serum of Different Marine and Terrestrial Animals. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 707—717).—Measurements are given of the time of outflow of the blood-serum of different animals from an Ostwald viscosimeter, compared with the values obtained with distilled and sea-water at the same temperatures.

W. A. D.

Chemico-physical Investigations on Animal Liquids. Ib. Viscosity of the Blood-sera of Certain Marine and Terrestrial Animals. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 792—802. Compare preceding abstract).—The classification of marine and terrestrial animals according to the increasing time of efflux of their blood or body-fluid from a viscosimeter does not correspond with the ordinary zoological classification, so that the viscosity of the blood-plasma is not strictly dependent on the degree of organisation of the animal. The viscosity of the body-fluid of the marine invertebrates is only slightly greater than that of sea-water. The blood of cephalopods is distinguished from that of all other animals, vertebrate and invertebrate, by having the greatest viscosity. The viscosity of blood-serum increases with the proportion of colloids (sero-proteins) present.

T. H. P.

Chemico-physical Investigations on Animal Liquids. II. Content of Protein Nitrogen in the Blood-sera of Various Animals. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 16—26. Compare preceding abstracts).—The author has determined the proportions of nitrogen, precipitable by tannic acid, present in the blood-sera of various animals. The results show that, in this respect, marine and terrestrial animals are divided into four groups: (1) Those having sera or body-fluids containing less than 0.5% of protein nitrogen; this class includes *Siphunculi*, *Aplysia*, and probably, also, other low marine invertebrates. (2) Various vertebrates and invertebrates, including decapod crustaceans, birds, frogs, and the *Selachii*, with content of protein nitrogen varying from 0.52 to 0.67%. (3) Those with 0.8 to 0.9% of protein nitrogen, namely, herbivorous and carnivorous domestic mammals, such as cats, dogs, rabbits, and oxen. (4) Cephalopods, the serum of which contains, on an average, 1.66% of protein nitrogen. For the buffalo, the % of protein nitrogen is 1.3636, and for the pig, 1.230.

On comparing the numbers obtained with the viscosity results (see preceding abstract), it is found that, in general, the content of protein in the liquids examined increases with the viscosity. It is hence con-

cluded that the greater or less viscosity of the blood-plasma is due to the greater or less proportion of proteins present. This result is confirmed by experiments, in which the concentration of proteins in serum is increased artificially. T. H. P.

Chemico-physical Investigations on Animal Liquids. III. Variations of Electrical Conductivity, Viscosity, and Surface Tension of Blood-serum during Dialysis. FILIPPO BOTTAZZI, G. BUGLIA, and A. JAPPELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 49—57. Compare preceding abstracts).—The electrical conductivity and surface tension of blood-serum diminish considerably during dialysis, the diminution being at first rapid and afterwards slow; the same is the case when the serum is filtered before the conductivity or surface tension is measured. The viscosity of the serum diminishes if the liquid is filtered before determining the time of efflux; here, too, a slight increase in the time of efflux is observable at the beginning of the dialysis. The diminution of the conductivity is evidently due to the diffusion of the electrolytes, and this also causes the precipitation of the sero-globulin. T. H. P.

Action of Manganese and Iron Sulphates on Diastatic Ferments. ALFRED GIGON and T. ROSENBERG (*Chem. Zentr.*, 1908, ii, 84; from *Skand. Arch. Physiol.*, 1908, 20, 423—431).—A 1—2% solution of starch and a small quantity of manganese or iron sulphate were added to a freshly-prepared blood-serum, and the amount of sugar estimated by the polarimeter. The presence of these salts undoubtedly increases the amylolytic action of the blood-serum diastase, and is also favourable to the amylolytic ferment of the pancreatic juice. J. V. E.

Chemistry of Digestion in Animals. XVII. Digestion and Absorption of Proteins Rich in Bases. E. S. LONDON (*Zeitsch. physiol. Chem.*, 1908, 56, 378—383). **XVIII. The Importance of the Mouth in Gastric Digestion.** E. S. LONDON and J. D. PEWSNER (*ibid.*, 384—387). **XIX. Digestion and Absorption of Meat in the Intestine.** E. S. LONDON and TH. SULIMA (*ibid.*, 388—393). **XX. Laws of Digestion and Absorption in the Alimentary Tract.** E. S. LONDON and F. SANDBERG (*ibid.*, 394—403). **XXI. Further Investigations of the Same Laws.** E. S. LONDON (*ibid.*, 404—407). **XXII. The Importance of the Blood in Gastric Digestion.** N. A. DOBROWOLSKAJA (*ibid.*, 408—416). **XXIII. Digestion and Absorption of Carbohydrates.** E. S. LONDON and W. W. POLOWZOWA (*ibid.*, 512—544). **XXIV. Fat-splitting in the Alimentary Canal.** E. S. LONDON and M. A. WERSILOWA (*ibid.*, 545—550). **XXV. Composition, Digestion, and Absorption of Tubercle Bacilli.** E. S. LONDON and E. RIWKIND (*ibid.*, 551—553. Compare this vol., ii, 50).—The experiments were made on the dogs described in previous publications.

XVII.—If proteins, such as gelatin or histone (from the thymus), which are rich in bases are given, the products of digestion in the

jejunum and ileum contain only small amounts of free arginine. The chief substances obtained in the material issuing from the fistula are complexes which are precipitable by tannin. Absorption of gelatin occurs chiefly in the lower parts of the small intestine, and at the end of that tube it is fairly complete.

XVIII.—Details are given of the rate with which the stomach empties itself in dogs; this probably runs *pari passu* with the rate of digestion. Outside psychical influences do not affect this, but if the food is given by the mouth, it is much accelerated, probably because the normal reflexes due to taste impulses are set in motion.

XIX.—In flesh-feeding (200 grams), the total quantity of chyme which passes the various sections of the intestine decreases with each hour of the digestion period. The intervals between the peristaltic propulsions of the chyme are diminished by removal of the pylorus. The chyme is always a thick fluid, although its chemical and physical characters vary as it passes along; it also varies in the concentration of the digestion products in different segments of the intestine.

XX.—An attempt is made to construct mathematical formulæ to show the relationships between the digested, undigested, and absorbed portions of the food in relation to its quantity and the quantity of juices secreted. The experiments on which these are based were made with gliadin as the food.

XXI.—Similar experiments with white of egg; although this is more difficult to digest than gliadin, the same general laws are stated to hold.

XXII.—Loss of blood delays digestion; loss of one-third of the total volume of blood stops it for three hours; during this time the fall of blood-pressure persists. The quality of the blood is also important; in hydræmia there is diminution of gastric activity.

XXIII.—Starch, dextrin, sucrose, and dextrose are not absorbed in the dog's stomach in any concentration, whether dissolved in water or alcohol. Of these carbohydrates, only sucrose and erythro-dextrin undergo slight fission (2—4%) in the stomach, and this is due to the acid, not to enzymes; still large quantities of gastric juice are secreted. No formation of lactic acid was observed. In the duodenum, the carbohydrates undergo fission, the amount of which stated numerically varies in the case of different carbohydrates. Absorption has its main seat in the jejunum and upper ileum; again, the amount is stated numerically. Absorption is completed in the lower ileum; this is usually 100%, or nearly that. Only in the case of dry starch does any important amount (22%) pass through into the large intestine. The intestinal juice appears to be the main agent in the fission of carbohydrates; in starch digestion, however, the duodenal juice is of special importance. This intestinal activity leads to an increase of nitrogenous metabolism, which chiefly shows itself in the secretion of nitrogenous substances into the intestinal lumen.

XXIV.—The fission of emulsified fat begins in the dog's stomach soon after feeding, and reaches about 32%. This is partly due to gastric lipase, and partly to regurgitated duodenal contents. The pancreatic juice in the duodenum acts vigorously, cleaving 41% of the fat. Below this in the small intestine the percentage of free fatty

acids reaches its maximum, this in some portions reaching 95%; 69% of the fatty acids are still present in the large intestine.

XXV.—The main protein constituent of the tubercle bacillus approaches in composition those proteins with a mean percentage of diamino-acids. In the upper segments of the alimentary tract, it is digested, and it is absorbed throughout the length of the intestinal canal. In the lower ileum very little digestion of this protein takes place.

W. D. H.

Gastric Digestion in Fishes. M. VAN HERWERDEN (*Zeitsch. physiol. Chem.*, 1908, 56, 453—494).—This investigation definitely proves that the acid of the gastric juice in Selachian fishes is hydrochloric acid. An unimportant amount of formic acid is also present. The results in teleostean fishes are not so clear, mainly owing to the difficulty of collecting the juice during life. During digestion in selachians, the percentage of the acid may rise to 0.4. The proteolytic ferment present is probably pepsin, although some digestion may occur in a neutral medium, and in some teleostean fishes even in an alkaline medium. The acid is secreted at the cardiac region only of the stomach, but the epithelium differs from that seen in higher vertebrates. An amylolytic ferment is absent, but lipase is present.

W. D. H.

Influence of Bromine on Gastric Secretion. TOGAMI (*Biochem. Zeitsch.*, 1908, 13, 112—120).—Experiments on dogs with a Pawloff's "small stomach" show that aqueous solutions of bromine (in contradistinction to iodine) paralyse the stomach glands without any preliminary stimulation. Sodium bromide and bromo-protein compounds act, but not so constantly, in the same direction.

W. D. H.

[Importance of Calcium Salts for the Growing Organism]. ARNOLD ORGLER (*Biochem. Zeitsch.*, 1908, 12, 334—335. Compare this vol., ii, 606).—Explanation of a misunderstanding of the meaning of the term "balance" in a work by Aron and his collaborators (this vol., ii, 208), and criticised by the writer of the note.

S. B. S.

Behaviour of Lecithin with Bile Salts, and the Occurrence of Lecithin in Bile. JOHN H. LONG and FRANK GEPHART (*J. Amer. Chem. Soc.*, 1908, 30, 1312—1319).—Some authors have stated that bile contains small quantities of lecithin, whilst others have expressed the opinion that this substance is absent. Hammarsten (*Abstr.*, 1901, ii, 520; 1903, ii, 86; 1904, ii, 831), whilst leaving the universal occurrence of lecithin in bile an open question, asserts that it is present in the bile of the polar bear.

Experiments have now been made with ox bile and with human bile, but lecithin could not be separated. It has been found that the bile salts, as usually obtained, carry down a phosphorus complex, which has been regarded by Hammarsten and others as a lecithin. This complex could not be completely removed from the bile salts, as the latter retain it very tenaciously.

Bile salts are capable of dissolving 80% of their weight of egg-
lecithin, and much of this can be precipitated with acetone, but a
small quantity remains with the bile salts, and is probably much
greater than that contained in any bile. The addition of inorganic
salts hastens the solution of lecithin by bile salts, but does not
increase the amount dissolved. A few inorganic salts, however,
such as aluminium and ferric chlorides and lead nitrate, cause the
precipitation of the bile acids. When lecithin is dissolved in bile
salts, the optical activity is increased, whence it is calculated that the
lecithin has $[\alpha]_D + 7.75^\circ$.
E. G.

Action of Acids and Rennet on Human Milk. ENGEL (*Biochem. Zeitsch.*, 1908, 13, 89—111).—Hydrochloric, lactic, oxalic, and sulphuric acids precipitate human milk, and the optimal acidity is 2—3 c.c. of *N*/10 acid to 10 c.c. of milk. Phosphoric and acetic acids act best at a greater concentration (5 c.c.); the substance precipitated is caseinogen; rennet precipitates a calcium compound of this protein, and the amount necessary varies within wide limits, but the precipitation is most complete when combined with the optimal concentration of acid.
W. D. H.

Fat and Ester Hydrolysis in Tissues. PAUL SAXL (*Biochem. Zeitsch.*, 1908, 12, 343—360).—In organs containing only their own fat, or with additional added neutral fat, only a small amount of fat hydrolysis takes place during autolysis with exclusion of bacterial action. In the case of the addition of monoacetin, monobutylin, and ethyl butyrate to organs, the increase of acidity after twenty-four to forty-eight hours is due, at any rate partly, to the formation of acid products of autolysis. Amyl salicylate is, however, hydrolysed by all the organs investigated, with the exception of muscular tissue. The power of ester hydrolysis generally is smaller in the case of the muscles than in all other organs. The hydrolysing power of blood-serum is also small. Phosphorus poisoning does not activate a lipase. None of the methods hitherto employed for determining the fat-hydrolysing power of tissues is quite trustworthy; the quantities of acid formed are too small after short periods of incubation to allow an accurate estimation of their quantity to be made, and the product of autolysis and other circumstances interfere with the correct estimation after longer periods. Any conclusions as to the lipase content of organs under pathological conditions must therefore be accepted with reserve.
S. B. S.

Inosite in Animal Tissues and Fluids. FRANZ ROSENBERGER (*Zeitsch. physiol. Chem.*, 1908, 56, 373—377).—A new method of extraction is described which avoids the faults of Scherer's older method. Fresh flesh contains no inosite (cyclose); it is formed on keeping from a substance named *inositogen*. Ox-blood is free from both substances. Inositogen appears in the human placenta at the sixth month of foetal life; it is present in fresh eggs. The normal urine of men and dogs contains traces of inosite; that of the rabbit does not. The bodies of rabbits after inanition do not form inosite.

W. D. H.

Muscular Contraction and Receptive Substances. III.

JOHN N. LANGLEY (*J. Physiol.*, 1908, 37, 285—300).—The present experiments deal with the action of nicotine on denervated frog's muscles. Up to 100 days after nerve-section, the local punctiform application of nicotine to the muscles causes tonic contraction, as it does in normal muscles; more dilute solutions cause fibrillary twitchings; for this purpose, however, a somewhat stronger solution is required than in normal muscles. It is therefore certain that nicotine produces its effects on muscle and not on nerve-endings. Possibly the contractile molecule of the muscle fibre has a number of receptive side-chains; combination of one of these with nicotine causes one effect, with another, the other effect. Curare prevents nicotine from causing contraction in muscles, whether denervated or not.

W. D. H.

The Physiology of the Glands. IX. The Relationship between the Hourly Excretion of Nitrogen and Resorption from the Intestine, and its Dependence on Rest, Work, and Diuresis. ERNST HAAS (*Biochem. Zeitsch.*, 1908, 12, 203—247).—The hourly output of urine and its nitrogen content were estimated after meals containing known amounts of nitrogen, when the subject of the experiment was doing muscular work, when at rest, and when excessive diuresis was produced by drinking large amounts of tea. The curves representing the output were of a fairly constant form. They showed as a rule three maxima, the first in the second hour, the second in the fifth, and the last in the seventh hour. The first maximum is due to a washing-out of nitrogenous metabolism products owing to the introduction of liquids in the meal; the second and third are due to the resorption of the ingested nitrogenous matter from the intestine. Work or rest have no definite influence on the amount of excreted nitrogen in the first eight hours after a meal. With increased diuresis, there is to a certain extent an increased nitrogenous excretion, which is due, not to increased protein decomposition, but to the washing-out of nitrogenous metabolites already existing in the organism. If the diuresis be brought about before the ingestion of a meal, a smaller quantity of nitrogen is subsequently excreted; this quantity under the conditions of experiments performed was a constant, and amounted to 65% of the nitrogen of the ingested food.

S. B. S.

The Elimination of Non-dialysable Substances by the Urine under Normal and Pathological Conditions. ULRICH EBEBECKE (*Biochem. Zeitsch.*, 1908, 12, 485—498).—The amount of non-dialysable substance excreted in the urine depends on the amount of substance metabolised. In normal men it varies between 0.870 and 2.356 grams per day—averaging about 1.44 grams. These numbers are markedly higher than those found for females (about 0.8 gram per day). They are also higher than the numbers found in cases of nervous diseases, and of chronic disturbances of the digestive functions. On the other hand, in cases of increased metabolic processes, even with decreased ingestion of food, such as in cases of

fever and diabetes, the reverse is the case. The residue, in normal cases, gave, when tested with the majority of the protein reagents, negative results; on hydrolysis with hydrochloric acid it yielded a reducing substance; probably it consists of chondroitinsulphuric acid and nucleic acid. In the case of pneumonia, however, appreciable quantities of a peptone appeared to be present. In composition, this substance was not far removed from that of the mucin of bronchial mucous membrane, and it yielded on hydrolysis a reducing substance. It is possibly a glucopeptone. S. B. S.

Colloid Nature of Pigments in Relation to their Behaviour in the Frog's Kidney. RUDOLF HÖBER and S. CHASSIN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 76—80).—The experiments described previously (this vol., ii, 716) are extended to twenty-one other dyes. The experiments lead to the following rules: (1) When a dye is not taken up by the kidney epithelial cells it is highly colloidal. The converse is not true, since some colloids are taken up, for example, Biebrich-scarlet, acid-violet, and aniline-blue. (2) When a dye has little or no colloid character, it is readily taken up. T. E.

A Colour Reaction of Pathological Urine. OTTO GAUFF (*Biochem. Zeitsch.*, 1908, 13, 138—141).—Strzyzowski described in diabetic urine a reaction dependent on the amount of acetoacetic acid, the presence of which indicates a bad prognosis; it consists in the appearance of a green fluorescence at room temperature within twenty four to forty-eight hours when formaldehyde is added to the urine. In the present research, it is shown that the prognosis is not necessarily bad, and that the reaction is not specific for diabetic urine, but is found in a large number of other diseases. Ammonia is increased as well as acetoacetic acid in the urine, and a mixture of ammonia, acetoacetic acid, and formaldehyde gives the reaction. The chemical explanation of the reaction is still obscure. W. D. H.

The Relationship of the Thyroid Gland to the Physiological Action of Adrenaline. ERNST P. PICK and FRIEDRICH PINELES (*Biochem. Zeitsch.*, 1908, 12, 473—484).—The effect of adrenaline injection on the glycosuria and blood-pressure in thyroidectomised animals was investigated. It was found, in the case of rabbits, that the extirpation of the thyroid gland produced no effect on the action of adrenaline as regards its properties of producing glycosuria and diuresis, or of raising the blood-pressure. In the case of young goats, the removal of the thyroid, inhibited adrenaline-glycosuria; the diuretic and blood-pressure-raising properties remained, however, intact.

S. B. S.

The Behaviour of Bromides in the Human and in Animal Organisms. II. H. VON WYSS (*Arch. exp. Path. Pharm.*, 1908, 59, 186—195).—The kidneys possess no special capacity for elimination of bromides. After injection of these salts, owing to increased osmotic pressure, the kidneys will become active, but will eliminate, not the foreign salt necessarily, but also the chlorides. There will be,

consequently, a chlorine deficit in the organism, and the toxic effects due to bromides are caused by chlorine starvation; the bromides themselves play a purely passive rôle.

S. B. S.

Behaviour of Hydroxylamine in the Animal Organism. ROBERTO CIUSA and R. LUZZATTO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 834—840).—The authors have made a number of experiments on the toxicity of hydroxylamine and on the presence of the latter or its oxidation products in the urine of animals to which hydroxylamine has been administered, either by ingestion or hypodermically; the blood of the animals was examined spectroscopically.

As a poison, hydroxylamine is four to five times as powerful as nitrous acid. In blood *in vitro*, hydroxylamine is oxidised, first to nitrous acid and then to nitric oxide, most probably with intermediate formation of dihydroxyammonia, thus: $\text{NH}_2\cdot\text{OH} \rightarrow \text{NH}(\text{OH})_2 \rightarrow \text{N}(\text{OH})_3$ or $\text{NH}_2\cdot\text{OH} \rightarrow \text{HNO} \rightarrow \text{HNO}_2$ and $\text{HNO} + \text{HNO}_2 = 2\text{NO} + \text{H}_2\text{O}$. The blood-spectrum indicates the presence of the nitric oxide compound of hæmoglobin, together with methæmoglobin. T. H. P.

Physiological Action of Optical Antipodes on Higher Organisms. GIUSEPPE BRUNI (*Gazzetta*, 1908, 38, ii, 1—5).—*l*- and *d*-Camphors were administered to a number of pairs of rabbits of about equal weight in the proportion of 1.5 gram of 10% camphor oil per 100 grams-weight of the animal, the times of survival of the rabbits after the injection being measured. In the case of *l*-camphor, the mean period of survival was 25.4 minutes, and for *d*-camphor, 336.7 minutes, so that the toxicity of *l*-camphor is thirteen times as great as that of the *d*-isomeride. Similar results were obtained by experiments on guinea-pigs. The tastes of the two forms of camphor are markedly different, the *l*-isomeride being almost tasteless.

T. H. P.

Behaviour of Dextrosephenylosazone in the Organism. LUCIANO PIGORINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 132—136).—Experiments on frogs, chickens, guinea-pigs, and dogs to which dextrosephenylosazone was administered, either by ingestion or by subcutaneous or peritoneal injection, show that the animals are not affected by the osazone. The conclusion is drawn that the osazone is not resolved in the organism into dextrose and phenylhydrazine, or that, if such resolution does occur, phenylhydrazine is not set free; phenylhydrazine, when administered in the free state, reduces the oxyhæmoglobin of the blood to methæmoglobin, besides depressing the nerve centres.

T. H. P.

The Pharmacology of Phenanthrene and its Hydro-derivatives. HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1908, 59, 140—144).—The reduced phenanthrenes are less toxic than phenanthrene itself. The latter is eliminated from the organism in the form of a phenanthrol glycuronate. Dodecahydrophenanthrene, in a rabbit, also gives rise to a glycuronate. In the case of

frogs, phenanthrene itself gives rise to a glycuronate, but not 9:10-dihydrophenanthrene, or derivatives containing more hydrogen.

S. B. S.

The Quantitative Estimation of Synthetical Muscarine by Physiological Methods. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1908, 59, 179—185).—Injection of muscarine solutions into the heart of a toad (*Bufo vulgaris*) produces in weak solutions diminutions of amplitude of the beat; in stronger solutions, short cessation, with spontaneous recovery, with periodic beats, and with still stronger solutions, total cessation, lasting for some minutes. By perfusing the heart with Ringer's solution, it readily recovers, and can be employed for further experiments. To test the strength of a solution, the heart is first treated with known strengths of a muscarine solution, and the effects produced by each strength noticed. The heart is then perfused with the muscarine solution under investigation, and from the dilution necessary to produce the various effects, the concentration of the muscarine therein can be ascertained.

S. B. S.

The Action of Methyl-green. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1908, 59, 161—178).—Methyl-green is a true quaternary ammonium base, which cannot be extracted from aqueous solutions by ether. It has, accordingly, a curare-like action, and produces paralysis, acting peripherally. This effect is produced in frogs by doses of 2—4 milligrams. 0.03 Gram per kilo. is the toxic dose for rabbits when injected subcutaneously. Five times this dose, when administered *per os*, is without action. It exerts no muscarine-like action on the heart, but acts on the blood-vessels, causing fall of blood-pressure. Pharmacologically, it stands in the same relationship to the methyl-violet, from which it is produced by methylation, as curarine to curine; methyl-violet, like curine, exerts no curare-like action, but a digitalis-like action on the heart, which is wanting both in methyl-green and curarine. Methyl-violet is adsorbed by filter-paper and charcoal much more readily than methyl-green, and pigments strongly colour the tissues surrounding its point of application and the organs on which it exerts pharmacological action. Methyl-green, on the other hand, does not pigment very much, and is readily excreted by the kidneys. For this reason, the tinctorial power of methyl-green has failed to throw light on the question of the localisation of its curare-like action.

S. B. S.

The Pharmacology of the Quinotoxins. HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1908, 59, 127—139).—The products formed in the isomeric change produced by heating the cinchona alkaloids in acetic acid have been termed the quinotoxins. The experiments indicate that the increased toxicity of these products, as compared with the parent substances, is due to the presence of the piperidine group and the free imino-group. The comparative effects of cinchotoxin, methylcinchotoxin, and other derivatives were investigated.

S. B. S.

Biochemical Investigations of *p*-Iodophenylarsinic Acid. FERDINAND BLUMENTHAL and FRIEDRICH HERSCHMANN (*Biochem. Zeitsch.*, 1908, 12, 248—251).—*p*-Iodophenylarsinic acid was prepared from atoxyl by slowly diazotising it, and then adding potassium iodide. It is soluble in methyl and ethyl alcohols, but insoluble in other organic solvents, and can be heated to 300° without melting. For physiological investigations, the sodium salt was employed. It is more toxic than atoxyl; 0.1 gram can be injected into rabbits of from 1.5—2 kilograms in weight without marked ill-effects; 0.2 gram is a lethal dose. The animals killed exhibit acute nephritis. The iodine is excreted in the urine apparently in the form of an organic compound, and can be detected therein for some days after the injection. S. B. S.

Beeswax. RAGNAR BERG (*Chem. Zeit.*, 1908, 32, 777—780).—From a study of this wax, the author concludes that yellow beeswax contains aromatic and yellow colouring matters soluble in 80% alcohol and insoluble in light petroleum; chemically-bleached wax contains no such insoluble substances. The odour of the wax appears to be due, in part, to esters of a cholesterol derivative and acetic acid, butyric acid, valeric acid, and an unsaturated liquid acid. The operation of bleaching the wax causes the lower fatty acid esters to decompose. Both bleached and unbleached wax contain at least 0.6% (probably more) of cholesterol esters, which are difficult to saponify, and have high saponification values; only the alcohols give the cholesterol reaction, not the acids. The free wax-acids, which are soluble in 80% alcohol, consist chiefly of unknown acids, together with small quantities of cerotic acid; the bleached wax contains palmitic acid. A supersaturation method is described for showing stearic acid adulteration of beeswax. Dilute acetone, D 0.8450, is used instead of alcohol, enabling so small a quantity as 0.3 gram of stearic acid to be detected in the presence of palmitic and cerotic acids. J. V. E.

Fatty Acids from Mummies. W. A. SCHMIDT (*Chem. Zeit.*, 1908, 32, 769—770).—All mummies of whatever age contain fatty acids, and it is of interest to ascertain the alteration in composition of these acids as time progresses. With this object, mummies from about A.D. 500 and about B.C. 1000 have been investigated. From the lungs and muscles of the more recent, 60% and 20—25% respectively of higher fatty acids have been obtained, 40% of which is oleic acid; practically no volatile fatty acids were present. The lungs and spleen of the older mummies contained respectively 12.5% and 30% of higher fatty acids, relatively less oleic acid, and in proportion to the more recent mummies, a considerable quantity of volatile acids.

The liver of a mummy (B.C. 1000) was found to contain 1.6% volatile fatty acids, which are, for the most part, present as the sodium salt.

The author considers that the presence of higher acids is probably due, in part, to the transformation of the mummified albumin, and that the volatile acids may be derived from the slow decomposition of the higher acids, and not directly from the albumin. J. V. E.

Optical Activity of "Protagon." A New Physical Phenomenon Observed in Connexion with the Optical Activity of So-called "Protagon." OTTO ROSENHEIM and M. CHRISTINE TEBB (*J. Physiol.*, 1908, 37, 341—347, 348—354).—"Protagon" dissolved in pyridine possesses at 30° a slight dextrorotatory power, which changes to optical inactivity at higher or lower temperatures, showing finally a maximum lævorotation of -242° , and a final constant lævorotation of $[\alpha]_D^{20} - 13.3^\circ$. The prolonged action of boiling or warm alcohol during its preparation or recrystallisation has no influence on these phenomena. Wilson and Cramer's "decomposition" theory of protagon, based on the change of the specific rotation of protagon in pyridine from $+6.8^\circ$ to $(+?)13.3^\circ$ after the action of warm alcohol, is erroneous, and cannot be used for the revival of the view that protagon is a definite chemical compound.

The explanation of the change is as follows: the diamino-phosphatide, sphingomyelin (the constituent of "protagon" rich in phosphorus), is precipitated, when a solution of protagon is kept; it is the appearance of this precipitate which gives rise to the high lævorotation; as the precipitate settles, the lævorotation decreases, and the final lævorotation is due to a small amount of the precipitate which does not settle. But if the precipitate is removed by filtration or centrifugation, the portion of the protagon which remains in the pyridine solution, and is phosphorus-free, is optically inactive. If the precipitate is once more shaken up with this, high lævorotation is again obtained, which lessens as the precipitate once more settles. The high lævorotation is expressed in the usual way, but the optical activity of the precipitated substance does not follow Biot's laws.

On microscopic examination, the precipitate of sphingomyelin is found to consist of anisotropic globules (fluid sphæro-crystals), and their appearance in polarised light is figured. The term *sphaerorotation* is proposed for this phenomenon.

The majority of the experiments recorded were performed with protagon or sphingomyelin prepared from brain, but a similar substance with the same remarkable properties was also prepared from the cortex of the suprarenal body.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Enzymes [Diastase]. WILHELM SCHNEIDEWIND, DIEDRICH MEYER, and F. MÜNTER (*Bied. Zentr.*, 1908, **37**, 503—504; from *Arb. Agric.-chem. Versuchstat. Halle*, 1906, **2**, 67).—Alcohol and ether have a very injurious effect on the action of diastase, and freshly-prepared solutions of diastase are much more vigorous in action than the precipitated substance. It is therefore impossible to obtain information as to the composition of enzymes by studying substances prepared by precipitation.

Albumin, asparagine, and peptone act favourably, so also do weak acids (citric and acetic) at low concentrations (0.001%), but at higher concentrations (0.010%) they retard the action of diastase. Chlorides of the alkalis and small quantities of monophosphates and of aluminium sulphate accelerate the action. One to 2% of monocalcium phosphate or of aluminium phosphate inhibits action altogether. E. J. R.

Action of Small Quantities of Metals on Lactic Acid Fermentation. CHARLES RICHET (*Bied. Zentr.*, 1908, 37, 576; from *Compt. rend. Soc. Biol.*, 1905, 60, 455—456).—Minute amounts of barium, platinum, cobalt, manganese, and vanadium were found to cause a slight acceleration in the rate of production of lactic acid.

E. J. R.

The Catalases of Bacteria. AUGUST JORNS (*Arch. Hygiene*, 1908, 67, 134—162).—The power of bacteria in bouillon cultures to decompose hydrogen peroxide is due to the presence of a specific catalase, which exists in the form of both an ecto- and endo-ferment. Catalase-formation appears to be a very general property of bacteria, although individual species vary very greatly as regards the intensity of the action.

S. B. S.

The Chemical Changes Involved in the Assimilation of Free Nitrogen by Azotobacter and Radiobacter. JULIUS STOKLASA (*Centr. Bakt. Par.*, 1908, ii, 21, 484—509).—Both *Azotobacter chroococcum* and *Radiobacter* are widely distributed in nature, especially in soils where the bluish-green algæ are numerous; they were not found, however, in the high-lying soils of the Alps. Full details are given of the methods of isolating and studying the organisms.

Experiments on the amount of nitrogen-fixation showed that, contrary to the generally-accepted view, *Radiobacter* has only slight powers of assimilating free nitrogen; thus cultures in 10 and 20 days respectively fixed only 2.2 and 5 milligrams of nitrogen per litre, whilst *Azotobacter* cultures under the same conditions fixed 74.9 and 98 milligrams per litre. Nor is the nitrogen-fixing power of *Azotobacter* greatly increased by symbiosis with *Radiobacter*.

In order that nitrogen-fixation should go on, it is essential that carbohydrate should be supplied, and experiments were made to ascertain the relative values of several sugars. *l*-Arabinose was the most effective, causing 180 milligrams of nitrogen per litre to be fixed; under the same condition, *l*-xylose, dextrose, *d*-galactose, and lævulose enabled 140 to 155 milligrams to be fixed, sucrose 125, maltose 86, but rhamnose only 49.8. The figures for duplicate experiments show somewhat wide variations, but a series of tests with dextrose showed that 99 to 224 grams of this sugar were converted into carbon dioxide and water for every gram of nitrogen fixed. In view of the above results, the author suggests that the furfuroids of the soil furnish the best source of food for *Azotobacter*.

The influence of sodium nitrate on the process was also investigated. This substance inhibits nitrogen-fixation; nevertheless, it is not nearly as useful a food-stuff as free nitrogen. *Radiobacter* is a power-

ful denitrifier, decomposing the nitrate with liberation of free nitrogen.

Respiration is more intense than in any other organism yet studied, 1 gram of the bacterial mass evolving 1.3 grams of carbon dioxide in twenty-four hours. In addition to carbon dioxide, the following substances are also produced from the sugar: ethyl alcohol, hydrogen, formic, acetic, butyric, and lactic acids. E. J. R.

Effect of Pasteurisation on the Development of Ammonia in Milk. W. G. WHITMAN and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1288—1295).—Experiments which have been made on the pasteurisation of milk at 65° and 85° have shown that it does not entirely destroy the bacteria which attack the proteins with formation of ammonia, but does destroy, sometimes at 65° and always at 85°, the bacteria or enzymes which cause the decrease of ammonia in raw milk. The estimation of ammonia for the purpose of determining the amount of decomposition of proteins in milk is particularly useful in samples which have been pasteurised at a high temperature, but is of less value in samples which have been pasteurised at low temperatures or not at all, since the amount of ammonia present at any given time cannot be assumed to be proportional to the extent to which protein decomposition has taken place. In the case of samples of New York milk, it was found that, in general, pasteurisation was less efficient in checking the development of ammonia than in retarding the production of acid, and this was especially true of milk pasteurised at the higher temperature (85°), which before becoming sour often showed an amount of ammonia considerably in excess of that produced in raw milk of the same age and origin. It was also found that pasteurisation greatly retarded souring, but favoured the development of an offensive odour and bitter taste, this effect being much less noticeable in samples pasteurised at 65° than in those pasteurised at 85°. E. G.

The Photodynamic Action of Plant Extracts Containing Chlorophyll. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1907, 12, 331—334).—Extracts of various plants containing chlorophyll were shown to exert no hæmolytic action on suspensions of red blood-corpuscles when kept in the dark; if the mixture of corresponding quantities was exposed to light, hæmolysis readily took place.

S. B. S.

Recent Researches on Chlorophyllian Photosynthesis. EVA MAMELI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 739—744).—A destructive criticism of the work of Usher and Priestley (Abstr., 1906, ii, 299, 881; compare also Ewart, this vol., ii, 217). The statement made by Usher and Priestley that green leaves of *Elodea*, still attached to the plant, do not become reddish-violet when immersed in Schiff's reagent is incorrect. Moreover, when *Elodea*, killed by immersion in boiling water, is placed in pure water, the same bleaching is seen as was observed by Usher and Priestley in a solution of carbon dioxide; it is probably due to the action of oxygen on the chlorophyll, and not to that of carbon dioxide. The experiments on the production of formaldehyde from carbon

dioxide in an artificial "cell" composed of glycerol and chlorophyll are valueless, because solutions of chlorophyll always give Schiff's reaction. The evolution of oxygen from these artificial cells as described by Usher and Priestley could not be observed. In conclusion, it is pointed out (1) that these workers did not make any direct experiment to prove the presence of hydrogen peroxide in plants; (2) the function of the catalytic enzymes supposed to decompose the hydrogen peroxide is not demonstrated; (3) that all deductions based on the existence of formaldehyde in the plant after the death of the protoplasm and the bleaching of the chlorophyll are erroneous, because formaldehyde is present in the living green cells; (4) that the photolytic decomposition of carbon dioxide in presence of chlorophyll cannot be realised, much less the production of starch under the conditions given by Usher and Priestley. The only facts established are that the phenomena of assimilation are intimately connected with the production of formaldehyde, and that the latter is localised in the chloroplastids, as was already observed by Kimpflin. W. A. D.

The Translocation of Nitrogen Compounds into the Embryo of Barley from the Endosperm and from Artificial Culture Solutions. HORACE T. BROWN (*Trans. Guinness Lab.*, 1, ii, 288. Compare following abstract).—Germinating barley has been shown to contain in the early stages of its life a variety of nitrogenous substances arising from the protein of the original seed; within the first ten days, at least 35% of the seed protein must be transformed. Not all of the nitrogen compounds found after germination are degradation ("down-grade") products; a certain amount represents the surplus nitrogen over and above that required for immediate tissue formation in the growing embryo, and temporarily accumulated for future use ("up-grade" products). It would be possible to discriminate between the two by stopping the vital activity of the embryo in germinating grain without stopping enzyme action, for example, by treatment with chloroform vapour. Useful light is also thrown on the subject by determining the relative nutrient value of the various nitrogenous constituents of the growing grain when these are presented to the detached embryo in water cultures (compare Brown and Morris, *Trans.*, 1890, 57, 483).

The barley was softened somewhat by steeping, and the embryo removed without injury by means of a small knife. A certain number of the embryos were then placed, scutellum downwards, on disks of porous porcelain immersed in Petri dishes containing the nutrient solution in such quantity that the disk was covered without drowning the embryos. The amounts of mineral matter and of sugar supplied were the same in all experiments, but the nitrogen compounds were varied. The compounds used, and the order of their effectiveness, are as follows: tyrosine and phenylalanine (both poisonous at the concentration used); leucine, malt albumoses, and malt peptones (tend to inhibit growth of the plantlets); choline, betaine, allantoin (directly effective as nutrients, and causing assimilation of nitrogen amounting to nearly 50% of that originally present); ammonium sulphate,

aspartic acid, glutamic acid, potassium nitrate, and asparagine show progressive increases in their power to supply nitrogen to the plant.

It is significant that asparagine, the best nutrient found, is much more effective than its hydrolytic products, just as sucrose was found by Brown and Morris to be superior as a nutrient to dextrose and levulose.

E. J. R.

The Soluble and Non-coagulable Nitrogen Compounds in Malt. HORACE T. BROWN (*J. Inst. Brewing*, 1907, 13, 394—416).—An aqueous extract of malt contains a very complex mixture of nitrogenous substances, even after boiling and removal of the coagulated compounds, and ordinary precipitants were found insufficient to effect complete separations. Thus phosphotungstic acid precipitates about half the nitrogen, but it does not sharply differentiate the complex compounds, and it is possible to isolate both from the precipitate and the filtrate substances having substantially the same properties. Special methods were devised for estimating the nitrogen present as ammonia, and that existing as amides and amino-acids (and therefore liberated by nitrous acid), but these only accounted for 12·5% of the total nitrogen in the extract. An elaborate series of experiments was then made to separate and characterise the remainder of the nitrogen compounds, including salting-out with zinc sulphate and ammonium sulphate, various treatments with alcohol, precipitation with phosphotungstic acid, and the use of dialysis in a special form of dialyser; as far as possible, the experiments were made quantitatively. In this way, some substances were isolated resembling in their main characteristics the albumoses and peptones which result from the digestion of animal proteins under the influence of animal pepsins. The malt albumoses are neutral, soluble in water, not coagulated by heat, and salted-out by ammonium and zinc sulphates. The malt peptones are readily and permanently soluble in water and strong alcohol, are readily diffusible, and precipitable by phosphotungstic acid. In all these respects they agree with the corresponding animal products; they differ, however, in not giving the biuret reaction, and in that the malt peptones are not precipitable by ferric ammonium alum. The division of the “non-coagulable” nitrogen in aqueous and dilute alcohol extracts of malt was found to be as follows:

	Aqueous extract of malt.	Dilute alcohol extract of malt.
Nitrogen as ammonia	3·5	2·0
„ „ amino-acid and amide	8·5	16·0
„ „ organic bases	4·0	8·0
„ „ malt albumoses	20·0	16·0
„ „ malt peptones	31·0	58·0
„ „ undetermined substances...	33·0	—
	<hr/> 100·0	<hr/> 100·0

The amino-acids and amides include asparagine, tyrosine, leucine, and allantoin; the organic bases are mainly betaine and choline; the albumoses consist of at least three distinct compounds, and the peptones can be differentiated into at least two.

In examining the several fractions obtained during the investigation of the albumoses and peptones, the author has found the "amino-index" a useful factor. These substances, although neither amides nor amino-acids, liberate a certain amount of their nitrogen on treatment with nitrous acid, and the percentage so liberated is called the amino-index.

Malt albumose I, which represents about one-third of the total albumoses separable by ammonium sulphate, is insoluble in 85% alcohol, and possesses a remarkable power of producing a persistent froth in aqueous solution, a property of considerable interest in connexion with the formation of "head" or foam on malt-worts and beers; its amino-index is 4. Albumose II is soluble in 85% alcohol, and does not possess this frothing power; its amino-index is 5. Albumose III, with amino-index 20, is salted-out with zinc sulphate after removal of Albumoses I and II.

The malt peptones I and II closely resemble each other in general properties, but the amino-index of one is 10.9, and of the other, 19.3.

The author considers that the albumoses and peptones are derived from hordein, the alcohol-soluble protein of barley. E. J. R.

The Protein Changes Taking Place in Green Plants when Kept in the Dark. WL. BUTKEWITSCH (*Biochem. Zeitsch.*, 1908, 12, 314—330).—The plants employed in the investigations were beans and oats. The total nitrogen was estimated by Kjeldahl's method, the protein nitrogen by that of Stutzer, the aspartic acid nitrogen by that of Sachsse, and the ammonia nitrogen by that of Bosshard. In the case of beans, the undigestible nitrogen and the nitrogen of the substances precipitable by phosphotungstic acid were also estimated. The analyses were carried out with samples of the original material, and also with samples of material which had remained for different lengths of time in the dark. It was found that there was a decrease of protein nitrogen and an increase in aspartic acid nitrogen. The nitrogen, which was due neither to aspartic acid nor protein, at first increased, and then diminished. The conclusion is drawn that part of the aspartic acid (and another accompanying amide) is formed by a secondary change from products of protein degradation, which include leucine and tyrosine. S. B. S.

The Function of Calcium in Plants. VIKTOR GRAFE and LEOPOLD RITTER VON PORTHEIM (*Bied. Zentr.*, 1908, 37, 571—572; from *Naturw. Rundschau*, 1907, 22, 255).—The authors find that the injurious effects observed when plants are grown without a proper supply of calcium compounds either fail to appear or are greatly delayed when sugar is supplied. The experiments were made with beans (*Phaseolus vulgaris*), and the sugars investigated were lævulose, dextrose, and sucrose; of these, lævulose was most effective in delaying the effects of calcium starvation. These results lend support to the view that calcium is concerned in the conversion of starch into sugar in the plant.

Experiments were also designed to ascertain whether calcium acts as a protector against the formaldehyde, which may be supposed to

be produced during the assimilation of carbon dioxide. Plants were grown in normal solutions and in solutions free from calcium; some were kept in the dark and some in the light. Formaldehyde occurred in all plants exposed to light, but it did not occur in plants kept in the dark, even where calcium was withheld. Nevertheless, the characteristic effects of calcium starvation were seen in the latter case, and these experiments do not show any relation between calcium starvation and presence of formaldehyde. E. J. R.

Occurrence of Calcium Oxalate in the Barks of the Eucalyptus. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1905, 39, 23—32).—The following amounts of calcium oxalate were found in the bark of different species of *Eucalyptus*: *E. gracilis*, 16.66; *E. Behriana*, 16.50; *E. salubris*, 16.00; *E. oleosa*, 10.64; *E. dumosa*, 9.80; *E. salmonophloia*, 8.34; *E. occidentalis*, 6.82; *E. viridis*, 5.01; *E. redunca*, 4.46; *E. polybractea*, 2.14; *E. stricta*, 0.69, and *E. Morrisi*, 0.08%. The calcium oxalate differs from that usually found in plants in having only one mol. H_2O , and in its crystalline form, being similar to the mineral whewellite.

It is suggested that the production of large amounts of oxalic acid may be the cause of stunted growth, and that *Eucalyptus gracilis* is the degenerate form of a larger tree.

The tannin in the barks containing much calcium oxalate is decidedly superior to the tannin of barks in which only small amounts are present. N. H. J. M.

Aluminium, the Chief Inorganic Element in a Proteaceous Tree, and the Occurrence of Aluminium Succinate in Trees of this Species. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1904, 37, 107—120).—Four specimens of *Orites excelsa*, one of the trees known in Australia as "Silky Oak," were found to contain large amounts of aluminium. When excessive amounts of aluminium are taken up by the trees, deposits of basic aluminium succinate are formed. The deposits contain also free butyric acid.

Samples of the wood from (1) Queensland, (2) Mullimbimby, (3) Dorrigo, and (4) Bangalow, contained 0.639, 0.684, 0.673, and 0.706% ash, the composition of which was as follows:

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Al ₂ O ₃ .	Mn ₃ O ₄ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.	CO ₂ .
1.	6.98	trace	1.99	3.59	79.61	trace	0.96	0.85	3.64	0.25	2.54
2.	10.91	1.59	11.25	13.87	36.04	3.01	1.31	0.13	0.62	3.03	18.82
3.	14.96	1.13	2.63	16.12	43.03	trace	1.70	0.26	0.36	1.54	(18.62)
4.	—	—	—	—	38.77	0.48	1.26	—	—	—	—

The ash of (2) contained traces of cobalt. Iron was present only in traces.

The sap of *Grevillea robusta* was found to contain butyric acid. No aluminium could be detected in the ash of five varieties of *Grevillea*.

N. H. J. M.

Ochoco Fat. JULIUS LEWKOWITSCH (*Analyst*, 1908, 33, 313—315).—A fat, consisting of about 98% of myristin and 2% of olein, is yielded by the seeds of *Scyphocephalum ochocoa*, a tree

found on the West Coast of Africa. The kernels of the seeds yield about 58·8% of the fat, but by whatever process the fat is prepared, a dark brown colouring matter is at the same time extracted; this colouring matter is contained, not only in the husks, but also in the spermoderm which passes through the whole of the endosperm in the form of irregular lamellæ. The white endosperm, cut out carefully by hand, yielded a fat having the following chemical and physical constants: D_4^{20} 0·8899; saponification number, 238·5; iodine number, 1·72; Reichert-Meissl number, 0·65; m. p. 45—48°; unsaponifiable matter, 0·37%; mean molecular weight of the fatty acids, freed from unsaponifiable matter, 221·9; m. p. of fatty acids, 47·2°; the extracted fat had the acid number 1·42. The seeds are obtainable in large quantity.

W. P. S.

Carrotene from Carrots. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1908, 56, 554. Compare Euler and Nordenson, this vol., ii, 724).—The author has shown previously that carrotene when oxidised does not yield a derivative of cholesterol.

J. J. S.

Absence of Gum and Presence of a New Diglucoside in the Kinos of the Eucalyptus. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1905, 38, 21—36).—Freshly-exuded kinos of *Eucalyptus paniculata* yielded a diglucoside, *emphloin*, which is insoluble in alcohol. When hydrolysed, it yields 44·47% of a sugar, from which an *osazone*, m. p. 176—178°, was obtained. The sugar, which is probably isomeric with melibiose, is without optical activity, presumably owing to internal compensation.

When the glucoside is boiled with dilute acid, a precipitate of “kinored” is produced. This yields protocatechuic acid when heated with potassium hydroxide.

The astringency values of about 100 species of *Eucalyptus* were determined. Compared with gallotannic acid, containing 14·43% of water, = 1000, the values for *E. pilularis*, *E. macrorrhyncha*, and *E. eugenioides* (containing about 18% of water) were 838, 835, and 811 respectively. The kinos of *E. paniculata* and other “iron-barks” have only about half their values, owing to their glucosidal nature, and it will be necessary to hydrolyse the glucoside while in the pits (perhaps by means of an enzyme) to render them suitable as tanning materials.

N. H. J. M.

Barks of Rhamnus Frangula and Rhamnus Purshiana. ALEXANDER TSCHIRCH and J. F. A. POOL (*Arch. Pharm.*, 1908, 246, 315—325).—The emodins isolated from the two barks are identical; a substance, m. p. 165°, which was, in addition, obtained from *Frangula* bark, is probably chrysophanic acid; neither bark contains rhein. Tschirch and Edner's assay-method for rhubarb (*Abstr.*, 1907, ii, 515) is not applicable to the barks in question, but Warin's colorimetric method (*Abstr.*, 1905, ii, 659) appears to be of more importance. The addition of magnesia to the powdered drug before percolation, in order to remove the bitter taste from the extract, does not greatly affect the total hydroxymethylanthraquinone-content of the

percolate, but increases in it the amount of combined hydroxymethyl-anthraquinones.
G. B.

Origin of the Colour of Red Grapes. PHILIPPE MALVEZIN (*Compt. rend.*, 1908, 147, 384—386.* Compare Laborde, this vol., ii, 774).—When unripe, green berries of red grapes are heated with distilled water for seventeen hours at 85°, an intense yellow colour is developed, which at the end of twenty-four hours changes to red. The red coloration is due to oxidation by the air, since in absence of air only the yellow colour is obtained. A similar series of colour changes occurs when green berries of white grapes are treated in the same way. The leaves and stalks of the vine, however, give only the yellow colour.

The author ascribes the red colour of grapes to the existence of a single chromogenic compound, which in his experiments is transformed into the red substance under the influence of air, heat, and probably light, the same transformation being brought about in nature by a specific enzyme. The absence of colour in white grapes is considered to be due to the absence of this enzyme. The chromogenic substance is unstable, and is precipitated when the heating at 85° is prolonged; on raising the temperature, however, the original brilliant red colour reappears, and this process can be repeated a certain number of times.

W. O. W.

The Action of Sulphur Dioxide on Plants. A. WIELER (*Bied. Zentr.*, 1908, 37, 572—573; from *Naturw. Rundschau*, 1907, 22, 229).—Assimilation of carbon dioxide is profoundly influenced by the presence of sulphur dioxide, but respiration is not affected. Examination of the leaves of plants from districts where sulphur dioxide causes injury showed that this substance is present in the leaf, although only in small quantities, except in cases where the leaves are close to the source of origin of the gas, when larger amounts are found. The sulphur dioxide enters through the stomata, and causes greater injury in wet than in dry weather, because the stomata are more widely open.

There is evidence that some other factors come into play besides the direct action of sulphur dioxide in the leaf; for instance, the soils in the districts where injury arises are acid. It is concluded that injury can usually be overcome by suitable manuring, and, in particular, by liming.

E. J. R.

The Quantity of Arsenic contained in Wines obtained from Vines which have been Treated with Arsenical Washes. PIERRE BRETEAU (*J. Pharm. Chim.*, 1908, [vi], 28, 154—158).—Ten samples of wine obtained from vines which had been treated with arsenical washes or sprays were found to contain quantities of arsenic varying from 0.003 to 0.20 milligram per litre; one sample was free from arsenic. Four other samples, also coming from vines similarly treated, but which had received the addition of quantities of sulphuric acid, bisulphite, &c., contained from 0.03 to 0.10 milligram of arsenic per litre.

W. P. S.

* And *Bull. Assoc. chim. Sucr. Dist.*, 1908 26, 187—189.

Tobacco-smoke. JOSEF HABERMANN and RICHARD EHRENFELD (*Zeitsch. physiol. Chem.*, 1908, 56, 363—372. Compare Abstr., 1901, ii, 680).—An investigation of the amount of ammonia, sulphur, and nicotine in the smoke of various brands of Austrian cigars.

W. D. H.

Composition of the Air in Soils. ERICH LAU (*Bied. Zentr.*, 1908, 37, 433—434).—The author discusses the variations in the amount of carbon dioxide present in the air of the soil. The soil air is richest in carbon dioxide in summer and poorest in winter, the maximum being reached in July, and the minimum in February. Only small amounts are found in sandy soils, more in clays and loams, and a still larger quantity in peaty soils, corresponding with the increasing amounts of humus present; the physical properties of the soil also influence the quantity. Less is found at the surface than lower down; the difference is more marked in the case of peaty than of sandy soils. The amount of oxygen in the soil air depends on the amount of carbon dioxide, hence it is clear that the latter is formed by oxidation of humus.

Some of the carbon dioxide is also produced by the plants growing in the soil, and the amount present in soils carrying crops is always greater than in fallow soils; the amount also increases with the temperature and the weight of the crop. Potatoes and lupins especially cause an increase in the carbon dioxide, indicating that their respiratory processes are more intense than those of other plants.

Dung also increases the amount of carbon dioxide present.

E. J. R.

Some Properties of the Organic Matter in the Soil. The Osmotic Pressure of the Soil Moisture. JOSEF KÖNIG, JULIUS HASENBÄUMER, and H. GROSSMANN (*Landw. Versuchs.-stat.*, 1908, 69, 1—92).—The authors have examined a method suggested by Copenrath (*Landw. Versuchs.-stat.*, 1907, 66, 401) for determining the amount of available plant food in soils, namely, heating the soil (500 grams) with water (5 litres) for five hours under 5 atm. pressure. The plant food goes into solution either as complex salts or as organic substances. Great differences in composition, such as would be found in soils of widely different types, are thus brought out, but not the slight differences produced by adding to a given soil artificial manures in quantities commensurate with those used in practice. Hydrogen peroxide also dissolves plant food from the soil, and in somewhat higher quantities than the above method, but it also fails to discriminate between manured and unmanured soils of the same type when the amount of added manure is only small.

The analytical value of the method was established by pot experiments, which showed that the amount of potash taken by the plant, and therefore "available" for the plant, was much the same as that dissolved by the above processes. Since the amount of plant food dissolved by these methods is higher than that extracted by pure water, or water saturated with carbon dioxide, it follows that some of the soil humus must furnish mineral matter to the plant. For the same

reason, potash appears to be set free from some of its insoluble compounds during the growth of the plant.

An apparatus is described by means of which a measure of the osmotic pressure of the soil solution can be obtained. It is suggested that such measurements might throw much light on the solubility of soil constituents.

E. J. R.

Isolation of Picolinecarboxylic Acid from Soils and its Relation to Soil Fertility. OSWALD SCHREINER and EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1908, 30, 1295—1307).—A sample of soil from Takoma Park, Md., was found to contain 3% of organic matter, 0.1% of nitrogen, and sufficient mineral substances for ordinary crops. Nevertheless, this soil was very unfertile, and did not respond readily to treatment with manures. It was found that this was due to the presence of toxic substances, and a careful investigation was therefore carried out, with the result that picolinecarboxylic acid was isolated.

2-Picoline-4-carboxylic acid was obtained by Böttinger (Abstr., 1881, 612; 1884, 758) by the action of heat on uvitonic acid, the latter being easily prepared by treating pyruvic acid with alcoholic ammonia. Indications were obtained of the presence of pyruvic acid in the soil, but no evidence could be obtained of the presence of uvitonic acid.

A series of experiments has been carried out with a view to ascertaining the toxicity of various organic substances on wheat seedlings (compare Schreiner and Reed, this vol., ii, 420). It has been found that picolinecarboxylic acid in very low concentrations acts as a stimulant, but is decidedly injurious when present to the extent of 100—200 parts per million. The amount of picolinecarboxylic acid in the Takoma Park soil was not sufficient to account for the full toxic effect, but this was chiefly due to the presence of dihydroxystearic acid. Uvitonic acid is much more toxic than picolinecarboxylic acid. Pyruvic acid exerts a toxic action, but its sodium salt is inactive. Pyridine and picoline are very injurious, and piperidine is even more so.

E. G.

Effect of Lime on the Availability of the Soil Constituents. FREDERICK B. GUTHRIE and L. COHEN (*J. Roy. Soc. New South Wales*, 1907, 41, 61—66).—About 10 lb. of a light sandy soil, a garden loam fairly rich in humus, and a very stiff clay were mixed with 1% freshly-slacked lime and, along with duplicate portions without lime, exposed to the sun and rain for a month, being kept moist the whole time.

The clay to which lime was added became friable in a fortnight. In the soils which had no lime, the water-soluble phosphoric acid decreased considerably, and in the case of the clay soil the water-soluble potassium decreased as well. Application of lime lessened the decrease in water-soluble constituents, and in the sandy soil increased the proportions both of phosphoric acid and potassium soluble in water above those originally present.

The amounts of constituents soluble in citric acid changed very slightly, and the effect of liming was less marked.

As regards the soluble nitrogen, application of lime was found to increase the amount of nitrites, whilst the amount of nitrates remained almost the same, except in the case of the clay soil, which showed a loss of nitrate under the influence of lime. The largest amount of soluble nitrogen in the unlimed soil was in the form of ammonia, of which the limed soil contained very little.

N. H. J. M.

Chemical Examination and Calorimetric Test of Indiana Peats. R. E. LYONS and C. C. CARPENTER (*J. Amer. Chem. Soc.*, 1908, 30, 1307—1311).—Twenty-nine samples of peat from the lake region of Northern Indiana have been tested for calorific value, and five typical specimens of Indiana peats have been submitted to complete analysis. The maximum heating effect was given by a specimen of sphagnum moss peat from a bed 20 feet thick, exhibiting almost complete decomposition and a dark chocolate colour, whilst the minimum effect was given by an impure, highly oxidised peat derived from grass and sedge. In general, the results showed that the best Indiana peat has a calorific value equal to the best grade of peat found in other parts of the United States and in Europe.

E. G.

Manurial Trials with Calcium Cyanamide and (Swedish) Calcium Nitrate. HJALMAR VON FEILITZEN (*Bied. Zentr.*, 1908, 37, 498—499; from *Landwirtsch. Presse*, 1907, 229 and 243; see also *Abstr.*, 1906, ii, 487).—The experiments show that calcium cyanamide acts almost as favourably as ammonium salts, although not as well as sodium nitrate, on oats, barley, wheat, and potatoes growing on sandy or clay soils. It also acts well on the better moor soils (*Misch- u. Niederungsmooren*), but on the poorer soils (*sphagnum* and high moorland) it was not as good.

Calcium nitrate gave much better results, and was fully as good as sodium nitrate even on the high moorland soils; indeed, on oats it was better than sodium nitrate.

E. J. R.

Pot Experiments to Determine the Limits of Endurance of Different Farm Crops for Certain Injurious Substances. FREDERICK B. GUTHRIE and R. HELMS (*J. Roy. Soc. New South Wales*, 1904, 37, 165—171. Compare *Abstr.*, 1905, ii, 755).—The following numbers indicate the percentages of the different substances employed, and their effect on maize grown in a fairly rich garden loam.

	NaCl.	Na ₂ CO ₃ .	NH ₄ CNS.	NaClO ₃ .	As ₂ O ₃ .
Germination affected ...	0·20	0·20	0·005	0·004	0·50
„ prevented..	0·50	0·50	above 0·02	above 0·006	above 0·80
Growth affected	0·10	0·10	0·001	0·001	0·05
„ prevented	0·25	0·25	above 0·02	0·004	0·60

N. H. J. M.

Amount and Composition of Drainage Waters collected during the Year 1906-7. J. M. HAYMAN (*Rep. Cawnpore Agric. Stat.*, for the year ending June 30, 1907, 57—58. Compare *Abstr.*, 1907, ii, 127).—Results of analyses, made twice a month, of the drainage

through four drain-gauges, two 72 inches and two 36 inches deep, from June 1 to October 31.

The total amounts of rain and drainage, and of nitrogen as nitrates in the drainage, for the five months were as follows :

No.	Depth of soil, in inches.	Rainfall, in inches.	Drainage, in inches.	Nitrogen	
				Per million.	Lb. per acre.
1.....	72	34·38	19·126	41·66	180·31
2.....	72	34·38	16·709	53·03	200·51
3.....	36	34·38	18·257	14·70	60·75
4.....	36	34·38	19·952	18·96	85·62

N. H. J. M.

Analytical Chemistry.

The Importance of Hygroscopy in General Analysis. C. REICHARD (*Pharm. Zentr.-h.*, 1908, 49, 759—763).—Attention is directed to the deductions which may be drawn as to the nature of a salt from an observation of its hygroscopic properties. Instances are given of salts which are similar in appearance, but may be distinguished from one another by one having the power of absorbing water from the atmosphere. Thus, a crystal of sodium iodide, exposed side by side with a crystal of potassium iodide, will absorb enough water to give a complete solution, whilst the potassium salt remains practically dry. Barium chloride is readily distinguished from the hygroscopic calcium and strontium chlorides. Sodium metaphosphate is hygroscopic, and differs from sodium orthophosphate in this respect. Other salts exhibiting this difference are potassium acetate and sodium acetate, copper sulphate and copper nitrate, &c. W. P. S.

Qualitative Centrifugal Analysis. B. C. P. JANSEN (*Chem. Weekblad*, 1908, 5, 591—593).—The author finds that the use of the centrifuge in qualitative analysis affords a method which is superior to the ordinary filtration process in speed, ease of manipulation, and cleanliness. Its use is not more expensive than that of good filter-paper. A. J. W.

Gas Analysis. J. P. WUITE (*Chem. Weekblad*, 1908, 5, 623—625).—A theoretical paper, criticising Anema and van Deventer's conclusions (this vol., ii, 221). A. J. W.

Compound Gas-Pipette. HANS FLEISSNER (*Chem. Zeit.*, 1908, 32, 770).—The troublesome operation of filling the compound Hempel pipette is avoided by having a small vertical tube sealed to the communication tube of the central top bulb. When the pipette is filled with the aid of a funnel and a piece of rubber tubing, the tube is closed with a rubber tube carrying a glass rod. L. DE K.

Physico-chemical Analysis of Wines. PAUL DUTOIT and MARCEL DUBOIX (*Compt. rend.*, 1908, 147, 351—353. Compare this vol., ii, 781).—Berthelot's method for determining the end point in acidimetry by means of the electrical conductivity of the solution, furnishes higher results when applied to the analysis of the distillation products of wines than the usual process. The total quantity of basic substances exceeds the amount of ammonia determined gravimetrically or colorimetrically; the difference represents the volatile organic bases, the quantity of which varies considerably with the nature and age of the wine. The method has also been employed to estimate the volatile acids, but the results are found to depend to a certain extent on the method of carrying out the distillation.

Estimations of the organic bases and colloidal tannins have shown a deficiency of one or both of these constituents in inferior wines ("piquettes") and wines prepared from raisins. W. O. W.

Qualitative and Quantitative Separation of Metals. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim. Belg.*, 1908, 22, 327—338).—A new course shown in six tables and including the rarer metals. The process much resembles the ordinary course, but deviates from this in the treatment of the filtrate resulting from the action of hydrogen sulphide. This, after expelling the hydrogen sulphide by boiling, is mixed with an excess of sodium hydrogen phosphate, sodium hydroxide, and sodium hypobromite, and again boiled. L. DE K.

Detection and Estimation of Free Mineral Acids in Red Wines. CHARLES ASTRE (*Bull. Soc. chim.*, 1908, [iv], 3, 928).—The process depends on the partial separation of the mineral acid from the other constituents of the wine by dialysis. For quantitative purposes, parallel experiments are made with the suspected wine and with one of similar type, the dialysed products being titrated with *N*/10 alkali. Details as to the quantities to be used, &c., are given in the original. T. A. H.

Simple Method for the Estimation of the Halogen in Mercuric Chloride and Mercuric Bromide. MORITZ KOHN (*Zeitsch. anorg. Chem.*, 1908, 59, 271—272).—Mercuric chloride and bromide are decomposed by alkaline solutions of hydrogen peroxide more readily than the iodide (compare this vol., ii, 696). Metallic mercury separates, and is filtered off after the solution has been heated to near its boiling point to remove the excess of hydrogen peroxide. The halogen in the solution is then estimated by means of silver nitrate. H. M. D.

Rapid Estimation of Sulphur in Coals. ABRAM KOMAROWSKY (*Chem. Zeit.*, 1908, 32, 770).—A combination of Brunck's process of combustion with cobaltic oxide and sodium carbonate in a current of oxygen (Abstr., 1905, ii, 762) and the author's barium chromate method (Abstr., 1907, ii, 577). L. DE K.

Estimation of Sulphur in Mineral Sulphides. V. HASSREIDTER (*Bull. Soc. chim. Belg.*, 1908, 22, 308—316).—A review of the recent methods proposed, particularly that recommended by Lunge. The author is of opinion that the problem of exact estimation of sulphur is not as yet quite solved, especially in the case of zinc ores.

L. DE K.

Estimation of Sulphurous Acid in Gelatins and other Foods. L. PADÉ (*Ann. Chim. anal.*, 1908, 13, 299—301).—Twenty grams of dry gelatin, or 100 grams of jelly, are placed in a flask containing 500 c.c. of boiled water. The flask is fitted with a cork through which pass the usual inlet and outlet tubes and also a separating funnel containing 25 c.c. of syrupy phosphoric acid. After twelve hours, a current of carbon dioxide is passed; the liquid is heated at 70°, and the free sulphur dioxide absorbed in nitrogen bulbs containing iodine solution. After an hour, the bulb-tube is changed, the phosphoric acid is introduced from the funnel, and the operation continued for another hour. In this way, the sulphur dioxide present as sulphites is expelled.

The sulphur dioxide is converted by the iodine into sulphuric acid, which is then estimated gravimetrically.

L. DE K.

Ammonia Distillation in the Presence of Magnesium or Calcium Salts. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1908, 30, 1279—1281).—The time required for distilling off the ammonia in Folin's method of estimating carbamide (*Abstr.*, 1903, ii, 116) is three or four times greater than that required for ordinary ammonia distillations. Further, the results of such ammonia distillations show considerable variation, especially when made in the presence of magnesium or calcium salts. These facts are discussed, and an explanation is given.

The solvent action of ammonia or its salts on magnesium hydroxide is due to the following reaction: $\text{MgCl}_2 + 2\text{NH}_4\cdot\text{OH} \leftarrow \text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl}$. The liquid from which the ammonia is distilled in Folin's estimation contains a large excess of magnesium chloride, and some ammonium chloride, magnesium hydroxide, and ammonia. As the concentration of the magnesium hydroxide is extremely small and that of the magnesium chloride relatively great, equilibrium will not occur until most of the ammonia is in the form of ammonium chloride. A small amount of the ammonia is removed by distillation, and the equilibrium is disturbed, so that a further quantity of ammonium hydroxide is formed. This gradual change explains the slowness with which the ammonia passes over in carbamide estimations made with magnesium or calcium chloride. It has been found very difficult, if not impossible, to distil ammonia from an alkaline saturated solution of magnesium or calcium chloride. It is therefore evident that quantitative ammonia distillations should not be carried out in the presence of large quantities of magnesium or calcium salts.

E. G.

Electrolytic Estimation of Nitric Acid. OWEN L. SHINN (*J. Amer. Chem. Soc.*, 1908, 30, 1378—1381).—Easton (*Abstr.*, 1904, ii, 84) has studied the reduction of potassium nitrate to ammonia by

electrolysis in presence of copper sulphate. A further investigation was made by Ingham (Abstr., 1905, ii, 61), who, by employing a high current density and a rotating anode, obtained very accurate results. As several subsequent workers have been unable to obtain satisfactory results by this method, a series of experiments has been made in order to determine the best conditions. It has been found that Ingham's results can be obtained if the anode is rotated slowly so as to prolong the precipitation of the copper. The current should be about 4—5 amperes and 10 volts, and not more than about 20—25 c.c. of $N/5$ sulphuric acid should be present. It is sometimes necessary to add a second or even a third quantity of copper sulphate in order to complete the reduction.

E. G.

Detection of Nitrates in Wine and Must. T. MARSIGLIA (*Chem. Zentr.*, 1908, i, 2204; from *Staz. sperim. agrar. ital.*, 1908, 41, 162—170).—One hundred c.c. of the wine are concentrated in a flask to 15 c.c., and, when cold, 6 c.c. of a saturated solution of ferrous sulphate and 4 c.c. sulphuric acid are added and the liquid slowly boiled. By means of a condenser, the vapour is collected in a suitable vessel containing 2 or 3 c.c. of a specially prepared, acidified starch-potassium iodide solution. When nitrates are present in the wine, a blue ring is produced in the starch solution, either at once or in the second or third small fraction, according to the quantity present.

The starch solution is prepared by shaking starch with water, then warming on a water-bath, and adding zinc chloride; after again heating and allowing to cool, the potassium iodide is added. This method of detecting nitrates is not applicable to must, or wine of a high extract content; with such, the following method of Zecchini is advised. The must is evaporated to dryness with fresh lime on a water-bath, and then extracted with 96% alcohol and filtered; the filtrate is evaporated, extracted with water, and then submitted to the test described above for wine.

J. V. E.

Detection of Phosphoric Acid in Stones, Ores, and other Minerals. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 817—822).—The presence of phosphoric acid in minerals may be readily detected as follows: The finely-powdered mineral is first strongly heated in a crucible or iron tube in order to free it from water, organic matter, and carbon dioxide. From 0.080 to 0.100 gram of the cooled mineral is then mixed with approximately 0.3—0.35 gram either of magnesium or of a mixture of about 65% of magnesium and 35% of aluminium. The mass is introduced into an iron tube about 5—6 cm. long and 5 mm. in diameter, a loose plug of asbestos being placed above it. The tube is then heated until the lower end becomes dull red, after which it is rapidly cooled and the contents mixed with a thick wire and introduced into a test-tube with a spherical enlargement at the upper part. In this tube, the substance is gently heated with 20% potassium hydroxide solution, the gases evolved being passed through a calcium chloride tube and a plug of cotton wool, and over a strip of filter paper moistened with copper acetate slightly acidified with acetic acid. If phosphorus is present,

the filter paper blackens, owing to the formation of copper phosphide, and in moist air, gradually becomes decolorised, in consequence of the oxidation to colourless copper phosphite.

A dark coloration of the filter paper moistened with copper acetate is also determined by arsenic or nitrogen in the mineral. In the former case, the hydrogen arsenide sometimes gives a characteristic metallic arsenic deposit, which is not easily confused with the blackening due to the formation of copper phosphide, and which remains unchanged in the air. When nitrogen is present in small proportion, the small amount of ammonia evolved simply forms ammonium acetate, and the colour of the filter paper remains unchanged; when much ammonia is evolved, a dark blue solution of copper oxide in ammonia is formed on the filter paper, which changes to the cinnamon colour of cuprous oxide on heating. Experiment shows that magnesium does not absorb an appreciable proportion of nitrogen at a red heat.

T. H. P.

Titration of Phosphoric Acid in Superphosphates. S. KOHN (*Chem. Zeit.*, 1908, 32, 718—719).—A slight modification of the author's process (this vol., ii, 531). Fifty c.c. of the aqueous solution of the sample are diluted with 300 c.c. of water, and titrated with standard sodium hydroxide, using a mixture of methyl-orange and indigotin as indicator. Another 50 c.c. are then mixed with an excess of calcium chloride, and titrated without further dilution, using phenolphthalein as indicator. Salts of iron or aluminium do not interfere.

L. DE K.

Estimation of Phosphoric Acid as Phosphomolybdic Acid. P. CHRISTENSEN (*Zeitsch. anal. Chem.*, 1908, 47, 529—545. Compare Abstr., 1907, ii, 652).—The estimation of phosphoric acid by direct ignition of the precipitate of ammonium phosphomolybdate was found to be trustworthy for the analysis of soils if carried out in the following manner. A known volume of the extract of the soil (equivalent to about 33 grams of the latter) is evaporated to dryness after the addition of a few drops of nitric acid; the residue is then moistened with a little nitric acid, again evaporated, and heated to a temperature of about 120° for fifteen minutes. The residue is next treated with about 25 c.c. of boiling water and a few drops of nitric acid, the silica is collected on a filter, and washed with water until the filtrate measures about 40 c.c. The filtrate is neutralised by the addition of ammonia, D 0.91, a further 8 c.c. of ammonia are added, and then 10 c.c. of concentrated nitric acid. The mixture is heated to about 50°, and, when all the precipitated ferric hydroxide has re-dissolved, molybdic acid solution is run in with constant stirring. About 10 c.c. of the latter solution are added for every 0.1 gram of phosphoric oxide present. After the lapse of three hours, the precipitate is collected on a filter, washed with a 5% ammonium nitrate solution containing 1% of nitric acid, dried, and ignited at a temperature not exceeding a dull red heat; the filter paper is burnt before adding the precipitate to the crucible, and the latter is not covered until the ignition is nearly

completed. The weight of the precipitate multiplied by 0.0394 gives the quantity of phosphoric oxide.

W. P. S.

Direct Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. EMIL RABEN (*Zeitsch. anal. Chem.*, 1908, 47, 546).—As ammonium nitrate is readily soluble in alcohol, the yellow precipitate of ammonium phosphomolybdate obtained in the usual way in the estimation of phosphoric acid may be washed with alcohol, and weighed. The precipitate is collected on an asbestos filter, washed with ammonium nitrate solution, then a few times with warm 70% alcohol, once with absolute alcohol, and, finally, with a little ether. The precipitate is dried to constant weight at a temperature of 110–120°.

W. P. S.

Pemberton's Method for the Estimation of Phosphoric Acid. G. H. G. LAGERS (*Zeitsch. anal. Chem.*, 1908, 47, 561–571. Compare Abstr., 1907, ii, 907).—The method was found to give trustworthy results if the solution containing the water-soluble phosphoric acid received the addition of at least 58 milligrams of sulphuric acid before the phosphoric acid was precipitated with the molybdate reagent. When smaller quantities of sulphuric acid (compare Abstr., 1905, ii, 419) were added, the results obtained were too low.

W. P. S.

Detection of Traces of Arsenic in Various Substances, and the Sensibility of the Usual Methods. C. H. NIEUWLAND (*Chem. Weekblad*, 1908, 5, 558–561).—Sjollema's method (this vol., ii, 224) can be applied to the detection of traces of arsenic in milk, urine, wheat-meal, beef-suet, calico, beer, wall-paper, bones, bone-marrow, and yams. The arsenic was introduced by means of a solution of potassium arsenite containing 0.1 milligram of arsenious oxide per c.c. Gutzeit's test is more delicate; but with not less than 0.05 milligram of arsenious oxide, Sjollema's method enables arsenic to be distinguished from antimony and phosphorus.

A. J. W.

Detection of Boric Acid in Foods by means of Turmeric Paper. FRANCISCO P. LAVALLE (*Chem. Zeit.*, 1908, 32, 816–817).—In order to render turmeric paper more delicate, it has been recommended to extract the turmeric powder with benzene before preparing the tincture. The author states that a reaction for boric acid obtained by means of this paper must on no account be taken as proving a wilful addition of boric acid; the reaction is too delicate, showing the (apparent) presence of boric acid even in such reagents as pure hydrochloric acid, sodium chloride, &c.

L. DE K.

The Estimation of Graphite. FRANK BROWNE (*Chem. News*, 1908, 98, 51).—The author has studied the influence of heat on the conversion of ferric oxide into the magnetic oxide, and, as a result, has devised the following process for the estimation of graphite: Some ferric oxide is heated to redness in a covered crucible for two to three hours; the resulting oxide is a nearly black, slightly coherent magnetic powder. About 5 grams of this oxide are heated in an uncovered

wide mouthed crucible at a pale red heat for an hour, with occasional stirring; after weighing, 0.5 gram of graphite is added and heated as before for one or two hours, with occasional stirring, again weighing. The carbon is burnt off, and the oxide remains unchanged. The results agree fairly closely with those obtained by the potash fusion method. The mineral matter of coal may be estimated in the same way, but the amount found will be about 0.5 per cent. higher than when estimated in the ordinary manner, owing, probably, to interaction of the constituents of the ash.

P. H.

Estimation of Potassium in Silicates. WILHELM AUTENRIETH (*Centr. Min.*, 1908, 513—517).—The mineral is decomposed by heating with hydrofluoric and sulphuric acids. When dry, the mass is extracted with boiling water, and the solution freed from iron, etc., by boiling with excess of sodium acetate. After concentrating to about 20 c.c., the potassium is precipitated as cobalt-yellow by addition of 5—10 c.c. of de Koninck's cobalt reagent. As, however, the precipitate is not of constant composition, it is dissolved in hydrochloric acid, and the residue left on evaporation is treated for potassium by the well-known perchlorate method. The potassium may be estimated also by the usual platonic chloride method; in this case, the cobalt must be eliminated by gently igniting the precipitate and extracting the mass with hot water.

The cobalt reagent is prepared by dissolving 30 grams of crystallised cobalt nitrate in 60 c.c. of water, adding 100 c.c. of a saturated solution of sodium nitrite, and then 10 c.c. of glacial acetic acid. After a few days, the reagent is poured off from any deposit, and is then fit for use; it keeps, in the dark, for about a month.

L. DE K.

Estimation of the Alkaline Earths [in Waters] by means of Potassium Stearate and Phenolphthalein. C. BLACHER and J. JACOBY (*Chem. Zeit.*, 1908, 32, 744—745).—The carbonates are first titrated with *N*/10 hydrochloric acid, using methyl-orange as indicator, and the carbon dioxide is removed by a current of air. Phenolphthalein and a few drops of alcoholic *N*-alkali are added, and the liquid is decolorised with *N*/10 hydrochloric acid. After adding an extra 0.02 c.c. of acid, the total hardness is determined by titrating with *N*/10 potassium stearate until the liquid turns red. The calcium is estimated in the presence of magnesium by placing 200 c.c. of the water in a flask and weighing the same. After neutralising with *N*/10 hydrochloric acid, the carbon dioxide is boiled off, 1—3 c.c. of *N*-alcoholic alkali is added, and the loss in weight restored by adding water free from carbon dioxide. The liquid is filtered while still hot, and, when cold, 100 c.c. are neutralised as directed, and the calcium is titrated with the stearate solution. Sulphates may be titrated indirectly by precipitating with a slight excess of barium chloride and determining the excess with the stearate solution, allowance being made for any calcium and magnesium present.

The reagent is prepared by dissolving 28.4 grams of stearic acid in 400 c.c. of hot alcohol and 250 grams of glycerol, and neutralising

with alcoholic potassium hydroxide. When cold, the whole is diluted with alcohol to one litre. If desired, the solution may be checked with lime-water and *N*/10 acid.

L. DE K.

Volhard's Copper Titration. H. THEODOR (*Chem. Zeit.*, 1908, 32, 889—890).—Volhard's process (precipitation of copper in presence of sulphurous acid with ammonium thiocyanate and estimation of the excess of the latter with silver solution) is strongly recommended.

L. DE K.

Analysis of Bronzes, Brass, and Similar Alloys. E. SCHÜRMANN and H. ARNOLD (*Chem. Zeit.*, 1908, 32, 886—887).—The solution of the alloy, which should contain, besides tartaric acid, about 5% of free nitric acid, is submitted to electrolysis; conditions, $1\frac{1}{2}$ amperes and 4 volts. This precipitates the copper only (which, however, should be examined for traces of tin), whilst antimony and tin remain in solution. After rendering alkaline with potassium hydroxide, lead and any copper still present are precipitated by cautious addition of potassium sulphide, and then treated by the usual methods. The filtrate is boiled with addition of 0.5 c.c. of hydrogen peroxide, and, after neutralising with oxalic acid, an aqueous solution of 5 grams of that acid is added. The liquid is diluted to 400 c.c., heated to boiling, and treated with hydrogen sulphide to precipitate the antimony, which is then collected, dissolved in sodium sulphide, and submitted to electrolysis. The filtrate from the antimony is neutralised with ammonia, acidified with acetic acid, heated to boiling, and treated with hydrogen sulphide. The tin sulphide is then converted as usual into tin oxide.

A number of test-analyses are given.

The process is also applicable to the analysis of brass. After the copper has been separated electrolytically, the liquid is treated with hydrogen sulphide, and the precipitate submitted to the usual process. The filtrate containing the zinc is then analysed for zinc in the ordinary way.

L. DE K.

Estimation of Manganese in Iron and Manganese Ores. MAX ORTHEY (*Zeitsch. anal. Chem.*, 1908, 47, 547—560).—The results of a critical examination of some of the methods now in use for the estimation of manganese are given, particular attention being paid to the more rapid volumetric processes. For the estimation of manganese in iron and manganese ores, the methods proposed by Volhard-Wolff, von Knorre (*Abstr.*, 1902, ii, 108), and Blair (*Abstr.*, 1904, ii, 683) were found to be trustworthy, the results obtained agreeing well with those yielded by the ordinary gravimetric method.

W. P. S.

Direct Combustion of Steel for Carbon and Sulphur. HELEN ISHAM and JOSEPH AUMER (*J. Amer. Chem. Soc.*, 1908, 30, 1236—1239).—Experiments showing that the carbon in steel is almost completely eliminated by direct ignition in a current of

oxygen, whereas the sulphur cannot be expelled completely in this manner.

The results for carbon average 0.004% more than those obtained by the usual copper chloride method. L. DE K.

Loss of Carbon during Solution of Steel in Potassium Cupric Chloride. ERNEST P. MOORE and JAS. WATSON BAIN (*J. Soc. Chem. Ind.*, 1908, 27, 845—846).—In order to ascertain whether there is actual loss of carbon when steel is dissolved in potassium cupric chloride solution, the authors carried out experiments in which the samples of steel were dissolved in the solution in a flask through which a current of air free from carbon dioxide was passed. After leaving the flask, the air was passed over heated cupric oxide, and then through barium hydroxide solution. The barium carbonate formed was collected and estimated. From the results obtained, it is seen that the loss of carbon from 1 gram of steel amounted to from 0.0004 to 0.0005 gram. The two samples of steel used in the experiments contained 0.653 and 1.18% of carbon respectively.

W. P. S.

Pure Ferric Oxide as a Standard Substance for the Estimation of Iron in Hydrochloric Acid Solution. L. BRANDT (*Chem. Zeit.*, 1908, 32, 812—814, 830—832, 840—843, 851—853).—A lengthy article, unsuitable for adequate abstraction. The chief point is the preparation of a pure oxide of iron, which may then be dissolved in hydrochloric acid, and serve for the standardising of the permanganate after the usual reduction with stannous chloride.

About 50 grams of a commercially-pure iron free from zinc are dissolved in hydrochloric acid, and a current of hydrogen sulphide is passed. The filtrate is boiled, and oxidised with nitric acid. The solution is concentrated, and evaporated twice with hydrochloric acid. The mass is dissolved in hydrochloric acid, D 1.104, and shaken repeatedly in a separating funnel with ether, which dissolves the ferric chloride. Should the iron contain cobalt, this will also pass into the ether, but may be removed by shaking the ether with 1/10 of its volume of hydrochloric acid, D 1.104, saturated with ether. The ether is evaporated, and the residual ferric chloride converted into nitrate by repeated evaporation with excess of nitric acid, and, finally, with addition of ammonium nitrate. The dry mass is now ignited in a platinum dish, finally with addition of ammonium carbonate, until the weight is constant to about 0.01 gram.

L. DE K.

Detection and Estimation of Nickel and Cobalt. M. EMMANUEL Pozzi-Escot (*Chem. Zeit.*, 1908, 32, 804).—A reply to Grossmann (this vol., ii, 230). The author upholds the accuracy of his own molybdate process.

L. DE K.

Ammonium Molybdate as a Reagent for Nickel. HERMANN GROSSMANN and BERNARD SCHUCK (*Bull. Soc. chim.*, 1908, [iv], 3, 894. Compare this vol., ii, 230).—A reply to Pozzi-Escot (this vol., ii, 231).

T. A. H.

Detection of Chromium. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 333).—The solution, which, besides chromium, may contain a large excess of iron, manganese, cobalt, nickel, copper, &c., is heated to boiling, a solution of sodium hypobromite containing a large excess of alkali is added, and the boiling is continued for a few minutes. When cold, the solution is filtered, and the chromate formed is identified by the usual tests, such as lead acetate and acetic acid.

L. DE K.

Estimation of Chromium and Tungsten in Steel. F. WILLY HINRICHSEN and LUDWIG WOLTER (*Zeitsch. anorg. Chem.*, 1908, 59, 183—197).—Attempts were made to separate tungsten and chromium by precipitating the former as tungstic acid with nitric acid, but the precipitation was incomplete. On the other hand, reduction of the chromate to chromic salt and precipitation with ammonia gave too high results. Good results were finally obtained by precipitating the tungsten (and a small part of the chromium) with benzidine hydrochloride according to Knorre (*Abstr.*, 1905, ii, 286), the amount of chromium in the precipitate being determined by oxidising to chromate and estimating with potassium iodide and thiosulphate in the usual way. With certain precautions, the presence of tungstic acid does not interfere with the iodometric estimation of chromium.

In the presence of chromium, the results for tungsten obtained by the benzidine method are somewhat too low, and this point is under investigation.

On the other hand, satisfactory results for both metals were obtained by precipitating both chromium and tungsten from an aliquot part of the solution by means of mercurous nitrate (Berzelius) and estimating the chromium in another portion of the solution by the iodometric method. The precipitation is done as follows: To a portion of the solution containing chromate and tungstate, heated to boiling, a saturated solution of mercurous nitrate is added, and then 10% ammonia added drop by drop until the precipitate becomes dark brown. The mixture is then boiled, filtered, dried, ignited, and the mixture of acids weighed.

G. S.

Estimation of Vanadium, Molybdenum, Chromium, and Nickel in Steel. ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, 1908, 30, 1229—1233).—Two grams of the sample are converted into syrupy ferric chloride, which is then dissolved in a little hydrochloric acid, D 1.1. The solution is shaken first with 80 c.c. and then again with 50 c.c. of ether, which dissolves the iron and also the molybdenum. The ether is then shaken with water, and the aqueous solution evaporated with excess of sulphuric acid. The ferric sulphate is then dissolved in water, and reduced by boiling with ammonium hydrogen sulphite. The molybdenum is precipitated by means of a current of hydrogen sulphide, collected in a Gooch crucible, and converted into trioxide by cautious ignition. As it always contains a little iron, it is dissolved off the filter by means of dilute ammonia, and the crucible is re-weighed.

The liquid which has been extracted with ether is repeatedly

evaporated with nitric acid to a syrupy condition, dissolved in 20 c.c. of hot water, and, after reducing any chromate formed by means of sulphurous acid, poured into a boiling 10% solution of sodium hydroxide. The precipitate contains the oxides of chromium and nickel, also the bulk of the manganese, and traces of iron and copper. The filtrate, which contains the vanadium and sometimes a trace of chromium, besides any silica and alumina, is acidified faintly with nitric acid, and then again rendered slightly alkaline and boiled to remove the last traces of chromium. To the filtrate are added 10 c.c. of 10% lead nitrate and then a little acetic acid, and, after boiling for a few minutes, the lead vanadate is collected and evaporated with a large excess of hydrochloric acid to effect reduction. The hydrochloric acid is then completely expelled by evaporation with 10 c.c. of sulphuric acid, and the residue, after being diluted to 150 c.c., is titrated for vanadium at 60—70° with standard permanganate. The filters containing the two precipitates from the soda solution are burnt, and the ash fused with 2 grams of sodium carbonate and 0.5 gram of potassium nitrate. The mass is then extracted with water. The insoluble portion contains nickel, copper, iron, and part of the manganese. It is dissolved in hydrochloric acid, the copper is removed by hydrogen sulphide, and the filtrate evaporated with excess of sulphuric acid. The residue is diluted with water, excess of ammonia is added, and the nickel deposited electrolytically. The filtrate, which contains the chromium and the remainder of the manganese, is mixed with excess of ammonium nitrate and evaporated with addition of ammonia; this precipitates the manganese, also any silica and alumina. The filtrate is then boiled, reduced with sulphurous acid, and the chromium precipitated by ammonia and weighed as oxide.

L. DE K.

Estimation of Vanadium in Iron and Steel. EDWARD DE MILLE CAMPBELL and EDWIN LEGRAND WOODHAMS (*J. Amer. Chem. Soc.*, 1908, 30, 1233—1236).—Five grams of the sample are dissolved in dilute sulphuric acid, and the insoluble matter, which contains part of the vanadium, is collected and burnt, and finally treated with hydrofluoric acid to expel silica. The soluble portion is treated with hydrogen sulphide and evaporated to about 35 c.c., and the greater portion of the ferrous sulphate precipitated by addition of 100 c.c. of alcohol. The filtrate is oxidised with hydrogen peroxide, boiled, and precipitated with sodium carbonate. The precipitate is collected, and to it is added the residue from the first step of the analysis. The whole is fused with sodium carbonate, and then 300—400 milligrams of charcoal are added and the heating continued for ten minutes in the covered crucible. The object of the charcoal is to reduce any chromate formed; sodium vanadate is not affected.

The mass is now extracted with hot water, 10 c.c. of sulphuric acid, D 1.51, are added, and then 3—4 c.c. of 3% potassium permanganate. After boiling for five minutes, sulphurous acid is added until the permanganate has been reduced and the vanadic acid converted into the blue divanadyl sulphate. The solution is then evaporated until sulphuric fumes appear, and, when cold, water is added up to

60 c.c. and the warm liquid titrated with $N/20$ permanganate, 1 c.c. of which = 0.00256 gram of vanadium. L. DE K.

Estimation of Alcohol in Fermented Liquids. WM. ANTONI (*J. Amer. Chem. Soc.*, 1908, 30, 1276—1278).—The wine or other alcoholic liquid is introduced into a specially constructed pyknometer of the Sprengel type, brought to the required temperature by immersion in a bath, and weighed. By means of a rinsing arrangement, the wine is introduced into the distilling flask, and the distillate is collected in the pyknometer, which is then carefully filled up with water and reweighed. For details, the original paper and illustrations should be consulted. L. DE K.

Detection of Formaldehyde. FRANZ VON FILLINGER (*Zeitsch. Nahr. Genussm.*, 1908, 16, 226—231).—The paper is written with the object of drawing general attention to the usefulness of the test described by Hehner for the detection of formaldehyde. The author discusses the chemistry of the reaction (compare Abstr., 1907, ii, 512), and gives general directions for its application. W. P. S.

The Value of the Different Methods Used for Estimating Sugar in Urine. CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1908, 56, 507—511).—Bertrand's method for estimating sugars (Abstr., 1907, ii, 136) gives very good results for urines, except when β -hydroxybutyric acid is present.

Bang's method gives good results with pure sugar solutions, but not with urines. Borchardt's suggestion, that diabetic urine contains an unknown laevorotatory sugar, is not accepted. J. J. S.

Estimation of Reducing Sugars. FRITZ ZERBAN and W. P. NAQUIN (*J. Amer. Chem. Soc.*, 1908, 30, 1456—1461 *).—The cuprous oxide formed by the action of the reducing sugar on Fehling's solution is collected in a Munro-Neubauer crucible, and the precipitate is converted into copper oxide by heating for ten minutes over a Bunsen flame.

In some cases there may be present co-precipitated mineral matter; the real amount of copper oxide must then be estimated by some accurate method, such as Low's volumetric process.

Some sugars contain reducing substances other than sugar. In such cases, clarification with normal lead acetate is resorted to, which will partly remove such matters. L. DE K.

Detection and Identification of Certain Reducing Sugars by Condensation with *p*-Bromobenzylhydrazide. E. C. KENDALL and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1908, 30, 1451—1455).—The reagent is prepared by heating on a water-bath a mixture of 10 grams of ethyl *p*-bromobenzoate, 8.2 grams of a 50% aqueous solution of hydrazine hydrate, and 12 c.c. of 95% alcohol. After four hours, the alcohol is distilled off, and the residue, after being washed with ether, is recrystallised from alcohol.

The test is applied by heating about 0.03 gram of the sugar with

* and *Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 177—182.

twice its weight of the reagent in presence of alcohol. After evaporating three or four times with alcohol, the residue is boiled with chloroform and a few drops of water, which leaves the condensation product undissolved. The reaction is obtained with dextrose, galactose, mannose, and arabinose; not with lævulose, maltose, or lactose, and only to a slight extent with xylose.

The *p*-bromobenzylhydrazone of galactose is insoluble in boiling alcohol, those of mannose and arabinose are dissolved partly, whilst that of dextrose is completely dissolved. The non-reacting sugars, however, interfere with the formation of the dextrose hydrazone to an extent comparable with the interference of maltose and lactose in the ordinary osazone reaction for dextrose.

L. DE K.

Test for Pentoses with Orcinol and Hydrochloric Acid. J. PIERAERTS (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 46—62).—Sugars with a keto-group, such as lævulose, produce colorations with orcinol and hydrochloric acid which obscure the colour given by pentoses; hence lævulose and its anhydrides should first be eliminated by fermentation with yeast. In employing the orcinol reagent of Tollens, it is advisable to add an additional volume of concentrated hydrochloric acid to the mixture of one volume of the reagent with one volume of the pentose solution.

G. B.

Formic Acid in Glacial Acetic Acid. H. OST and F. KLEIN (*Chem. Zeit.*, 1908, 32, 815—816).—Wegener's process for formates is recommended. Ten c.c. of the sample are heated with 50 c.c. of sulphuric acid in a flask from which the air has been expelled by a current of carbon dioxide. The mixture is heated on the water-bath for one hour, and the gas evolved collected, with the usual precautions, over aqueous potassium hydroxide; 100 c.c. of carbon monoxide = 0.2056 gram of formic acid.

Good results are also obtainable in the case of weaker acids with Lieben's permanganate or Macnair's dichromate process, or with the mercuric chloride reduction method.

L. DE K.

Estimation of the Acidity of Wines. G. FAVREL (*Ann. Chim. anal.*, 1908, 13, 315—316).—Three official methods are in use. Titration with sodium hydroxide, using phenolphthalein as indicator; the same, using red litmus paper; titration with lime water until a grey, flocculent precipitate forms. The author states that there is a great discrepancy between the results obtained by the first and the last two methods, and expresses the hope that analysts will adopt a definite process.

L. DE K.

Indirect Estimation of the Acidity of Wines. G. FAVREL (*Ann. Chim. anal.*, 1908, 13, 343—346).—Ten c.c. of the wine free from carbon dioxide are placed in a separating funnel, and 20 c.c. of *N*/20 sodium hydroxide free from carbonate are added. A quantity of benzoic acid, known from a previous experiment to neutralise exactly the soda, is introduced, and the whole is well shaken. The liquid, which now contains free benzoic acid equivalent to the acidity of the

wine, is shaken twice in succession with 40 c.c. of ether, and this is slowly distilled until about 20 c.c. are left. The residue is allowed to evaporate in a beaker, and the flask is rinsed first with 10 c.c. and then with 5 c.c. of alcohol, which is poured into the beaker. The alcoholic solution is then titrated with $N/20$ sodium hydroxide, using phenolphthalein as indicator.

L. DE K.

New Method of Estimating the Fixed and Volatile Acids in Wine. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1908, 147, 245—247; *Bull. Soc. chim. Belg.*, 1908, 22, 338—340; *Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 68—69).—The method is based on the transformation of the barium salts of the fixed acids into carbonates by suitable heating and titration of these by standard acid. Two samples, each of 100 c.c., are concentrated to 3—4 c.c. in flat porcelain capsules. The product of the first is treated with an excess of alcohol, filtered, and the filter calcined in a muffle furnace. The alkalinity of the ash is determined by titration with standard nitric acid, using methyl-orange as indicator. The second sample, after evaporation, is neutralised with baryta, and treated with 100 c.c. of a 2% solution of barium bromide in alcohol (96%). The barium salts of the fixed organic acids (except lactic acid) are precipitated immediately and completely; they are filtered off, washed with strong alcohol (in which the barium salts of the volatile acids are soluble), drained, and calcined in a porcelain capsule in a muffle furnace. The carbonates formed are titrated against standard nitric acid, and the result, after deduction of the value obtained from the first experiment, corresponds with the acidity of the wine due to the fixed acids. Subtraction of the acidity due to the fixed acids from the total acidity of the wine, determined on 100 c.c., using phenolphthalein as indicator, gives the acidity due to the volatile acids. The author claims that the method is rapid and simple. It is only applicable to the estimation of organic acids, and is inexact in the presence of lactic acid, but the presence of the latter in wines is quite exceptional.

E. H.

The Natural Citric Acid of Wine. E. DUPONT (*Ann. Chim. anal.*, 1908, 13, 338—343).—A study of the Denigès mercury test for citric acid. Most wines from the South of France give the reaction, but, unless they are preserved by mean of sulphur dioxide, the acid disappears within a few months. The author thinks the reaction may be made approximately quantitative. As comparison liquid should be used a wine itself free from citric acid, but to which a known quantity of the acid has been added.

L. DE K.

Estimation of Malic Acid in Food Products. H. W. COWLES, jun. (*J. Amer. Chem. Soc.*, 1908, 30, 1285—1288).—The process is devised for the estimation of malic acid in maple products, but may, of course, be applied to other products, such as cider, cider vinegar, etc.

6.7 Grams of the sugar or syrup are dissolved in 5 c.c. of water, and 2 c.c. of 10% calcium acetate are added, followed by 100 c.c. of 95% alcohol, and the whole is warmed on the water-bath until the precipitate has settled completely. The precipitate is washed free from soluble

matters with 85% alcohol and then burnt to carbonate. This is then estimated as usual by dissolving in *N*/10 hydrochloric acid and titrating back with *N*/10 sodium hydroxide. The alkalinity represents the malic acid. L. DE K.

Estimation of Tartaric Acid in the Presence of Malic and Succinic Acids. L. GOWING-SCOPES (*Analyst*, 1908, 33, 315—319).—The author has submitted the method proposed by Ferentzy (Abstr., 1907, ii, 991) to a critical examination, and finds that it is trustworthy. It is stated, however, that more accurate results may be obtained by titrating the magnesium basic tartrate with potassium permanganate than by igniting it as recommended by Ferentzy. The method may be applied to the estimation of tartaric acid in fruit juices, and in wines if the tannic acid is first removed. W. P. S.

Estimation of Lactic Acid ; Comparison of Methods. JOSEF TRUMMER (*Chem. Zentr.*, 1908, ii, 101 ; from *Zeitsch. landw. Vers.-Wesen Oesterr.* 1908, 11, 492—505. Compare Abstr., 1903, ii, 189).—The method of Kunz (Abstr., 1901, ii, 700), with some slight modification, is applicable in all cases for the estimation of lactic acid, and gives more trustworthy results than does the method of Möslinger (Abstr., 1902, ii, 181). J. V. E.

A New Process for the Estimation of Lactic Acid in Organs and Animal Fluids. I. Estimation of Lactic Acid in Aqueous Solutions. ERNST JERUSALEM (*Biochem. Zeitsch.*, 1908, 12, 361—378).—The lactic acid is estimated by oxidising to acetaldehyde : $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CHO} + \text{CO}_2 + \text{H}_2\text{O}$, and estimating the aldehyde thus formed by treating with excess of iodine in alkaline solution, and afterwards estimating the excess not used for the formation of iodoform from the aldehyde. To get trustworthy results, the oxidation must be carried out by warming the liquid containing the lactic acid with sulphuric acid, and adding permanganate solution to the boiling mixture. The aldehyde as it is formed must be removed as quickly as possible from the boiling liquid ; this is accomplished by means of a current of air. The apparatus for the absorption of the aldehyde must also be very efficient, and one, specially devised, is figured in the original paper. In animal tissues, other substances are found which will interfere with the accuracy of the determinations, especially the sugars and acetone. Tissues must therefore be evaporated down and extracted with ether, and the lactic acid estimated in the ethereal extract. S. B. S.

A New Process for the Estimation of Lactic Acid in Organs and Animal Fluids. II. Estimation of Lactic Acid in Animal Fluids. ERNST JERUSALEM (*Biochem. Zeitsch.*, 1908, 12, 379—389).—In estimating the lactic acid in animal tissues and liquids, the acid must be first extracted with ether (see preceding abstract). Quantitative extraction can only be accomplished when the liquid to be extracted is so concentrated as to be of pasty consistency. A special apparatus for the extraction of such liquids is figured and described in

the paper, and also the application of the method to special cases, such as the estimation of lactic acid in blood, milk, urine, &c. S. B. S.

Detection and Estimation of Boric Acid, Salicylic Acid, and Benzoic Acid in Foods, etc. WILHELM VON GENERSICH (*Zeitsch. Nahr. Genussm.*, 1908, 16, 209—225).—The results of a critical examination of many of the methods proposed for the detection and estimation of these acids are given. Amongst others, the method described by Windisch (*Abstr.*, 1905, ii, 554) was found to be trustworthy for the estimation of boric acid, as was also Freyer's iodometric process for estimating salicylic acid. Benzoic acid is best extracted from food materials by means of benzene, or mixtures of the latter with light petroleum. The benzene solution of the acid may be evaporated after the addition of ammonia, or a portion of it may be titrated with standard alkali solution. W. P. S.

Detection of Benzoic Acid in Butter. GEORGES HALPHEN (*J. Pharm. Chim.*, 1908, [vi], 23, 201—203 *).—The test proposed is a modification of that described originally by Mohler, in which the benzoic acid is converted into ammonium diaminobenzoate; this salt, when treated with alkalis, gives a brownish-red coloration. The butter to be tested is melted, together with sufficient lime-water, to render the aqueous portion distinctly alkaline; after cooling, the aqueous portion is separated, rendered acid with phosphoric acid, and shaken out with ether. The ethereal extract is evaporated at the ordinary temperature, and the dry residue is dissolved in 2 c.c. of sulphuric acid, the mixture being heated slightly to dissolve the benzoic acid. When cold, 0.2 c.c. of fuming nitric acid is added, the solution is transferred to a test-tube, and heated, with constant agitation, over a small flame until it boils. The heating is then continued, without agitating the contents of the tube, until sulphuric acid vapours commence to be evolved. After cooling, 6 c.c. of water are added, and then saturated sodium sulphite solution, drop by drop, until all the yellow vapours have disappeared. Ammonia is then allowed to flow over the surface of the liquid, when, if benzoic acid is present, an orange-red coloration is obtained, the intensity of which depends on the quantity of benzoic acid in the sample. W. P. S.

Separation and Estimation of Salicylic Acid and Methyl Salicylate; Hydrolysis of Methyl Salicylate. H. D. GIBBS (*J. Amer. Chem. Soc.*, 1908, 30, 1465—1470).—*Estimation of Free Salicylic Acid in Oil of Gaultheria.*—Five to twenty c.c. of the ester are shaken with an equal volume of water, and titrated with *N*/50 sodium hydrogen carbonate, using Congo-red as indicator.

Preparation and Estimation of Salicylic Acid and Methyl Salicylate in Foods and Drugs.—The substance is extracted with *N*-sodium hydrogen carbonate, which dissolves the salicylic acid and also a portion of the ester; the remaining ester is recovered by acidifying with dilute sulphuric acid, and distilling in a current of steam; the ester is then shaken out with chloroform. The filtrate is shaken with chloroform to remove the dissolved ester, and the salicylic acid is

* and *Ann. Chim. anal.*, 1908, 13, 382—384.

recovered from the alkaline solution by acidifying and shaking with chloroform; finally, the acid is determined colorimetrically.

The chloroform extracts containing the ester are boiled in a reflux apparatus with excess of potassium hydroxide, and the salicylic acid formed is then estimated as directed.

For the methods of studying the rate of saponification of the ester by sodium hydroxide and carbonate, the original article and curve should be consulted. Methyl salicylate, on keeping, always becomes slightly hydrolysed.

L. DE K.

Characteristic Test for Hippuric Acid [in Urine]. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1908, 30, 1507—1508).—A few c.c. of the urine are treated in a test-tube with sodium hypobromite just sufficient to decompose the carbamide and impart a permanent, yellow colour. The solution is then heated to boiling, when, should hippuric acid be present, an orange or brownish-red precipitate is formed, which, however, consists partly of earthy phosphates.

The nature of the red precipitate, which contains nitrogen and bromine, has not yet been fully investigated. It is soluble in most of the organic solvents and in carbon disulphide.

L. DE K.

Apparatus for Estimating the Expansion of Oils and Other Liquids which Boil above 100°. WILHELM THÖRNER (*Chem. Zentr.*, 1908, i, 2001—2003; from *Zeitsch. chem. Apparatenkunde*, 1908, 3, 165—168).—The estimation of the expansion of oils and fats between 0° and 100° is advised as an additional means of identification. A Jena glass flask, having a long neck, which is graduated in 1/10 c.c. from the top downwards, and having a capacity of exactly 100 c.c. of distilled water at 100°, is nearly filled with the oil to be tested. The flask is then heated in a suitably arranged steam jacket to 100°, when the volume is made up exactly to the zero mark. The flask and contents are then placed in an ice-chest to cool down to 0°, when the difference in volume may be observed on the graduated neck of the flask. A table of results obtained with thirty-three substances is given, and it is shown that by this method the amount of acetic acid in water solutions may be estimated with a fair degree of accuracy.

J. V. E.

A New Reaction for Distinguishing between Heated and Unheated Milk, and for the Detection of Hydrogen Peroxide in Milk. W. PERCY WILKINSON and ERNEST R. C. PETERS (*Zeitsch. Nahr. Genussm.*, 1908, 16, 172—175).—The test is similar to the well-known *p*-phenylenediamine test, but benzidine is used in place of the latter. Ten c.c. of the milk to be tested are treated with 2 c.c. of a 4% alcoholic benzidine solution, from two to three drops of acetic acid, and 2 c.c. of a 3% hydrogen peroxide solution. With unheated milk, a blue coloration appears at once, whilst if the milk has been heated to a temperature of, or exceeding, 78°, no change in colour takes place. The test is stated to be more sensitive than the *p*-phenylenediamine reaction, and may be used, conversely, for the detection of hydrogen peroxide.

W. P. S.

Detection of Small Quantities of Turpentine in Lemon Oil. E. M. CHACE (*J. Amer. Chem. Soc.*, 1908, 30, 1475—1477).—Fifty c.c. of the sample are distilled in a Ladenburg 3-bulb flask. The first 5 c.c. of the distillate are mixed with an equal volume of glacial acetic acid and cooled in a freezing mixture, 5 c.c. of ethyl nitrite are added, and, after mixing, 2 c.c. of strong hydrochloric acid are added drop by drop. After fifteen minutes, the deposit is collected on a Büchner funnel, using filter-paper under vacuum. The crystals are washed with about 50 c.c. of 95(vol.)% alcohol, and the filtrate is replaced in the freezing mixture in order to obtain a second crop of crystals; after passing the liquid through the same filter, the crystals are washed with strong alcohol and dried.

The crystals are now dissolved in a small quantity of chloroform, and hot methyl alcohol is added until crystallisation sets in, when the liquid is cooled. More methyl alcohol is then added, and the crystals are collected. For microscopical examination, they may be mounted in olive oil. Turpentine yields very characteristic crystals.

L. DE K.

Some Reactions of Terpin. E. ISNARD (*Ann. Chim. anal.*, 1908, 13, 333—334).—*Action of Reagents on Crystallised Terpin.*—Moistened on a watch-glass with sulphuric acid, a coloration varying from chrome-yellow to salmon-rose is developed. At the same time, the terpin dissolves and emits a characteristic, aromatic resinous odour. On adding a 10% solution of sodium hydroxide, the colour disappears, but the odour becomes still more pronounced. Syrupy phosphoric acid behaves similarly, but no coloration is noticed until heat is applied. If terpin is dissolved in sulphuric acid and then acted on with nitric acid, a yellow coloration is observed, with formation of brown streaks; the solution then becomes colourless and resinified. If nitric acid is added first, the terpin dissolves to a colourless solution, but if now a drop of sulphuric acid is put on the centre, a red spot is formed surrounded by a salmon-rose zone. Terpin shows reducing properties, reducing molybdic and chromic acids in presence of sulphuric acid, and also an acid solution of ferric chloride and potassium ferricyanide.

Action of Reagents on the Alcoholic Solution of Terpin.—Sulphuric acid turns salmon-rose, whilst the alcoholic solution remains colourless. The coloration disappears on shaking, unless the solutions are very concentrated. With a solution containing 200 c.c. of 15% ammonium molybdate, 10 c.c. of sulphuric acid, and 30 c.c. of nitric acid, a blue coloration is obtained, which takes a long time to develop. After about an hour, it becomes indigo-blue, and after twenty-four hours it has changed to bluish-green. The colouring matter is soluble in chloroform. A white deposit is also formed, but this is probably ammonium molybdate precipitated by the alcohol. When heat is applied, the coloration is developed more rapidly, but soon fades; in this case, the characteristic odour is also noticed.

L. DE K.

General and Physical Chemistry.

Ultraviolet Spectrum of Silicon. ANTOINE DE GRAMONT and CHARLES DE WATTEVILLE (*Compt. rend.*, 1908, 147, 239—242).—The ultraviolet spectrum of silicon containing both lines and bands has been mapped between $\lambda 2123\cdot0$ and $\lambda 2987\cdot8$. The spectrum of the oscillating spark passing between silicon poles in hydrogen in a quartz tube gave 23 lines and 14 bands, whereas the flame spectrum obtained by burning ordinary gas impregnated with silicon chloride vapour contained 26 bands and 11 lines. The relative intensities of lines and bands common to both spectra were not the same.

The oscillation frequencies of the bands seem to fall into series, but the heads are ill-defined. R. J. C.

Dispersion in the Electric Spectra of Benzene, Toluene, and Acetone. A. R. COLLEY (*J. Russ. Phys. Chem. Soc.*, 1908, 40 (*Phys.*), 228—244).—The author has investigated the electrical spectra of benzene, toluene, and acetone, a method being used which permits of accurate measurements with small troughs in the case of liquids with low refractive indices. The results, which are given in the form of tables and curves, bring out the intimate chemical relationship between toluene and benzene, two bands being common to the two spectra. Further, the spectra of toluene and acetone also exhibit one common band, which must be regarded as typical for the methyl group. T. H. P.

Discontinuous Cathode Luminescence Spectra of Some Aromatic Compounds. OTTO FISCHER (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 305—326. Compare Goldstein, *Abstr.*, 1904, ii, 689, 690).—The emission spectra of the substances exposed to cathode rays at the temperature of solid carbon dioxide were photographed. Difficulties were found in certain cases, owing to the rapid change of colour of some substances under the influence of cathode rays. The ultraviolet spectra were not examined.

The number of luminous bands is with most aromatic substances considerable. In all the cases examined, the sharp edges of the bands are turned towards the red, the blue side being more or less indistinct. It is frequently possible to group the bands in series, corresponding pairs of which show a constant difference of wave-length.

In the case of naphthalene compounds, blue and violet light is only emitted for a short time, the colour changing to yellow or red. Three characteristic blue bands of naphthalene reappear in the spectra of all the naphthalene derivatives examined, and also in those of diphenyl and phenanthrene, but, whilst the last two compounds continue to emit these bands, the structure producing them is rapidly destroyed by the bombardment in the case of naphthalene derivatives. The same

bands appear, strongly shifted towards the red, in anthracene and dibromoanthracene.

C. H. D.

Influence of Temperature and of the State of Aggregation on the Absorption Spectra of Molten Salts. T. RETSCHINSKY (*Ann. Physik*, 1908, [iv], 27, 100—112).—An examination of the absorption spectra of some thirty molten inorganic salts has shown that, in all cases, there is a well-defined limit to the absorption band on the ultra-violet side of the spectrum, all radiations of smaller wavelength than that corresponding with the limiting value being completely absorbed. With rise of temperature, this limit is displaced in the direction of greater wave-lengths. When the displacement is expressed in terms of wave-lengths, its magnitude, for a given rise of temperature, increases with the wave-length; when expressed in terms of frequencies, the displacement is independent of the wave-length. For a temperature rise of 100° , the absorption limit is displaced to an extent represented by 10 to $20 \times 10^5/\mu\mu$.

Some of the salts have been also investigated in the solid state. The influence of temperature on the absorption limit is of the same order of magnitude as in the case of the molten substances. On liquefaction, the absorption limit is displaced considerably in the case of the chlorides and bromides of potassium and sodium, but no sharp change is met with in the case of silver nitrate, silver chloride, or lead chloride.

In regard to the influence of chemical composition on the absorption, it is found that the salts of the heavy metals absorb more than those of the alkali and alkaline-earth metals. In general, for a given metal the sulphate absorbs most light; then follow the chloride, bromide, iodide, and nitrate with gradually decreasing absorptions. For salts of the same acid containing metals belonging to the same group of the periodic system, the absorption limit is nearer the red end of the spectrum the greater the atomic weight of the metal.

H. M. D.

Fluorescence of Sodium Vapour. HANS ZICKENDRAHT (*Physikal. Zeitsch.*, 1908, 9, 593—603).—The thermal and electrical condition of fluorescing sodium vapour has been examined. In contact with air, fluorescence begins at 280 — 290° ; this temperature is independent of the pressure, although the sharpness with which the phenomenon sets in is much greater at higher pressures than at low. Measurements have been made of the minimum potential required for electrical discharge through the vapour under different conditions. For sodium vapour in contact with air, the potential temperature curves show minima at 240° and 280° ; the latter is supposed to correspond with the commencement of fluorescence. In contact with nitrogen and carbon dioxide, the minimum potential differences corresponding with this are 300° and 340° respectively. In contact with hydrogen, an olive-coloured fluorescence can be observed at 370° , but no current could be passed through the vapour with the available potential of 400 volts.

The properties of the vapour in contact with air have been examined in greater detail. Curves are plotted which show the dependence of the current on the discharge potential under different pressures, and also the dependence of the potential on the pressure and on the temperature for a given current intensity. When a current has been passed through the vapour for some time, a smaller potential is required for discharge immediately after the cessation of the current than when some time has elapsed. The potential gradually increases, and attains a constant value after some minutes. The paper concludes with a theoretical discussion of the cause of the conducting power of sodium vapour.

H. M. D.

Fluorescence of Organic Substances. JOHANNES STARK and W. STEUBING (*Physikal. Zeitsch.*, 1908, 9, 661—669. Compare Abstr., 1907, ii, 147, 417; this vol., ii, 138, 746).—Further observations relating to the fluorescence of substances containing chromophoric groups are communicated, and a summary is given of the results obtained in the series of papers published by Stark on the connexion between fluorescence and absorption.

The new substances examined were acetone, methyl ethyl ketone, pyrotartaric acid, phorone, diacetyl, camphor, camphorquinone, dimethylfulven, potassium azodicarboxylate, azodicarbonamide, diethylketen, and diphenylketen. From the observations, the conclusion is drawn that if a substance possesses two absorption bands, one in the region of longer wave-lengths, the other in the remote ultraviolet region, it will fluoresce in the region of the first band when light is absorbed in the region of the second. The fact that the maxima for the intensity of the fluorescence and absorption do not coincide is due to the absorption which the fluorescent light undergoes in its passage through the absorbing medium. The two azo-compounds investigated are exceptions to this general statement, but this is supposed to be due to the absence of the radiation of the requisite very short wave-lengths from the aluminium light used in the experiments.

H. M. D.

Ultraviolet Fluorescence of Cyclic Compounds. HEINRICH LEY and K. VON ENGELHARDT (*Ber.*, 1908, 41, 2988—2995. Compare Stark, Abstr., 1907, ii, 147; Stark and Meyer, *ibid.*, ii, 418).—The ultraviolet fluorescent, and the absorption, spectra of mono- and di-substituted benzene derivatives in ethyl-alcoholic solutions of $N/0.005$ concentration have been measured in an apparatus very similar to that used by Stark; the results confirm this investigator's theory of the relation between fluorescence and selective absorption.

Toluene and propylbenzene are more strongly fluorescent than benzene, and the four bands which characterise the fluorescent spectrum of benzene have disappeared in the spectra of these two homologues. The auxochromic influence of the amino-group is accompanied by an auxofluoric influence, since aniline is more fluorescent than benzene; dimethylaniline, however, is less fluorescent than aniline, although the contrary might be expected from Kauffmann's

view that the dimethylamino-group is a stronger auxochrome than the amino-group. The hydroxyl and the methoxyl groups also act as auxofluors, phenol and anisole exhibiting a remarkably strong fluorescence, whilst the very feeble fluorescence of benzoic acid is markedly increased in the hydroxybenzoic acids, of which the ortho-compound fluoresces most strongly, even in the visible region, as is evident to the naked eye, when a quartz lamp and a quartz vessel are used. Although anisole is more fluorescent than phenol, the methoxybenzoic acids are less so than the hydroxy-acids; the fluorescence of *p*-methoxybenzoic acid cannot be detected with certainty. The introduction of a halogen into the benzene nucleus diminishes the fluorescence, the more so the greater the molecular weight; iodo-benzene does not fluoresce. Benzonitrile is remarkably fluorescent. Benzamide is non-fluorescent, showing that the amino-group only has auxofluoric influence when situated in the nucleus.

The presence of a nitro-group often entirely prevents fluorescence, even although *o*- and *p*-nitrophenols and *o*-nitroaniline exhibit marked selective absorption (according to Stark's theory, fluorescence is conditioned by the presence of bands in the absorption spectrum). The non-fluorescence may be attributable to quinonoid structure (compare Baly, Edwards, and Stewart, *Trans.*, 1906, 89, 514; Hantzsch, *Abstr.*, 1906, i, 353), since simple quinones never fluoresce.

Neither pyridine nor ethyl collidinedicarboxylate exhibit fluorescence. Ethyl dihydrocollidinedicarboxylate, however, shows violet fluorescence in alcoholic solution, and also a very intense band; thus providing a good confirmation of Stark's theory. C. S.

Natural and Magnetic Rotation of the Plane of Polarisation in Crystals. WALDEMAR VOIGT and K. HONDA (*Physikal. Zeitsch.*, 1908, 9, 585—590).—Measurements of the natural rotation of the plane of polarisation for a series of wave-lengths are recorded for *d*- and *l*-sodium chlorate and *d*-tartaric acid in the direction of the optic axis, and for sucrose in the direction of the two axes. The rotation induced by a strong magnetic field was measured for sodium chlorate, dolomite, apophyllite, apatite, and sucrose. In the case of sucrose, the values obtained for the two optic axes indicate that the magnitude of the rotation of the plane of polarisation is different in the two directions. H. M. D.

Relation between Rotatory Power and Chemical Constitution. II. D. HARDIN (*J. Chim. Phys.*, 1908, 6, 584—591. Compare this vol., ii, 470).—The theoretical deductions given in the previous paper have been further tested by application to certain derivatives of hexyl alcohol.

The atomic product for oxygen (the product of the distance between the oxygen and carbon atoms and the atomic weight of the former element) is approximately the same as that calculated from observations on the amyl derivatives, but is of opposite sign. The difference of sign has not been satisfactorily accounted for.

The theory also indicates that the distance between the centre of gravity of the benzene ring and the first carbon in the side-chain will be different according as the bonds between carbon and hydrogen are in the plane of the ring or perpendicular to it. The experimental data obtained with hexylbenzene support the latter view as to the structure of the benzene nucleus.

Active hexyl alcohol (γ -methylamyl alcohol) was prepared by saponification of Roman camomile oil with cold concentrated potassium hydroxide solution and repeated fractionation. The fraction boiling at $151-152^\circ/758$ mm. has $D^{20.5}_D$ 0.8262, $[\alpha]^{20.5}_D$ $+8.77^\circ$, D^{30}_D 0.7812, $[\alpha]^{30}_D$ 7.53° , and D^{47}_D 0.7276, $[\alpha]^{47}_D$ 6.10° . The corresponding *bromide* has D^{19}_D 1.1852, $[\alpha]^{19}_D$ $+19.97^\circ$, D^{27}_D 1.1150, $[\alpha]^{27}_D$ 17.12° , and D^{142}_D 1.0319, $[\alpha]^{142}_D$ 13.97° . Active hexylbenzene (α -phenyl- γ -methylpentane) (compare Klages and Sautter, Abstr., 1904, i, 302), prepared by the action of sodium on a mixture of bromobenzene and hexyl bromide, has D^{19}_D 0.8521, $[\alpha]^{19}_D$ $+16.62^\circ$, D^{105}_D 0.7873, $[\alpha]^{105}_D$ 14.99° , and D^{168}_D 0.7396, $[\alpha]^{168}_D$ 13.66° .
G. S.

Optical Isomerides. I. IWAN OSTROMISLENSKY (*Ber.*, 1908, 41, 3035—3046).—The observations of Gernez on the separation of a *dl*-conglomerate by means of the addition of a fragment of a substance isomorphous with one of the components have been extended.

The addition of *l*-asparagine to a supersaturated solution of *dl*-sodium ammonium tartrate causes the deposition of the pure *d*-tartrate.

Both *d*-tartrate and *l*-asparagine are hemihedral forms belonging to the rhombic system, and are isomorphous.

An optically active salt can also be obtained by impregnating a supersaturated solution of *dl*-sodium ammonium tartrate with a crystal of an active modification of any other alkali tartrate; for example, Rochelle salt, potassium tartrate, sodium tartrate, potassium hydrogen tartrate. In all cases the salt which is deposited is dextrorotatory if the impregnating material is dextro, and lævo if this is lævorotatory. Inoculation with ordinary ammonium malate causes the deposition of *d*-sodium ammonium tartrate. Substances which are isodimorphous with the sodium ammonium tartrate can also be used for bringing about the separation. Thus a crystal of *d*-potassium ammonium tartrate (usually monoclinic) causes the deposition of *d*-sodium ammonium tartrate, and similarly with potassium tartrate.

It is not necessary that the material used for inoculation should be optically active; thus glycine added to a supersaturated solution of *dl*-asparagine causes the deposition of either *d*- or *l*-asparagine, and it is not possible in any given experiment to predict which of the two will separate from an inspection of the glycine crystals, although the same glycine crystal always acts in the same way. The conclusion is drawn that glycine belongs to the hemihedral class of rhombic prisms.

This method of deposition is suggested as a method for determining whether the given substance is a *dl*-conglomerate or a *r*-compound.

If the crystals deposited on impregnating with an isomorphous substance are found to be inactive, then the original solution contained

a racemic compound, but if active, then the original was an inactive conglomerate.

J. J. S.

Chemical Action of Light. GIACOMO L. CIAMICIAN (*Bull. Soc. chim.*, 1908, [iv], 3, i—xxvii).—A lecture delivered before the French Chemical Society.

E. H.

Chemical Action of Tropical Sunlight. GILBERT JOHN FOWLER (*Mem. Manchester Phil. Soc.*, 1908, 52, xiv, 1—20).—Observations are recorded on the rate of liberation of iodine from an acidified potassium iodide solution under the influence of light. The reaction is practically unaffected by temperature under the ordinary conditions of exposure. The rate of liberation of iodine from a given solution diminishes with the duration of the exposure; this is due to the absorption of the chemically-active rays by the iodine liberated previously. The initial rate of liberation diminishes with increasing dilution of the solution, but, on longer exposure, results in closer agreement are obtained, owing, no doubt, to the greater retarding effect of the iodine liberated from the stronger solutions.

Tables of data obtained by measurements made in Calcutta and on the Mediterranean and Arabian Seas are recorded. The highest record corresponds with an actinic effect which is forty-two times as great as the lowest record obtained on a bright December day in Manchester. No relationship appears to exist between the photochemical and the sun-stroke effect of sunlight.

Solutions of bleaching powder lose their available chlorine with great rapidity on exposure to tropical sunlight. The effect is much more marked in the case of dilute solutions than it is in strong solutions.

Silver chloride, sealed in a glass tube and darkened by exposure to light, becomes quite white again when kept for some time in the dark. In the presence of a globule of mercury, the original colour is not restored. These observations support the view that the darkening of silver chloride on exposure to light is a dissociation effect, and is not due to the formation of an oxychloride.

H. M. D.

Photochemical Reactions. III. Decomposition of Ozone by Light. FRITZ WEIGERT (*Zeitsch. Electrochem.*, 1908, 14, 591—597).—The decomposition of ozone by light in presence of chlorine (this vol., ii, 5) is studied quantitatively. The light of a mercury quartz lamp is used, and the rate of decomposition measured by means of the change of pressure of the gas. There is no induction period, and decomposition stops when the light is cut off. The rate of decomposition is independent of the concentration of the ozone; it increases with the concentration of the chlorine, but not in proportion to it, and it is nearly proportional to the intensity of the light. By placing a vessel containing chlorine between the source of light and the ozone tube, a measurement of the quantity of light absorbed by the chlorine is obtained; in this way it is shown that the rate of decomposition of the ozone is proportional to the quantity of light absorbed by the chlorine mixed with it. A rise of temperature of 10° increases the rate of reaction 1.17 times

It is suggested that the light produces some intermediate product which is destroyed rapidly by the action of ozone; the rate of decomposition measured is then the rate of formation of this product, which is independent of the concentration of the ozone. T. E.

Catalytic Reactions and Photochemical Equilibria. BARTOLO L. VANZETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 285—288).—The author has carried out experiments to ascertain whether catalytic action necessitates immediate contact of the catalyst and the substance acted on, or whether the action can take place at a distance. When detonating gas is separated from platinum-black by a sheet of glass, the thickness of which is of the same order of magnitude as the wavelength of light, no combination occurs between the hydrogen and oxygen. But when the separating layer consists of an organic material, such as gelatin or a colloid, the hydrogen and oxygen combine slowly, but combination is found to be preceded by diffusion of the mixed gases through the membrane, as is shown by the observation that the diminution of the gas volume per unit of time is proportional to the concentration (pressure) of the gas mixture (compare Ernst, *Abstr.*, 1901, ii, 495).

Experiments with platinum and platinum-black placed at a distance of 0.5—1 mm. from rapid bromide plates show that both these substances exert a negative action on the plate, that is, they take away the darkening produced in the sensitive emulsion by the action of light (compare Piltchikow, *Abstr.*, 1906, ii, 414). This action is, however, quite different from that of light, and from the Russel effect produced by certain metals, in that it is only manifested at the surface of the photographic film and penetrates the latter only very slowly. This negative effect of platinum is especially marked in moist air, is greatly diminished in a cathode-ray vacuum, and is not exhibited in air in presence of phosphoric oxide. Experiments with other metals show that these may be arranged in the following series, in the first part of which the metals exhibit a diminishing positive effect on a photographic plate, whilst in the latter part an increasing negative effect is produced: cadmium, zinc, aluminium, lead, iron . . . copper, tin, silver, palladium, iridium, nickel, gold, platinum. If the condition in a silver bromide plate is represented as an equilibrium between the two reactions $3\text{AgBr} \rightleftharpoons \text{Ag}_2\text{Br} + \text{AgBr}_2$, the upper of which is produced by the action of light, and the lower by the action of darkness, the action of platinum at a distance is to accelerate the latter change. T. H. P.

Chemical Changes Produced by Different Kinds of Rays.
I. **Catalytical Reactions of Sunlight.** CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 13, 305—320).—A large number of substances undergo chemical change when exposed in solution to sunlight in the presence of uranium salts. The following changes have been observed: Alcohols to aldehydes; poly-alcohols to hydroxy-aldehydes or ketones; acids to aldehydes or keto-compounds, sometimes with fewer carbon atoms than the original substance; monosaccharides to osones; disaccharides undergo inversion; polysaccharides and glucosides are

hydrolysed; amino-acids undergo deamidisation and lose carbon dioxide, yielding aldehydes with a smaller number of carbon atoms than the original substance; glycerides are partly hydrolysed; peptones and proteins are partly hydrolysed, and the hydrolysis products undergo the fuller changes noted above.

Amongst the products actually isolated by decomposition in sunlight in presence of uranium salts were: glycerose in the form of the osazone, m. p. 130—131°, from glycerol; glyoxal in the form of the *p*-nitrophenylosazone from tartaric acid; acetaldehyde (in the form of the *p*-nitrophenylhydrazone) from alanine, from which ammonia was also obtained; dextrose (in the form of the osazone) from inulin.

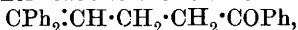
S. B. S.

Theory of Coloured Salts. HERMANN FECHT (*Ber.*, 1908, 41, 2983—2987).—The depth of the colour of many aromatic additive compounds appears to be conditioned by the magnitude of the difference of the electrical character of the two components; the more positive the one and the more negative the other, the deeper the colour. For example, quinone+phenol is red, quinone+sodium phenoxide is blue, and quinone+aniline in cold carbon disulphide yields a mass of dark violet crystals, which becomes colourless when the aniline is washed away. Again, diphenyldi-imine+benzidine gives a yellow solution, which becomes blue when the quinonoid component is made more negative by salt formation; the blue colour vanishes when the other component also enters into salt formation. Malachite-green becomes blue when chlorine is introduced into the phenyl group, and yellow when the halogen is attached to the still basic nitrogen atom. The effect on colour of the halogen atom or the hydroxyl or amino-group is not due to the influence of these *per se*, but depends on whether they increase or diminish the difference in the positive and negative characters of the components of the coloured substance.

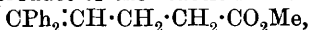
When chlorine is passed into a solution of di-iododiphenyl in chloroform, yellow crystals of the *dichloride*, $C_{12}H_8I_2Cl_2$, m. p. 146° (decomp.), are obtained. By heating the dichloride with benzidine in chloroform or carbon disulphide, a *substance*, $C_{24}H_{20}N_2Cl_2I_2$, is obtained in the form of a violet-blue powder, which sublimates and decomposes at 300°.

Equal molecular quantities of quinone and benzidine in chloroform yield a mass of bluish-violet needles with a red, metallic lustre, which melt indefinitely at 118°, resolidify, and decompose above 200°.

The reaction between methyl glutarate and excess of magnesium phenyl bromide in ether leads to the formation of the *ketone*,



m. p. 176°, which forms colourless crystals, and develops a bluish-green coloration with concentrated sulphuric acid. If the Grignard reagent is not in excess, the product of the reaction is the *ester*,



m. p. 120°.

C. S.

Rate of Decay of the Excited Radioactivity from the Atmosphere in Sydney. S. G. LUSBY and T. EWING (*J. Roy. Soc., New South Wales*, 1906, 40 158—160).—A copper wire, 10 metres

long, kept negatively charged at a potential of 25,000 volts, was after three hours' exposure rubbed with cotton wool moistened with ammonia. The cotton wool was incinerated, and the ashes tested for radioactivity; the time taken for the activity to fall to half value was on four days in December, 1905, found to be 41.5, 40.7, 41.9, and 39.5 minutes.

P. H.

Radioactivity of the Rocks in the Region Traversed by the Line to the Simplon. GINO GALLO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 209—214).—The author has examined the radioactivity of various rocks excavated in the laying of the railway line to the Simplon. The limestone-gypsums and the rocks of the calcareous schist zone are either quite inactive or very feebly radioactive. With the orthogneisses, however, the chemical composition and coefficient of acidity of which indicate that they belong to the eruptive granitic magmas, moderately intense radioactivity is observed, the maximum value found being 43.2 volt-hours. The radioactivity is, in general, accompanied by the presence of certain minerals, such as titanite and zirconia. The pyrites minerals are also moderately radioactive, but the radioactivity cannot be definitely attributed to the metallic sulphides, and not to the gneissic gangue accompanying them. Borne (*Jahrb. Radioaktiv. Elektronik*, 1905) has shown that, of the springs issuing from these rocks, those which are richest in emanation have their origin in the gneiss or in the granitic rocks.

T. H. P.

Preliminary Observations on Radioactivity and the Occurrence of Radium in Australian Minerals. D. MAWSON and T. H. LABY (*J. Roy. Soc., New South Wales*, 1905, 38, 382—389).—A number of Australian minerals were examined for radioactivity by the ionisation produced in an air gap, the activity being compared with that of black oxide of uranium. Radium was tested for, and found in the case of two Australian minerals, but a gadolinite known to contain helium gave no radium emanation.

P. H.

Preparation of Radium from Pitchblende. HEINRICH PAWECK (*Zeitsch. Elektrochem.*, 1908, 14, 619—623).—A description of the process of manufacture of radium salts used at the radium works of the Austrian Government at St. Joachimsthal. The ores of Joachimsthal have been worked since 1518, first for silver, then for cobalt, nickel, arsenic, and bismuth, and more recently for uranium. In 1907 the extraction of radium from the residues from the uranium ore was begun. The raw ore is ground and washed to remove the lighter rock constituents, it is then roasted at 800° to remove sulphur, and finally heated again with sodium carbonate. Uranium, arsenic, antimony, tungsten, molybdenum, and vanadium are washed out in the form of sodium salts. From the residue, iron, aluminium, calcium, silicon, and lead are removed by boiling with sodium hydroxide and then with hydrochloric acid, very thorough washing following each operation. The residue contains barium and radium sulphates, which are converted into carbonates by repeated treatment with sodium carbonate and thorough washing, and then dissolved in hydrochloric

acid and reprecipitated by sulphuric acid. This treatment is repeated several times. The solution of the chlorides is finally evaporated to dryness, and extracted with concentrated hydrochloric acid, which leaves a residue consisting mainly of barium and radium chlorides, which is submitted to fractional crystallisation. Of the radioactivity of the original ore, 73.9% is found in the residue from the uranium extraction, and the remainder in the solid uranium salts produced ; there is no loss in waste products. T. E.

Quantitative Estimation of Radium Emanation in the Atmosphere. GEORGE C. ASHMAN (*Amer. J. Sci.*, 1908, [iv], 26, 119—120).—The author has determined the radioactivity of 200 litres of Chicago air taken from the ground level. The purified air was passed through a long copper spiral immersed in liquid air to condense the emanation, which was afterwards volatilised into an electro-scope and estimated. Precisely the same results were obtained in simultaneous estimations by this method, which is considered to be the best hitherto devised for the purpose.

The radium equivalent of the emanation per cubic metre of air was found to be 86, 58, and 45×10^{-12} gram in three experiments. Immediately after a thaw and heavy rain, the amount rose to 200×10^{-12} gram ; under normal weather conditions with high barometer, the value 51×10^{-12} was found, whilst with a low barometer the amount was 131×10^{-12} .

The mean value, the equivalent of 1.0×10^{-10} gram of radium per cubic metre is 25% higher than the amount given by Eve. If the emanation has an appreciable vapour pressure at the temperature of liquid air, even the present estimate must be somewhat too low.

The active material had a half-period of decay of 3.5 days, indicating that it consisted only of radium emanation and that thorium emanation was absent. R. J. C.

Amount of Radium Emanation in the Atmosphere. JOHN SATTERLY (*Phil. Mag.*, 1908, [vi], 16, 584—615).—The amount of radium emanation present in the atmosphere of Cambridge has been measured by two methods. In the first, the emanation in a known volume of air was absorbed by charcoal ; in the second, it was condensed by means of liquid air. The electrical conductivity imparted to a given volume of air by the absorbed or condensed emanation was then compared with the conducting power brought about by the emanation emitted from a definite volume of a radium solution of known strength. The results of the two methods of measurement, which agree fairly well, show that the amount of radium emanation in the atmosphere varies very considerably. On the average, the quantity contained in a cubic metre of air is equal to the amount which would be in radioactive equilibrium with about 1×10^{-10} gram of radium. No connexion between the variation in the concentration of the emanation and the meteorological conditions could be detected. The observed values indicate that only a small proportion of the natural ionisation of the air is due to the presence of the radium emanation and its products. H. M. D.

Amount of Radium Emanation in the Atmosphere near the Earth's Surface. A. S. EVE (*Phil. Mag.*, 1908, [vi], 16, 622—632. Compare this vol., ii, 7).—Experiments according to the method already described have been continued at intervals for almost a year. An error in the previous calculations is pointed out, and this is corrected in the evaluation of the new experimental data.

The average amount of emanation present in a cubic metre of the air of Montreal during the period of the experiments is that which would be in equilibrium with 60×10^{-12} gram of radium. The observed variation in the concentration of the emanation is such that the maximum is to the minimum as 7 is to 1. Changes of temperature have little or no influence on the concentration of the emanation, but it increases on the approach of a deep cyclone accompanied by heavy rain or a thaw of snow, and decreases with anticyclonic conditions when the weather is dry or very cold. H. M. D.

The Heat Developed by Radium. EGON VON SCHWEIDLER and V. F. HESS (*Monatsh.*, 1908, 29, 853—862).—A quantity of over 1 gram of radium chloride was used for the experiments. A differential calorimeter was used consisting of two gilt-copper vessels in a chamber at constant temperature. One vessel contained the radium, and the other was heated by means of an electric current. Two copper-nickel thermo-junctions were balanced against one another, the heating current being adjusted until the temperatures were equal.

The results indicate a heat development of 118.0 cal. per hour for 1 gram of metallic radium, with a possible error of 1.4%. This is in good agreement with the value, 117 cal., obtained by Ångström (Abstr., 1906, ii, 63). C. H. D.

Relation between Uranium and Radium. III. FREDERICK SODDY (*Phil. Mag.*, 1908, [vi], 16, 632—638).—A further examination of the carefully-purified uranium salts prepared in 1905–06 has been made to ascertain the rate of production of radium (compare Soddy and Mackenzie, Abstr., 1907, ii, 730). In one case, the growth of radium is not greater than 5×10^{-11} gram per kilo. of uranium in $2\frac{3}{4}$ years, and in the other, it is not greater than 1×10^{-11} per gram kilo. of uranium in $1\frac{2}{3}$ years.

An examination of the residues from the highly-purified uranium salts has shown that the amount of radium present has increased about seven times during a period of one year. This indicates that a radium-producing substance is present in commercial uranium salts. Further, since the residues had been purified by the barium sulphate method with the object of removing radium and any intermediate products in the transformation of uranium into radium, it is established that the barium sulphate purification process does not remove the whole of this radium-producing substance. H. M. D.

Radiation of Uranium X. MAX LEVIN (*Physikal. Zeitsch.*, 1908, 9, 655—657. Compare Abstr., 1907, ii, 836).—As the distance between the radiating substance and the ionisation chamber is diminished, the ionisation produced by uranium X slowly increases at

first, attains a maximum value, and then rapidly diminishes. If the active substance is covered with a thin layer of aluminium, there is no evidence of this maximum ionisation value. The following explanation of the observed maximum in the case of the uncovered substance is given. As the distance between the source and the ionisation chamber increases, the actual number of ions which are discharged increases. When this distance is considerable, the strength of the electric field is not sufficient to bring about the discharge of all the ions before reunion takes place. If the ionisation per centimetre were constant, this should lead to a constant limiting ionisation when the distance is sufficiently great, but the fact that the strongly ionised layer in the immediate neighbourhood of the active substance is gradually removed from the measuring chamber influences the ionisation in such a way that, although an increase takes place at first with increasing separation, this is more than compensated for by the second effect when the distance has attained a certain value. H. M. D.

Actinium C, a New Short-lived Product of Actinium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1908, 9, 649—655).—Measurements of the ionisation produced by the α - and β -radiation emitted by the induced activity of actinium indicate that this consists of three disintegration products: actinium A, B, and C. Actinium C was separated from A by the action of finely-divided metals and animal charcoal on a solution of the active deposit, and its period of decay was found to be 5.10 minutes. It emits no α -rays, but the β -rays previously attributed to actinium B are found to be due to actinium C. The α -rays given off by the active deposit are entirely due to actinium B, whilst actinium A only emits a very readily absorbed type of β -radiation. In agreement with Bronson's determination, the decay period of actinium B is found to be 2.15 minutes, and that of actinium A, thirty-six minutes. These two products can be separated by heating the active deposit for about thirty seconds in a blow-pipe flame; the separation is not, however, complete even when the temperature is raised to 2000°.

Equations are given which represent the change in the α - and β -activity of the active deposit in agreement with the experimental observations. H. M. D.

Range of Activity and Absorption of α -Rays. Secondary Radiation Produced by α -Rays. E. ASCHKINASS (*Ann. Physik*, 1908, [iv], 27, 377—390).—An apparatus is described by means of which the charge on α -particles from polonium could be measured after passing through aluminium foil in a high vacuum. A magnetic field was employed to remove electrons and secondary radiation.

As found by other workers, layers of aluminium foil up to 13.7 μ in thickness allow the whole of the α -particles to pass. At about 24 μ , the particles are completely arrested. It is probable that complete absorption occurs suddenly at a definite thickness of aluminium.

Experiments with the same apparatus in the absence of a magnetic field indicate that the negative radiation from polonium considerably exceeds the positive in quantity. The secondary radiation produced by the α -particles may also be studied by its means. C. H. D.

Ionisation of Gases by α -Rays, and the Hypothesis of Initial Recombination of the Ions. M. MOULIN (*Chem. Zentr.*, 1908, ii, 474—475; from *Le Radium*, 1908, 5, 136—141. Compare Abstr., 1906, ii, 720).—The hypotheses of Bragg and Kleeman, and Langevin, as explanatory of the unsaturation of an electric current at low *E.M.F.* when passed through a gas ionised by α -rays, have been tested by the author. The evidence so far obtained appears to support Langevin's view, that the α -rays produce a larger number of ions, which, however, become arranged along the path of the α -rays.

J. V. E.

Quality of the Secondary Ionisation due to β -Rays. WILLIAM H. BRAGG and J. P. V. MADSEN (*Phil. Mag.*, 1908, [vi], 16, 692—697).—Experiments are described which show that the secondary rays reflected by different substances struck by the same bundle of primary rays are not uniform in quality, but vary from one substance to another. For the purpose of collecting all the secondary rays, the authors have made use of an ionisation chamber with a hemispherical wall.

It is found that the secondary rays returned by substances of low atomic weight contain a relatively large proportion of less penetrating rays. When the less penetrating portions of the primary beam are cut off, the emitted secondary rays are found to be more penetrating. On account of these facts, observations of secondary radiation cannot be accurately made when ionisation vessels of the ordinary type are employed.

H. M. D.

Attempts to Detect the Production of Helium from the Primary Radio-elements. FREDERICK SODDY (*Phil. Mag.*, 1908, [vi], 16, 513—530).—Experiments have been made to obtain a quantitative estimate of the amount of helium produced from uranium and thorium. By the process recently described (Abstr., 1907, ii, 251), it is possible to detect 2×10^{-10} gram of helium by observation of the D_3 line. In an experiment in which 350 grams of thorium in the form of nitrate were employed, helium to the extent of about 2×10^{-10} gram was detected after a period of accumulation of nearly seven months. This corresponds with a rate of production of 2×10^{-12} per year. The two estimated rates of production, on the assumption that the helium atom is identical with an α -particle, are, according to two different methods, 2×10^{-12} and 4.5×10^{-12} . It may be pointed out that the former value is almost eight times less than the value calculated three years ago.

H. M. D.

Rate of Production of Helium from Radium. Sir JAMES DEWAR (*Proc. Roy. Soc.*, 1908, 81, A, 280—286).—The rate of production of helium from radium was determined directly by observing the growth of pressure in a McLeod gauge connected with a vessel containing 70 mg. of radium chloride. A small tube containing cocoanut charcoal was sealed on to the gauge; the tube was kept in liquid air during an experiment, and served to condense any gases, other than helium or hydrogen, which might be generated in, or leak

into, the apparatus. Before starting an experiment, the apparatus was exhausted, first with a mercury pump, then with a large bulb containing charcoal immersed in liquid air, which was sealed off after some hours, and, finally, to a pressure of 0.00005 mm. by cooling the small charcoal bulb.

The second and more satisfactory experiment lasted 1100 hours. At intervals, the radium was heated to low redness, causing an increase of pressure after cooling to room temperature, which remained steady, showing that part of the helium had been occluded by the radium. Direct experiment showed that the helium was not appreciably occluded by the charcoal. It was further shown by examination of the spectrum, and by two other independent methods, that the helium was not contaminated with hydrogen.

A mean line drawn through the observations with the radium heated, shows a steadily maintained helium increment of approximately 0.37 c.mm. per gram of radium per day, a result which agrees almost exactly with that calculated by Rutherford on the assumption that the α -particle is an atom of helium carrying two ionic charges. On the other hand, Ramsay and Cameron (*Trans.*, 1907, 91, 1274) have determined the rate of production of the emanation from radium, the ratio of the amount of helium to that of the emanation being found by them to be 3.18; their value is about eight times as great as that of the author. It is pointed out in a footnote that Rutherford's experimental determination of the rate of production of the emanation gives a value about one-tenth that obtained by Ramsay, but in good agreement with the present results, on the assumption that the ratio of helium to emanation is 3 : 1.

G. S.

Accumulation of Helium in Geological Time. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1908, 81, A, 272—277).—The experiments were undertaken in order to obtain a comparison of the helium content of minerals with their geological age. It was found that phosphatic nodules and phosphatised bones, occurring in such strata that their relative age was well defined, possessed a radioactivity much higher than that of rocks, and that the activity was connected with the presence of uranium minerals.

The helium was liberated by dissolving the minerals in acids, and separated from other gases by special methods. The radium content of the minerals was determined in the usual way, and from the results the percentage of uranium oxide calculated by comparison with a standard uranium mineral.

The ratio of helium to uranium oxide is not strictly proportional to the age of the strata, but high ratios are not found in the younger strata, whereas they are common in the older ones. The absence of direct proportionality is ascribed to imperfect retention of the helium.

From the results, on the basis of Rutherford's estimate of the rate of production of helium from radium, an attempt is made to calculate the age of the strata. The following are provisional *minimum* values :

Phosphatic nodules of the crag, 225,000 years; of the upper green-

sand, 3,080,000 years; of the lower greensand, 3,950,000 years; and hæmatite overlying carboniferous limestone, 141,000,000 years.

G. S.

Helium in Saline Minerals, and its probable Connexion with Potassium. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1908, 81, A, 278—279).—The ratio of helium to uranium oxide has been determined (as described in the previous abstract) for the Stassfurt minerals, sylvine, carnallite, kieserite, and rock salt, and a number of other minerals from the same source have been examined qualitatively. Only for sylvine and carnallite is the ratio so high that it cannot be accounted for by the uranium present, and it is suggested that potassium may be the source of the helium in these two minerals (compare Campbell and Wood, *Abstr.*, 1907, ii, 217; McLennan and Kennedy, this vol., ii, 750).

G. S.

Electrical Conductivity of Alloys and their Temperature-coefficients. ERNST RUDOLFI (*Physikal. Zeitsch.*, 1908, 9, 607—609).—Polemical against Guertler (compare this vol., ii, 557).

H. M. D.

Conductivity of Fused Salts. KURT ARNDT and ALBERT GESSLER (*Zeitsch. Elektrochem.*, 1908, 14, 662—665).—The conductivities of a number of salts are measured by the method described by Arndt (*Abstr.*, 1906, ii, 418). The results (in reciprocal ohms per cm.) are:

	450°	500°	550°	600°	650°	700°	750°	800°	850°	900°	950°	1000°	1050°	1100°
CaCl ₂	—	—	—	—	—	—	—	1·90	2·12	2·32	2·50	2·66	2·76	—
KCl	—	—	—	—	—	—	—	2·19	2·30	2·40	2·50	2·61	—	—
KBr	—	—	—	—	—	—	1·65	1·75	1·85	1·95	2·05	—	—	—
KI	—	—	—	—	—	1·39	1·51	1·64	—	—	—	—	—	—
NaBr	—	—	—	—	—	—	—	3·06	3·23	3·30	—	—	—	—
NaI	—	—	—	—	—	2·56	2·63	2·70	2·76	2·83	2·90	—	—	—
AgCl	—	—	4·34	4·48	4·62	4·76	—	4·98	—	5·14	—	—	—	—
AgBr	2·93	3·02	3·10	3·18	—	3·34	—	3·50	—	3·68	—	—	—	—
AgI	—	—	2·46	2·52	2·59	2·64	—	2·72	—	—	—	—	—	—
NaPO ₃	—	—	—	0·30	0·425	0·55	0·675	0·80	0·925	1·05	1·175	1·30	1·42	1·54
B ₂ O ₃	—	—	—	—	—	—	—	(0·7	1·2	2·1	3·3	4·6	× 10 ⁻⁵)	—

The conductivity is in all cases a linear function of the temperature; for the alkali salts it is approximately proportional to the absolute temperature. The conductivities of mixtures of potassium and sodium chlorides and of calcium and strontium chlorides are very nearly the mean of those of the constituents.

T. E.

Density and Equivalent Conductivity of Some Fused Salts. KURT ARNDT and ALBERT GESSLER (*Zeitsch. Elektrochem.*, 1908, 14, 665—667).—The density is determined by means of a platinum sinker and Westphal balance. The results are (in grams per c.c.):

	850°	900°	950°	1000°	1050°
CaCl ₂	2·03	2·01	1·99	1·97	—
SrCl ₂	—	2·69	2·67	2·645	2·62
BaCl ₂	—	—	—	3·12	3·09

For mixtures of calcium and strontium chlorides, the densities found are slightly smaller than the mean :

	700°	800°	900°	1000°	1100°
NaPO ₃	2.22	2.18	2.14	2.10	—
B ₂ O ₃	—	—	1.520	1.508	1.495

Mixtures of sodium metaphosphate and boron trioxide were measured at 900°; very considerable contraction occurs. In the following table, x is the percentage of sodium metaphosphate :

x	50	25	10	5	1.0	0.5
Density ...	2.115	1.820	1.655	1.585	1.552	1.522

The equivalent conductivities are calculated by means of the figures in the preceding abstract.

T. E.

Limiting Conductivity of Some Electrolytes in Ethyl Alcohol. PAUL DUTOIT and H. RAPPEPORT (*J. Chim. Phys.*, 1908, 6, 545—551).—The alcohol used in the measurements had a specific conductivity of the order 10^{-7} reciprocal ohms. The values of the limiting molecular conductivity, μ_{∞} , were obtained directly by measurements in very dilute solution (up to a dilution of 20,000 litres) and indirectly by extrapolation from measurements in more concentrated solutions. The values of μ_{∞} at 18°, expressed in Siemens units, are 39.2, 39.1, 35.8, and 35.0 respectively for the iodides of potassium, sodium, lithium, and ammonium, and 41.1 and 38.0 for the thiocyanates of potassium and ammonium respectively. Ammonium bromide gives 36.4, and sodium acetate, 31.8.

Kohlrausch's law holds for the electrolytes examined within the limits of experimental error, but the dilution law does not apply.

The order of the speed of the ions is the same in water and in alcohol, but the ratio of the speeds in the two solvents is by no means constant, varying from 1.8—3 : 1.

G. S.

A Light Accumulator. R. GOLDSCHMIDT (*Bull. Soc. chim. Belg.*, 1908, 22, 317—327).—An accumulator in which the electrodes are zinc and oxide of nickel, and the electrolyte a concentrated solution of potassium carbonate, is described. The changes taking place on charging and discharging are represented by the upper and lower arrows respectively in the equation $\text{Ni}_2\text{O}_3 + 2\text{Zn} \rightleftharpoons \text{NiO} + 2\text{ZnO}$, the electrolyte taking no direct part in the reaction. The nickel peroxide electrodes are prepared by electrolysis of a solution of nickel silicofluoride containing a little cobalt silicofluoride, nickel plates being used as anode, and the nickel deposited on a sheet of iron covered with nickel serving as cathode. A constant *E.M.F.* of about 2.75 volts is employed. After seven to eight hours' electrolysis, it is necessary to add a little cobalt silicofluoride and free hydrofluosilicic acid to the electrolyte to prevent the formation of a green mass on the cathode. The plate thus prepared is washed and oxidised electrolytically in a solution of sodium carbonate.

The zinc electrodes are prepared by electrolysis of a strong solution

of zinc silicofluoride containing a little free acid, zinc plates being used as anode, and the zinc deposited on iron as cathode. It is remarkable that much better deposits of zinc are obtained after the electrolyte has been in use for some time.

The plates thus prepared are immersed in a 43% solution of potassium carbonate or a 25% solution of sodium carbonate to form an accumulator; the potassium salt is preferable. An accumulator of this type has a capacity of at least 60 ampere-hours per kilo. of positive electrode; with a current of 15—20 amperes, the yield is about 100 watts, and the mean *E.M.F.*, 1.57 volts. It has the further advantage that it can be charged with a very large current, up to 50 amperes per kilo. of positive electrode, without damage. G. S.

Formation of Gas in Discharge Tubes. RUDOLF VON HIRSCH (*Physikal. Zeitsch.*, 1908, 9, 603—606. Compare Hirsch and Soddy, this vol., ii, 12).—The author has investigated the gas which is evolved from aluminium electrodes containing sodium as an impurity when cathode rays are generated by means of an influence machine. About 50% of the gas is absorbed by glowing copper oxide, and consists of hydrogen. The remainder appears to be carbon dioxide, for the spectral bands of this gas become much stronger after the removal of the hydrogen. This mixture of gases differs from others previously examined in that the product p^2V is constant, p being the gas pressure and V the discharge potential. It has been suggested previously (*loc. cit.*) that the constancy of p^2V is characteristic of pure gases, and this has led to a detailed examination of mixtures of hydrogen and carbon dioxide.

The value of p^2V for pure carbon dioxide is about 1/22 of that for hydrogen; the connexion between the value of the product and the molecular weight of the gas does not hold therefore in this case. For mixtures of the two gases, p^2V is not constant; the curve, which represents the deviations of the product from a constant value, exhibits maxima for mixtures containing a large excess of one or the other gas, and a minimum for which $p^2V = 4$.

Analysis of two mixtures giving this minimum value showed that approximately equal quantities of the two gases are present. This mixture is the one produced from the aluminium electrodes, the constancy of the proportions between the two gases being maintained automatically. The formation of the gases is due to the action of water and carbon dioxide on the sodium contained in the aluminium.

H. M. D.

Chemical or Physical Theory of Volatilisation (of Cathodes). FRANZ FISCHER and OTTO HÄHNEL (*Zeitsch. Elektrochem.*, 1908, 14, 677—681). VOLKMAR KOHLSCHÜTTER (*ibid.*, 681—683).—Fischer and Hähnel regard the volatilisation as a purely physical phenomenon; Kohlschütter upholds his chemical hypothesis (this vol., ii, 457, 653, 799, and 800).

T. E.

Volatilisation of Cathodes in Attenuated Gases. B. WALTER (*Zeitsch. Elektrochem.*, 1908, 14, 695).—In Fischer and Hähnel's experiments (this vol., ii, 653), the current passing in the argon

and hydrogen tubes is the same, but the energy consumed is greater in hydrogen; hence for equal quantities of energy the volatilisation would be greater in argon.

T. E.

Behaviour of Calcium and Sodium Amalgams as Electrodes in Solutions of Neutral Salts. HORACE G. BYERS (*J. Amer. Chem. Soc.*, 1908, 30, 1584—1586).—Le Blanc and Novotný (Abstr., 1907, ii, 22) found that the values of the equilibrium constant of the reaction between sodium carbonate and calcium hydroxide, obtained by direct determination, did not agree with those calculated from the solubilities of calcium hydroxide and calcium carbonate. An attempt has therefore been made to determine this constant by measuring the *E.M.F.* of the cell $\text{CaHg}-\text{CaCO}_3-\text{Na}_2\text{CO}_3 \mid \text{NaOH}-\text{Ca}(\text{OH})_2-\text{CaHg}$, K being calculated from the equation $\pi = RT/7 \times \ln K/a$. The value of π , however, could not be satisfactorily determined, owing to the rapid action of water on the calcium amalgam, but interesting results were obtained on the action of solutions of salts on the amalgam. Similar experiments were made with sodium amalgam and solutions of salts. The results are tabulated.

It has been found that when amalgams are treated with solutions of salts of alkali or alkaline-earth metals, replacement occurs, and the determination becomes that of the *E.M.F.* of an electrode consisting partly of the amalgam of the metal of the added solution. Replacements of this character in concentrated amalgams have been recorded previously.

E. G.

Anomaly of the Strong Univalent Electrolytes M. KATAYAMA (*J. Coll. Sci Tōkyō*, 1908, 25, vii, 1—42).—By combining the views of Nernst (Abstr., 1901, ii, 647) and Jahn (Abstr., 1900, ii, 522; 1901, ii, 491; 1902, ii, 597) with those of Storch (Abstr., 1896, ii, 288) and Bancroft (Abstr., 1900, ii, 186), the author has deduced the following empirical formula:

$$K = \frac{c_i^n (c_i)}{c_n (c_n)} - 0.3 \frac{c_i^2}{c_n},$$

that is, $\log K = n \log \frac{\lambda}{\lambda_\infty} c - \log \frac{\lambda_\infty - \lambda}{\lambda_\infty} c - 0.3 \frac{\lambda^2 c}{(\lambda_\infty - \lambda) \lambda_\infty} \log \frac{\lambda}{\lambda_\infty - \lambda}$, where K is a constant, c_i the concentration of the ions in gram-mols per litre, c_n the concentration of the neutral, undissociated molecules, $c_i + c_n = c$ the total concentration, n a constant, λ the equivalent conductivity for the concentration c , and λ_∞ the equivalent conductivity for infinite dilution. The values obtained with this formula are in close agreement with the observed conductivities for every kind of univalent electrolyte.

In conjunction with Nernst's theory of solutions (*loc. cit.*), the following assumptions were made: $\pi_1 = a_1 c_n c_i^s$; $\pi_2 = a_2 c_i \left(\frac{c_i}{c_n} \right)^{0.3 \frac{c_i^2}{c_n}}$; where π_1 is the vapour pressure of the neutral molecule, π_2 the vapour pressure of the cation or anion, and a_1 , a_2 , and s are constants. The

values for the *E.M.F.* calculated on the second assumption are in fair agreement with the observed values. The partition-coefficient values obtained by Rothmund and Drucker for picric acid (Abstr., 1904, ii, 231) are well explained with the aid of the first assumption. By combining the two, it is possible to calculate the lowering of the freezing point of an aqueous solution of a strong electrolyte, which as a rule is in agreement with the observed depression. W. H. G.

The Size of Molecules and Charge of the Electron. JEAN PERRIN (*Compt. rend.*, 1908, 147, 594—596).—The number (*N*) of molecules in a gram-molecule, the charge (*e*) of the electron, and the ratio (*a*) of the mean energy of a molecule to its absolute temperature are universal constants, all of which are known when the value of one is determined, since (1) in the electrolysis of a univalent salt 96550 coulombs are conveyed by *N* atoms, whence $Ne = 3 \times 10^9 \times 96550$ electrostatic units; (2) the kinetic energy of a gram-molecule is measured by $3RT$, so that $2Na = 3R = 3 \times 83 \cdot 2 \times 10^6$.

The values 3×10^{-10} (Townsend), $3 \cdot 4 \times 10^{-10}$ (J. J. Thomson), $6 \cdot 8 \times 10^{-10}$ (J. J. Thomson), and $3 \cdot 1 \times 10^{-10}$ (H. A. Wilson) have been found for *e*, and from them values varying from 43×10^{22} to 96×10^{22} derived for *N*. Planck has obtained the value $2 \cdot 02 \times 10^{-16}$ for *a* and deduced 61×10^{22} for *N*, but Lorentz from the same data finds $N = 77 \times 10^{22}$. The author has determined *N* by a method based on the assumption that equal particles distribute themselves in a dilute emulsion in the same manner as molecules of the same mass which obey the gas laws. This leads to the equation $2 \cdot 3 \log_{10} n_0/n = N/RT[4/3\pi a^3 g(d-\sigma)h]$, in which *n* and *n*₀ signify the concentrations of the particles at levels separated by the distance *h*, *a* the radius of the particles, and (*d* - *σ*) the excess of their density over that of water. After finding that particles of very different size gave the same value for *N*, the value 71×10^{22} was obtained, and the values $4 \cdot 1 \times 10^{-10}$ and $1 \cdot 7 \times 10^{-16}$ thereby deduced for *e* and *a* respectively. From this value of *N*, the mass of the oxygen molecule is $0 \cdot 45 \times 10^{-23}$ gram, of the hydrogen atom $1 \cdot 40 \times 10^{-24}$ gram, and of the corpuscule $0 \cdot 75 \times 10^{-27}$ gram. E. H.

Magnetic Susceptibility of Solutions. P. PASCAL (*Compt. rend.*, 1908, 147, 242—244. Compare this vol., ii, 756).—The rule that a magnetic atom becomes more diamagnetic the more it enters into complex ions or colloidal molecules, and becomes removed from its characteristic chemical properties, has been verified in the cases of certain ferrous, cobalt, chromium, copper, and mercury salts. Ferropyrophosphates, ferro-oxalates, and ferrometaphosphates are oxidised at rates which are in order of their magnetism. The decrease of magnetism on adding sodium carbonate to these salts is accompanied by a slower rate of oxidation. R. J. C.

Relation of Melting Point to the Surface of the Granules of a Solid Substance. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1022—1066).—From theoretical considerations, the author shows that the relation between the melting point, *T*, of a substance and the

radius, r , of its granules is expressed by the following differential equation:

$$dT/dr = [A(v_2 - v_1)p \cdot 2k/r^2 \cdot dR\sigma] / [\rho + A(v_2 - v_1)p \cdot 2k/r \cdot dR\sigma T],$$

where A is a constant independent of the magnitude of the granules for any given temperature, and is given by the expression: $\log Ap = 2k/r dR\sigma T$; k is the surface tension at the separation of the solid from vapour; r the radius of the spherical granules; σ the specific volume of the vapour; ρ the specific heat of liquefaction; v_2 and v_1 the volumes of unit masses of the liquid and solid respectively at the melting point.

Granules of commercial salol having a magnitude of 8μ melt 3.5° lower than those 32μ in size. After one recrystallisation, granules of 6μ — 40μ melt within an interval of 1.5° . Dust having dimensions less than 2μ melts, in the case of salol 7° , with antipyrine 5 — 7° , and with phenacetin 4° , lower than large granules of diameter 0.5 — 2 mm.

T. H. P.

Apparatus for Determining the Freezing Point of Mixtures.

OTO SCHEUER (*J. Chim. Phys.*, 1908, 6, 620—624).—Two forms of apparatus suitable for determining the freezing point of mixtures are described. The first is a modified Beckmann apparatus. The essential feature of the second is that the stirring is concentric, and is effected by means of the thermometer, to the lower part of which two strips are attached for this purpose.

G. S.

Negative Adsorption. REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1908, 57, 315—316).—Tezner and Roske state (this vol., ii, 810) that negative adsorption does not occur. This, however, is only true when the adsorption of a single substance is dealt with, and instances are given where, under other conditions, the phenomenon does take place.

W. D. H.

The Fusion Curves of the System Naphthalene-Phenol.

T. YAMAMOTO (*J. Coll. Sci. Tōkyō*, 1908, 25, xi, 1—23).—The freezing-point curve of mixtures of naphthalene and phenol was determined by the cryoscopic method, a correction being made for supercooling. The eutectic point lies at 29.7° and 15.7 mol. % naphthalene. The form of the phenol curve is explained as being due to the association of phenol in the liquid state, represented by the equilibrium $3C_6H_5O \rightleftharpoons (C_6H_5O)_3$. The equilibrium constant of this association is expressed as a function of temperature, the heat of association being also determined.

C. H. D.

The Fusion Surfaces of the System Naphthalene-Chlorobenzene-Phenol, and the Molecular Association of Phenol.

H. HIROBE (*J. Coll. Sci. Tōkyō*, 1908, 25, xii, 1—50. Compare preceding abstract).—The fusion surfaces (freezing-point surfaces) of naphthalene and phenol in the ternary system have been determined, an accurate cryoscopic method being employed. The two surfaces are separated by a eutectic curve, the projection of which on the plane of composition is nearly a straight line. The form of the surfaces is

consistent with the assumption that naphthalene and chlorobenzene are non-associated, and that phenol is partly associated to triple molecules. The latter conclusion was supported by determinations of the partition-coefficient of phenol between chlorobenzene and an aqueous solution of sodium chloride and sodium sulphate. C. H. D.

Arrangement for Liquefying and Distilling Easily Condensable Gases and Low-boiling Liquids. AUREL VON BARTAL (*Chem. Zeit.*, 1908, 32, 891).—A U-shaped form of receiver which can be completely immersed in a freezing mixture contained in a vessel consisting of two concentric cylinders between which there is a layer of asbestos; in this way, a very effective condensation is ensured. When removed from the freezing mixture, the apparatus can be employed as a distillation flask by gently warming it; the distillate may be condensed in a second similar apparatus cooled in a freezing mixture. P. H.

Practical Studies in Vacuum Sublimation. RICHARD KEMPF (*J. pr. Chem.*, 1908, [ii], 78, 201—259).—The employment of sublimation in a vacuum as a means of purification entails a smaller loss of substance than does recrystallisation, whilst, on the other hand, in consequence of the slower volatilisation, a more complete separation of a mixture is secured than by fractional distillation. The author describes an arrangement for sublimation experiments suitable for use in a laboratory, consisting of a glass tube on to one end of which is ground a glass cap with a tap and nozzle for connecting with the pump, and on to the other a bent pear-shaped glass bulb. This bulb, containing the substance to be sublimed, is heated in a suitable air-oven; the straight tube projecting through a hole in the side of the oven serves as the receiver for the sublimate. The phenomena of sublimation are discussed, and details given of experiments with fifty-three inorganic and organic compounds. G. Y.

Heat of Combination of Acidic Oxides with Sodium Oxide and Heat of Oxidation of Chromium. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1908, [iv], 26, 125—137. Compare Abstr., 1907, ii, 738).—The heats of formation of sodium orthoborate, aluminate, chromate, and tungstate have been determined by firing mixtures of sodium peroxide with the metals or with metallic oxides in presence of carbon. Incidentally, the heats of formation of chromium sesquioxide and trioxide were calculated. Since the salts in question are largely hydrolysed by water, previous determinations by Thomsen, Berthelot, and others which referred to solutions are regarded as less trustworthy than those obtained by the sodium peroxide method. The heat of formation of sodium sulphate, on the other hand, is found to be the same by both methods. The principal results obtained were:

$3\text{Na}_2\text{O} + \text{B}_2\text{O}_3 = 2\text{Na}_3\text{BO}_3$	+ 104,200 cal.
$\text{Na}_2\text{O} + \text{Al}_2\text{O}_3(\text{amorphous}) = 2\text{NaAlO}_2$ +	40,000 „
$\text{Na}_2\text{O} + \text{CrO}_3 = \text{Na}_2\text{CrO}_4$	+ 77,000 „
$\text{Na}_2\text{O} + \text{WO}_3 = \text{Na}_2\text{WO}_4$	+ 94,700 „
$\text{Cr} + 3\text{O} = \text{CrO}_3$	+ 140,000 „
$2\text{Cr} + 3\text{O} = \text{Cr}_2\text{O}_3(\text{amorphous})$	+ 243,800 „

The heats of transformation of aluminium and chromium oxides from the amorphous to the crystalline state were also determined.

During the combustions which were made in a silver bomb, or a silver cup suspended in a steel bomb, a small amount of oxygen was always liberated, for which a correction was necessary. R. J. C.

Viscosity of Certain Metals and its Variation with Temperature. CHARLES E. GUYE and S. MINTZ (*Arch. sci. phys. nat.*, 1908, 26, 136—166, 263—278).—From observations on the rate of decrease of the amplitude of vibration of loaded wires when twisted, the authors have compared the viscosity of platinum, silver, gold, copper, and steel at different temperatures. To eliminate the damping effect of the air, the vibrating wire was enclosed in an apparatus which could be exhausted.

The viscosity increases with the temperature in the case of platinum, silver, gold, and copper, and the curves which express the relationship between the two factors are of the same type. In the case of steel, the viscosity increases up to about 100°, then falls, and passes through a minimum value at about 200°, above which it increases very rapidly. This phenomenon can be observed both with rising and falling temperatures, indicating that it is due to reversible changes.

The influence of temperature on the viscosity is diminished by previous annealing; it increases when the load on the wire is increased. H. M. D.

Viscosity of Dilute Alcoholic Solutions. TOSHIO HIRATA (*J. Coll. Sci. Tōkyō*, 1908, 25, v, 1—15).—Arrhenius has shown (Abstr., 1880, 336) that the viscosity of an aqueous solution of any two indifferent substances may be expressed by the formula $\eta = A^x B^y$, where A and B are two constants characteristic of the two solutes at a constant temperature, x and y being their respective volume percentages. With the object of ascertaining whether ethyl-alcoholic solutions follow the same law, the viscosities of ethyl-alcoholic solutions of various liquids, chiefly organic, have been measured. It is found that the formula can be applied to the solutions of all the substances examined, the error being less than 1% for solutions containing less than 10% by volume of the dissolved substance. Water, however, forms an exception; in this case, the formula can be applied only to very dilute solutions. When the concentration exceeds 3% by volume, the error is greater than 1%. W. H. G.

Viscosity and Ionic Volume. FREDERICK H. GETMAN (*J. Chim. Phys.*, 1908, 6, 577—583. Compare this vol., ii, 464).—Jones and Veazey (Abstr., 1907, ii, 438) have pointed out that the salts which diminish the viscosity of water have a large ionic volume, and there is evidence that for salts with the same anion the diminution of viscosity of the solvent is proportional to the atomic volume of the cation. In the present paper, this relationship is further illustrated by application to a number of nitrates and chlorides.

In order to show the relationship more clearly, the viscosity of solutions of the same salts is compared, when the degree of dissocia-

tion in each case is 75%. Under these circumstances, the viscosity, η , is represented by the formula :

$$10^4 \times \eta = 89 \pm 0.0242C_v,$$

where C_v is the atomic volume of the cation, and 89 represents the viscosity of water at 25°, there being good agreement between found and calculated values. On the other hand, there is no apparent connexion between the viscosity and the sum of the volumes of the ions and unionised molecules. G. S.

Changes in Internal Friction due to Protein Degradation.

KARL SCHORR (*Biochem. Zeitsch.*, 1908, 13, 173—176).—Experiments were carried out with dialysed salt-free serum, which was treated with sodium hydroxide in various dilutions. An Ostwald viscosimeter was used for the measurements.

On treatment with the alkali, there is at first an increase in the internal friction, which is followed by a steady fall. A similar phenomenon is brought about by hydrochloric acid ; in the latter case, however, the fall is followed by a second rise, which is accompanied by a gradual separation of a precipitate from the liquid, which is finally sufficient to impede entirely the flow of liquid through the viscosity tube. S. B. S.

Diffusion of Gaseous Ions. ÉDOUARD SALLES (*Compt. rend.*, 1908, 147, 627—629).—The author has measured the coefficient of diffusion of gaseous ions towards the walls of narrow metallic containing tubes. The coefficient for positive ions is 0.031, and for negative ions 0.041, the value being unaffected by interchanging tubes of German silver, brass, and steel. Contrary to J. J. Thomson's supposition, the nature of the metal has no specific influence on the rate of diffusion of gaseous ions towards it. R. J. C.

Osmotic Pressure of Concentrated Solutions of Non-electrolytes. OTTO SACKUR (*Chem. Zentr.*, 1908, ii, 472 ; from *Jahrb. Schlesisch. Ges. Vaterl. Kultur*, 1908, 86, 1—14).—According to the experiments of Morse and Frazer, aqueous sucrose solutions above 20° exert an osmotic pressure equal to the corresponding gas pressure, when the concentration is defined as the number of molecules of the dissolved substance in a volume of the solvent (Abstr., 1907, ii, 744). At lower temperatures, this agreement is not observed. If, however, the concentration is regarded as being expressed by the number of molecules of dissolved substance in a volume of the solution, the equation $p(v - b) = RT$ is applicable for all the observations with sucrose and dextrose. Contrary to the gas law, b , in the above equation, varies considerably with alteration of temperature ; for sucrose, it decreases from 0.31 (per litre) to 0.20 when the temperature rises from 0° to 20°, and for dextrose, from 0.16 to 0.093 under a like change of temperature. The author suggests that this is due to the hydration of the dissolved substance decreasing with rise of temperature. J. V. E.

Polymerisation and Dissociation of Molecules in the Liquid State. GEORGE G. LONGINESCU (*J. Chim. Phys.*, 1908, 6, 552—566. Compare Abstr., 1905, ii, 79).—With reference to the relation between

the boiling point and molecular weight, Walker has pointed out that the formula $T/\sqrt{m}=37$ (m =molecular weight; T =boiling point on the absolute scale) holds more particularly for a number of hydrocarbons, but is not generally applicable. The author now shows that the modified expression $T/(\sqrt{m}+(1000/\sqrt{m}))/T$ is about 64 for all the normal substances examined, and varies from 65 for slightly polymerised substances to 99 for water.

The above equation has two roots, $\sqrt{m_1}=T/37$ and $\sqrt{m_2}=T/27$. The ratio T/\sqrt{m} is termed x_1 , and $1000/\sqrt{m}/T$ is termed x_2 . It is only for certain hydrocarbons and some other substances that $x_1=37$ and $x_2=27$; for the majority of substances, x_1 is less than 37, and x_2 greater than 27. This is taken to mean that, in the liquid state, the molecules of most substances are partly polymerised and partly dissociated, the mean of the weights of the molecules being the theoretical molecular weight, and the views of other observers are adduced in support of this opinion.

The "factor of dissociation," $K_1=(x_1/37)^2$, and the "factor of polymerisation," $K_2=1.88K_1$, are given in tabular form for all the liquids considered. G. S.

The Chemical Theory of Solutions. I. K. IKEDA (*J. Coll. Sci. Tōkyō*, 1908, 25, x, 1—80).—An ideal solution is defined as a homogeneous liquid mixture, of which the volume and energy are the sum of the volumes and energies respectively of the components in the liquid state under the same pressure and at the same temperature. An attempt is made to explain all deviations from the properties of an ideal solution by assuming reversible chemical reactions within the solution and applying the law of mass action. The treatment is mathematical, and the results are applied to concrete cases. C. H. D.

Hardness of Solid Solutions of Metals and of Definite Chemical Compounds. NICOLAI S. KURNAKOFF and S. F. SCHEMTSCHUSCHNY (*Zeitsch. anorg. Chem.*, 1908, 60, 1—37; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1067—1104).—The degree of hardness of a number of binary alloys, the structure of which is known, is plotted against the composition, and in the majority of cases the electrical conductivity is represented on the same diagram. The data for the bronzes and brasses and certain other alloys are due to previous observers, and the authors have themselves determined the hardness of the binary alloys copper-nickel, gold-copper, and gold-silver. It is shown that practically the same results are obtained whether the hardness is determined by the sclerometer (ruling lines on a prepared surface of the alloy), by the resistance to penetration, or by other methods.

The more important results of the investigation are as follows: (1) the formation of mixed crystals is accompanied by an increase in hardness; (2) the hardness of an unbroken series of mixed crystals can be represented by a continuous curve showing a maximum; (3) in the latter case, the maximum of the curve of hardness coincides with the minimum of the curve of electrical conductivity. (4) At

points corresponding with the extremities of the series of mixed crystals (when the miscibility of the metals is incomplete), there are breaks in the curve of hardness.

Experiments have also been made on the pressures required to force certain plastic binary mixtures in a thin stream through a small opening, and the pressures just sufficient for this purpose are plotted against the composition. These limiting pressures are roughly proportional to the hardness of the alloys. The curves for the isomorphous mixtures of *p*-dichloro- and *p*-dibromo-benzenes and of silver chloride and bromide show maxima, but that for zinc-tin alloys shows no maximum, corresponding with the fact that these metals have little or no tendency to form solid solutions.

Finally, when the metals form a chemical compound, the latter may be harder or softer than either of the components, and the curve obtained by plotting hardness against composition may show either a maximum or minimum. A number of examples illustrating this case are cited.

G. S.

Causes Modifying the Dominant Faces of Crystals: Solid Solutions. PAUL GAUBERT (*Compt. rend.*, 1908, 147, 632—635. Compare Abstr., 1906, ii, 343).—Foreign matter is distributed between crystals and their mother liquor in a definite ratio. The crystalline habit may be modified, not only by crystallisable foreign matter, but by liquid molecules, and even by the mother liquor itself.

Crystals of phthalic acid from aqueous solutions are modified in the same sense by methyl, ethyl, and propyl alcohols, glycerol or aldehyde in small quantities. The minute amount of alcohol in the crystals augments as the proportion of alcohol in the mother liquor increases, but the alcohol is not merely in the state of occluded mother liquor. Methylene-blue, which favours a different crystalline habit in phthalic acid, also hinders the entrance of alcohol into the growing crystals.

R. J. C.

Ultra-microscopic Observations. J. REISSIG (*Ann. Physik*, 1908, [iv], 27, 186—212).—The colloidal solutions of brown, tellurium, selenium, and silver, and of red and blue gold, prepared by Paal (compare Abstr., 1902, ii, 500, 508; 1905, ii, 158) have been examined by means of the ultra-microscope. These solutions contain the sodium salts of protalbic and lysalbic acids (compare Abstr., 1902, i, 653), which act as protective colloids. From the number of particles contained in a given volume, the linear dimensions of the particles of the colloidal elements are calculated. It is found that the number of observable particles is not proportional to the concentration of the dissolved colloid, for all the particles can only be seen in dilute solutions. The number of particles seen through the ultra-microscope is, for a given solution, proportional to the intensity of the source of light used.

The ultra-microscope has also been employed to examine the behaviour of colloidal gold solutions on the addition of hydrochloric acid. The slowness with which flocculation takes place is supposed

to represent the stability of the solution, and for both red and blue solutions, one maximum and two minimum positions of stability have been identified. The position of maximum stability corresponds with the isoelectric point of the solution. In dilute solutions the stability of the colloidal gold is greater than it is in concentrated. The rate at which a given quantity of hydrochloric acid causes flocculation to take place depends on the concentration of the acid, the rate decreasing as the concentration of the acid decreases.

H. M. D.

The Dynamic Theory of a Reversible Chemical Reaction.

II. ERNST COHEN and TH. STRENGERS (*Chem. Weekblad*, 1908, 5, 719—721. Compare this vol., ii, 824).—Polemical. A reply to Smits and Wibaut.

A. J. W.

The Dynamic Theory of a Reversible Chemical Reaction.

ANDREAS SMITS and J. P. WIBAUT (*Chem. Weekblad*, 1908, 5, 771—772).—Polemical. A reply to Cohen and Strengers (this vol., ii, 824).

A. J. W.

Lecture Experiment to Demonstrate the Law of Mass Action. EMIL ABEL (*Zeitsch. Elektrochem.*, 1908, 14, 630—631).—The diminution of the concentration of the hydrogen ions in a solution of acetic acid by sodium acetate is shown by means of the reaction between hydriodic acid and hydrogen peroxide. In acid solutions, iodine is liberated; in almost neutral solutions, oxygen is given off. The difference between a solution of acetic acid, potassium iodide, and hydrogen peroxide, on the one hand, and the same solution with the addition of sodium acetate, on the other, is very striking (compare this vol., ii, 939).

T. E.

Application of the Kinetic Theory to the Metals. G. REBOUL (*Chem. Zentr.*, 1908, ii, 473; from *Le Radium*, 1908, 5, 129—136).—It is assumed that in metals there are free negative electrons and positive atom ions. The free electrons must, then, have a definite tendency to pass from the metal into the surroundings. It therefore follows that at the perimeter there must be a double film metal/gas, and also a potential difference, as in the Nernst theory for the perimeter metal/solution. The equilibrium between the electrons that leave the metal and the electrical energy is influenced by a change of temperature. In this is found a simple explanation of the phenomena of electric capillarity, thermal electricity, and electron rays when substances are strongly heated.

J. V. E.

Velocity of Reaction. JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1908, 5, 747—764).—A theoretical paper containing a continuation of the author's statement of his new thermodynamic theory (this vol., ii, 824).

A. J. W.

Equilibrium of Two Substances in a Mixed Binary Solvent. E. D. VOLCHONSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 941—993).—A theoretical paper, in which the author considers: (1) The coefficient of distribution in a homogeneous system,

(2) Le Chatelier's principle of the opposition of action and reaction, and the conditions of existence of inverse systems. (3) Equilibrium of heterogeneous systems. (4) The energy relations between the members of a system. (5) The influence of temperature on the equilibrium of the system. (6) The classification of the reactions effecting the equilibrium of the system. T. H. P.

Equilibria in Quaternary Systems. FRANS A. H. SCHREINERMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 138—142. Compare this vol., ii, 571).—The system copper sulphate, ammonium sulphate, lithium sulphate, and water has been studied at 30°. In addition to the three sulphates named, there are two solid compounds involved in the equilibria, namely, $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$. The equilibria are represented with the aid of a tetrahedron, all saturation lines and surfaces being projected perpendicularly on one of the side planes of the tetrahedron. J. C. P.

Kinetics of Successive Reactions. Reduction of Chromic Acid by Oxalic Acid. K. JABŁCZYŃSKI (*Zeitsch. anorg. Chem.*, 1908, 60, 38—49.* Compare Luther and Rutter, *Abstr.*, 1907, ii, 555).—The rate of reaction between chromic acid and excess of oxalic acid in dilute solution has been measured at 15°, the course of the reaction being followed by estimating the concentration of chromic acid in a portion of the solution from time to time with iodide and thiosulphate. The velocity is proportional to the concentration of the chromic acid when different initial concentrations of the latter are used, but the constants calculated according to the unimolecular formula increase considerably during the reaction. Excess of chromic salt does not influence the rate of the reaction.

On the assumption that the reaction takes place in the three stages $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{V}}$ (1), $\text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{IV}}$ (2), $\text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$ (3), and that all three reactions are unimolecular, an equation is deduced from which, by an approximation method, the following values are obtained for the constants of the three successive reactions $k_1 = 0.0344$, $k_2 = 0.1322$, $k_3 = 0.0238$. Other measurements were made in which the conditions were varied considerably, but, although the ratio of the constants calculated from these observations varied somewhat, the order remained the same.

The above conclusion, that the reaction $\text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{I}}$ is very rapid and that the other reaction, $\text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$, is comparatively slow, is in accordance with what is known of the behaviour of quinquevalent and quadrivalent chromium salts. G. S.

Formation of Salts and Basicity of Acids. GIUSEPPE BRUNI (*Zeitsch. Elektrochem.*, 1908, 14, 701—706).—Measurements are made of the conductivity of an acid and of mixtures of the acid and its potassium salt. In each series of measurements, the total concentration of the acid is kept constant, the series extending from pure acid at one end to pure potassium salt at the other. Acetic, formic, monochloroacetic, cyanoacetic, and di- and tri-chloroacetic acids are used; they form a series of gradually increasing strength. Each acid is used in eleven different concentrations from N to $N/1024$.

* and *Bull. Acad. Sci. Cracow*. 1908, 603—620.

The results are given in the form of tables and curves. For acetic acid of normal strength, the molecular conductivity increases as the neutralisation proceeds; in weaker solutions a minimum occurs near the acetic acid end of the curve. This minimum becomes more pronounced, and is found nearer the normal salt end of the curve, with formic acid; with the stronger acids the conductivity of the acid is greater than that of its potassium salt (except in the stronger solutions), and the minimum becomes less marked as the acid used is stronger, until with trichloroacetic acid it disappears altogether, the curves being straight lines. The theoretical discussion of the results is reserved for a later paper. T. E.

Reduction of Solutions of Potassium Permanganate Acidified with Sulphuric Acid in the Presence of Mineral Salts. T. WARYNSKI and P. TCHEICHVILI (*J. Chim. Phys.*, 1908, 6, 567—576).—The experiments were made with approximately 1/100 molar solutions of potassium permanganate and 1/30 molar sulphuric acid, and varying concentrations of salts. In some cases observations extended over four months. After the experiment, the amount of change was determined by titration with ferrous sulphate.

Most of the salts used as catalysts exerted an accelerating action in the dark, but a retarding action in daylight. Also, in green and blue light most salts retarded the action, but in orange light a slight acceleration was observed; the retarding effect, therefore, probably depends on the actinic rays.

Rise of temperature also affects the catalytic power of salts on the reaction; it increases the activity of the sulphates of iron, chromium, and aluminium, but retards the action of cadmium sulphate. The activity of certain catalysts, such as ferric alum, increases with the concentration. G. S.

Esterification of Trichloroacetic Acid. ANTON KAILAN (*Monatsh.*, 1908, 29, 799—844. Compare this vol., ii, 28).—The esterification of mandelic acid is not retarded by the presence of water up to 4 gram-mols. per litre. The influence of water on the esterification of phenylpropionic acid is much less when trichloroacetic acid is used as a catalyst than when hydrogen chloride is employed.

The relation between the velocity constant and the concentrations of the water and hydrogen chloride in the esterification of trichloroacetic acid is expressed by the equation: $1/k = 6.554 + 4.850/c + 0.0985/c^2 + (-40.15 + 35.39/c - 0.9550/c^2)w + (-16.90 + 12.98/c - 1.259/c^2)w^2$. The ratio of the velocity constants with hydrogen chloride and trichloroacetic acid respectively as catalysts is for phenylpropionic acid four times as great as for trichloroacetic acid. The presence of ethyl trichloroacetate does not retard the esterification. The ester is very little hydrolysed by the catalysts in nearly dry alcohol, but considerably in presence of water. The results are not in accordance with the theory of catalysis by hydrogen ions. C. H. D.

Method of Calculating Atomic Weights. LOUIS DUBREUIL (*Compt. rend.*, 1908, 147, 629—632).—The method introduced by Hinrichs (*Abstr.*, 1907, ii, 945) of calculating the atomic weights of

all the elements present in a single reaction depends on a graphic construction, and is thus limited to reactions in which not more than three elements participate. The author develops Hinrichs' theorem analytically, obtaining equations whereby true atomic weights can be calculated from any reaction, however complex. The method consists in finding the minimum deviations from round number atomic weights which will account for experimental values within their limits of error. The true deviations are then to be obtained by averaging results obtained by different experimenters and methods. R. J. C.

Connexion between Residual Affinity and Additivity. WALTER PETERS (*Ber.*, 1908, 41, 3175—3186).—Although the compounds of ammonia with the salts of heavy metals have been fully examined, the compounds with the salts of more strongly electro-positive metals have not been so closely examined, owing to their high dissociation pressure. The investigation has been made by means of Ley and Wiegner's apparatus (*Abstr.*, 1905, i, 749), as the formation of the additive ammonia compound occurs in an atmosphere of ammonia, and it also allows of the effect of temperature being determined.

Well-defined increase in the number of ammonia molecules absorbed by lowering the temperature was only given by silver chloride, platinochloride, bromide, and platinocyanide; in the other cases, ammonia was absorbed, and liquids were obtained containing a large percentage of ammonia.

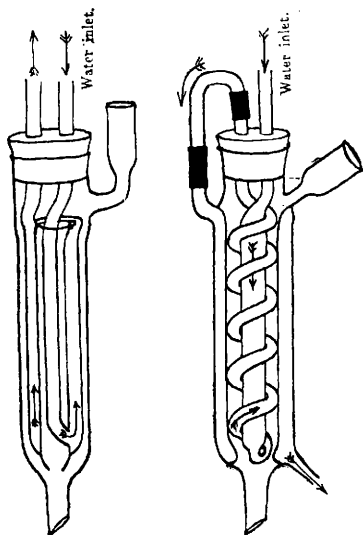
The table summarises the results obtained at the ordinary temperature, I giving the number of ammonia mols. absorbed, and II the number retained after evacuation:

	I.	II.		I.	II.
Cobalt cyanide	2	0	Potassium aurithiocyanate var.	4	
Cobalt thiocyanate	6	2	Platinous chloride	5	4
Nickel thiocyanate	6	3	Silver platinochloride	6	3
Nickel dithionate.....	6	4	Potassium platinocyanide.	1	0
Mercuric thiocyanate	4	1	Silver platinocyanide	4	2
Mercuric acetate	4	2	Cobalt platinothiocyanide.	6	2
Mercuric propionate.....	4	2	Potassium platinothiocyan-		
Silver chloride	1.5	0	ate	2	2
Silver bromide	1.5	0	Silver platinothiocyanate.	6	4
Silver iodide	0.5	0	Sodium platinichloride ...	6	5
Silver cyanate	1	0	Silver platinichloride	8	4
Silver thiocyanate	2	0	Potassium platinithiocyan-		
Potassium aurichloride ...	3	0	ate	12	6
Potassium aurothiocyanate	5	2	Silver platinithiocyanate...	14	6

The platinic salts, in general, absorb more ammonia than the platinous, and the metals, gold or platinum, more than silver or mercury. W. R.

An Apparatus for Extraction by Hot Ether. WILHELM KULKA (*Biochem. Zeitsch.*, 1908, 13, 134—137).—An extraction apparatus somewhat similar to Soxhlet's, but so modified that the vessel containing the substance to be extracted is surrounded by the ether vapour, its contents therefore being nearly at the temperature of boiling ether (about 30°). S. B. S.

New Forms of Condenser. H. STOLTZENBERG (*Chem. Zentr.*, 1908, ii, 277; from *Zeitsch. Chem. Appar.*, 1908, 3, 243—245).—The condensers described have the advantage of exposing four cooling surfaces to the vapour, are light and compact, and may be readily cleansed by removing the inner portion with the stopper. The accompanying figures should explain their construction. J. V. E.



A New Aspirating Reflux Condenser. HENRI VIGREUX (*Bull. Soc. chim.*, 1908, [iv], 3, 855—857).—This consists of a Liebig condenser in which the water outflow pipe is fused to a small aspirator acting on the principle of an ordinary filter-pump. The air-exhaust tube of this aspirator is connected with the upper end of the inner condensing tube. The latter is provided on its inner surface with points and mounds in order to facilitate condensation. The effect of a current of water through the condenser envelope is thus to produce an upward current of air in the inner condensing tube, and it is

claimed that such a condenser placed above an open vessel (basin, beaker or flask) containing the boiling liquid condenses the whole of the vapours, returning the condensed liquid to the vessel even when the liquid consists of ether, alcohol, light petroleum, or carbon disulphide. The apparatus is also of use in reactions involving hydrogen chloride or bromine or iodine vapours. E. H.

A New Aspirating Condenser and Recuperator for Rapid Evaporations. HENRI VIGREUX (*Bull. Soc. chim.*, 1908, [iv], 3, 858).—This is simply the condenser described previously (preceding abstract), of which the inner tube is provided, immediately below the outer jacket, with a side-tube arranged to collect the condensed liquid and to convey it through a trap (to prevent the aspirator from drawing air through this side-tube) into a receiver. Solutions in ether, light petroleum, benzene, or carbon disulphide can be thereby rapidly evaporated without risk of ignition. The lower end of the condenser should be placed slightly above the surface of the liquid when the latter is contained in a basin, and in the middle of the neck of a flask when this vessel is used. E. H.

A Simple Form of Sprengel Vacuum Pump. JAMES ARTHUR POLLOCK (*J. Roy. Soc., New South Wales*, 1907, 41, 140—143).—A modified short fall Sprengel pump, in which the raising of the mercury is effected by evaporating the mercury at a lower and condensing it at a

higher level; the mercury on reaching the bottom of the fall tube enters a horizontal tube, the farther end of which is bent vertically upwards; this vertical limb bears a bulb in which the mercury is boiled, the vapours being condensed by passing through a Liebig's condenser the lower end of which is connected to the fall tube. The apparatus must be used in connexion with an efficient auxiliary pump. P. H.

Turbine Funnel for Mixing Solutions. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1908, 47, 697).—The apparatus is intended for the purpose of mixing a reagent with a solution. It consists of a funnel the stem of which is provided at the bottom with two arms placed at right-angles to the stem and ending in fine curved jets. A glass bulb is attached to the stem just below the funnel, and acts as a float, whilst the apparatus is kept in an upright position by means of a small quantity of mercury contained in a bulb below the two arms. The apparatus is floated in a solution contained in a beaker, and the reagent is poured into the funnel; as it escapes into the solution through the jets, the apparatus is caused to revolve, and the reagent and solution are thus mixed. W. P. S.

Inorganic Chemistry.

Catalysis of Hydrogen Peroxide by Iodine and Iodine Ions. EMIL ABEL (*Zeitsch. Elektrochem.*, 1908, 14, 598—607).—The reactions between hydrogen peroxide and iodine or iodine ions are: (1) $\text{H}_2\text{O}_2 + \text{I}_2 = 2\text{H}^+ + 2\text{I}^- + \text{O}_2$ and (2) $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ = 2\text{H}_2\text{O} + \text{I}_2$. The first is very rapid in alkaline solutions, and the second is rapid in acid solutions; in solutions containing a suitable small quantity of hydrogen ions, the two may take place with equal velocity, and the result is then simply decomposition of hydrogen peroxide, the concentrations of the iodine and iodine ions remaining unchanged. The ratio between the quantities of iodine and iodine ions which must be present in order to make the two reactions proceed equally fast depends on the concentration of the hydrogen ions. A large number of experiments, in which the concentration of the hydrogen ions is kept constant by adding acetic acid and sodium acetate to the solutions, are made which are in complete agreement with these views.

Bredig and Walton's observations (Abstr., 1904, ii, 319) on the catalysis of hydrogen peroxide by neutral iodides are explained by the same reactions, for in this case when reaction (2) has proceeded to a very small extent, the solution becomes alkaline and reaction (1) then proceeds exceedingly fast, the stage at which the two have equal velocity is therefore attained when a very small quantity of iodine has been liberated.

T. E.

Non-existence of a Polymeride of Chlorine. E. BRINER and E. DURAND (*Zeitsch. Elektrochem.*, 1908, 14, 706—707).—The authors have investigated the effect of the silent discharge on carefully-purified chlorine at a temperature but little above its boiling point. The experimental arrangements could have detected a contraction of 1/2000 of the volume of the gas, but no change was observed. The activity of chlorine observed by Kellner (Abstr., 1902, ii, 649) and Russ (Abstr., 1905, ii, 381) is possibly due to ozone or oxides of chlorine. T. E.

Absolute Density of Hydrogen Sulphide. GEORGES BAUME and F. LOUIS PERROT (*J. Chim. Phys.*, 1908, 6, 610—619).—Hydrogen sulphide from several sources, purified by fractional distillation, was employed. The density was determined by the method already described (this vol., ii, 372), except that an oil gauge was interposed between the gas and the mercury.

The mean value of nearly twenty experiments for the weight of a litre of the gas at 0° and 760 mm. is 1.5392 grams. From this result, the atomic weight of sulphur has been calculated by Guye's method from the critical constants. The mean result is $S = 32.070$ ($H = 1.00775$), in excellent agreement with the gravimetric determinations of Richards and Jones (Abstr., 1907, ii, 685). G. S.

Preparation of Azoimide. JOHANNES THIELE (*Ber.*, 1908, 41, 2681—2683).—Azoimide is obtained in good yield by the action of ethyl nitrite on hydrazine in presence of alkali. Hydrazine hydrate (1 mol.) is mixed with 4*N* sodium methoxide ($1\frac{1}{2}$ mols.), ethyl nitrite ($1\frac{1}{2}$ mols.), and ether, and the mixture allowed to remain, first in ice, and then at the ordinary temperature. After twenty-four hours, the sodium azoimide is collected and washed. The yield is nearly quantitative. Instead of the hydrate, hydrazine sulphate may be used; this is ground with $3\frac{1}{2}$ mols. of sodium methoxide for six hours, the sodium sulphate filtered off, and the filtrate treated with ethyl nitrite and ether. For the direct preparation of free azoimide, hydrazine sulphate is shaken for six hours with aqueous sodium hydroxide and ethyl nitrite; in this way, 80—84% of the hydrazine is converted into azoimide. Sodium azoimide is also formed by heating hydrazine hydrate with aqueous sodium nitrite, preferably in presence of hydrazine sulphate or sodium hydroxide, but the reaction is slow and incomplete. J. C. C.

Formation of Nitric Oxide in the High Tension Arc. FRITZ HABER and ADOLF KOENIG (*Zeitsch. Elektrochem.*, 1908, 14, 689—695).—The authors have continued their experiments (this vol., ii, 34) by passing the high tension arc through nitric oxide at about 100 mm. pressure. A platinum wire of 0.01 mm. diameter, stretched across the quartz tube in which the arc is produced, melts when the current is increased to 0.2 ampere. The temperature is therefore not much above the melting point of platinum. Using the same current and passing the gas through the tube at the same rate, the percentage of nitric oxide (about 14.5) leaving the arc is the same whether nitric oxide is used

or a mixture of equal volumes of oxygen and nitrogen. The temperature is at most some hundreds of degrees above the melting point of platinum, and the equilibrium is therefore electrical, that is, due to ionic collisions, and not thermal. T. E.

Interaction of Nitric Oxide and Oxygen. WILHELM HOLWECH (*Zeitsch. angew. Chem.*, 1908, 21, 2131—2135).—Mandl and Russ's observations (this vol., ii, 272) suggest that nitric oxide reacts only slowly with pure oxygen, the reaction being accelerated by the presence of catalysts. As this is of great importance for the practical working up of the nitric oxide which is formed in the electric furnace, the present author has endeavoured to prepare a non-reacting mixture of nitric oxide and ozonised oxygen with the object of studying the effect on it of catalysts. The apparatus employed is figured, and the results of the experiments represented by curves. It is found that 2 vols. of nitric oxide react with 1 vol. of oxygen almost completely at the atmospheric pressure with formation of NO_2 and N_2O_4 . The velocity of the reaction, by constant volume, is approximately the same for oxygen prepared from air by Linde's method, ozonised oxygen, oxygen from barium peroxide, and oxygen from potassium dichromate and sulphuric acid. G. Y.

Action of Nitrous Gases and Oxygen on Water. FRITZ FOERSTER and M. KOCH (*Zeitsch. angew. Chem.*, 1908, 21, 2161—2172).—A résumé is given of the work of various authors on the preparation of nitric and nitrous acids from the nitric oxide formed by combustion of atmospheric nitrogen. It is pointed out that the concentration of the nitric acid formed by the action of a mixture of nitrogen dioxide and oxygen on water must reach a limit, which is a function of the velocity with which the equilibrium $2\text{NO} + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + \text{HNO}_2$ is reached, and, therefore, of the concentration of the nitrogen dioxide, since the lower the partial pressure of the dioxide the smaller will be the concentration of its solution in the water, and hence the velocity of its reaction with the water. On the other hand, the larger volume of undissolved gases passing through the solution will cause more rapid evaporation, in which the nitric acid takes part even at concentrations far below 68%. The maximum concentration of nitric acid which can be obtained by the action of a mixture of nitrogen dioxide and oxygen on water, must lie about this percentage, since, when solutions containing higher percentages are evaporated, the nitric acid volatilises more rapidly than the water. For the same reasons, the limit concentration must be the lower the more rapid the current of gas. These views are confirmed by the results now obtained on studying the action on water of mixtures of nitrogen dioxide with oxygen and with air in varying proportions. The apparatus employed is figured, and the results are tabulated.

The formation of nitric acid takes place fairly rapidly until the solution contains about 54% of acid, a concentration corresponding with the composition $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$, when, in consequence of the greatly diminished amount of free water, the reaction becomes greatly retarded. It is found that, whilst the concentration of a 64.22% acid is raised to 67.6% by the action at 0° of a mixture containing 63.2% by volume of

nitrogen dioxide, at 60° the concentration is raised by the same mixture, passing into the nitric acid at the same rate and for the same period, only to 65.2%. The higher temperature is the more unfavourable to the reaction, which is, therefore, probably one between water, oxygen, and the bimolecular dioxide, N_2O_4 .

The influence of the partial pressure is shown in that, whilst almost the whole of the dioxide of a mixture of 2.5 vols. of nitrogen dioxide with 6.0 vols. of oxygen is absorbed by water with formation of a 37% acid, under the same conditions only 53% of the dioxide of a mixture of 2.5 vols. of dioxide and 122 vols. of oxygen is absorbed with formation of a 27.73% acid.

Whilst at low concentrations the velocity of the reaction is affected only slightly by the rate at which the gases are passed into the water, a marked effect is produced at concentrations over 50% of acid. Equal volumes of a mixture containing 5.0 vols. of dioxide and about 12 vols. of oxygen, when passed into water at the rates of 4.25, 8.5, and 17.0 litres per hour, yielded 58.78%, 55.36%, and 53.95% acids respectively. The bearing of the experimental results on the behaviour of nitrous acid also is discussed.

G. Y.

Molecular Weight and Hydrates of Hypophosphoric Acid.

ARTHUR ROSENHEIM and MAX PRITZE (*Ber.*, 1908, 41, 2708—2711).—The controversy between Rosenheim, Stadler, and Jacobsohn (*Abstr.*, 1906, ii, 744) and Parravano and Marini (*Abstr.*, 1906, ii, 744) as to the molecular weight of hypophosphoric acid has led the authors to determine the molecular weights of the methyl and ethyl esters of pyro- and of hypo-phosphoric acids in methyl or ethyl iodide by the ebullioscopic method, with results which indicate that the formulæ of the acids are $H_4P_2O_7$ and H_2PO_3 respectively.

The monohydrate, $H_2PO_3 \cdot H_2O$, m. p. 62°, appears to be the only hydrate stable between 0° and 60°; Joly's anhydride (*Abstr.*, 1886, 662), or Süssner's hydrate, $H_2PO_3 \cdot \frac{1}{2}H_2O$, could not be obtained.

C. S.

Coagulation of [Colloidal] Arsenious Sulphide by Barium Chloride. JACQUES DUCLAUX (*J. Chim. Phys.*, 1908, 6, 592—595).—When a colloidal solution of arsenious sulphide is precipitated by barium chloride, part of the barium is carried down with the precipitate and the remaining solution is acid. This is usually accounted for on physical lines as being due to absorption of the barium by the sulphide with consequent hydrolysis of the salt (Whitney and Ober, *Abstr.*, 1902, ii, 65), although Linder and Picton (*Trans.*, 1895, 67, 63) showed that the sulphide usually contains excess of hydrogen sulphide, and that in the presence of barium chloride barium sulphide is formed and hydrogen chloride set free.

The author now shows that when a colloidal solution of arsenious sulphide containing excess of hydrogen sulphide, which has been kept well stoppered for five years, is precipitated with barium chloride and filtered, the filtrate contains no hydrogen sulphide, but a certain amount of arsenious acid; the latter corresponds approximately with the amount of hydrogen chloride in the filtrate, and therefore with that of the barium absorbed. The author considers that neither of the above

explanations of the phenomenon are satisfactory; it is probable that there is double decomposition between the barium chloride and the sulphide, perhaps by replacement of an AsO group existing in the sulphide by barium. G. S.

Preparation of Carbon Monoxide. ERWIN RUPP (*Chem. Zeit.*, 1908, 32, 983).—A known weight of sulphuric acid is heated in a generating flask to 100°, and an equal weight of 98% formic acid is dropped in from a stoppered funnel. A regular stream of pure carbon monoxide is thus evolved; when the action slackens, a gentle heat is again applied by means of a small flame. L. DE K.

Simple Arrangement for Filling Glass Tubes with Liquid Carbon Dioxide. ALFRED THIEL (*Chem. Zentr.*, 1908, ii, 470—471; from *Zeitsch. Chem. Appar.*, 1908, 3, 240—243).—An arrangement is described for filling evacuated glass tubes with carbon dioxide to allow of the demonstration of the critical temperature of this gas. The glass tube to be filled is placed in a cooling bath of solid carbon dioxide and ether, and is connected by a stout capillary tube to a compression tube, which is regulated by an adjustable head of mercury. Air-free carbon dioxide is admitted to the compression tube by lowering the head of mercury, when, by closing a tap on the inlet tube and opening a tap connecting with the exhausted condensing tube and increasing the head of mercury, the enclosed carbon dioxide is transferred to the cooled tube, where it is condensed. By repeating this operation several times, any required quantity of carbon dioxide may be condensed in an expeditious manner. J. V. E.

Argon in Radioactive Zirconium Minerals. A. VON ANTROPOFF (*Zeitsch. Elektrochem.*, 1908, 14, 585—586).—The gas extracted from a feebly radioactive Brazilian mineral containing 97% of zirconia consisted mainly of carbon dioxide with smaller quantities of hydrogen and nitrogen and traces of helium and argon. This is the second mineral in which argon has been found; the first was also a radioactive zirconium compound (*Trans.*, 1906, 89, 1568). T. E.

Analysis of the Atmospheric Gases Non-liquefiable in Liquid Air. FRÉD BORDAS and TOUPLAIN (*Compt. rend.*, 1908, 147, 591—594).—A modified form of the apparatus described previously (this vol., ii, 430) has been employed for the analysis of the gases which escape liquefaction when liquid air is distilled and the oxygen and nitrogen condensed. A table is given of the wave-lengths of the lines observed in the spectrum of this gas after removal of all the oxygen and nitrogen. This includes, besides those observed by Baly for neon and helium, the red lines of wave-lengths 7267, 7050, 6943, 6732, 6610, 6572, 6535, 6509; the orange lines, 5905, 5890; the yellow lines, 5820, 5808, 5765, and the green lines, 5750, 5722, 5694, 5659, 5569, 5441, 5407, 5348, 5336, which the authors attribute to neon, but which have not been observed previously.

The conclusion is drawn that the gases in the atmosphere non-liquefiable in liquid air consist of neon and helium. E. H.

Liquefaction of Helium. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 168—185; *Compt. rend.*, 1908, 147, 421—424).—The actual work carried out with the object of liquefying helium was preceded by a study of the isothermal lines for such temperatures as can be attained by the use of liquid hydrogen. The results of this study made it very probable that the Joule-Kelvin effect would not only give a decided cooling at the melting point of hydrogen, but that this would be sufficient to make a Linde-Hampson process successful. The construction of the helium liquefier was therefore an imitation of the hydrogen liquefier described in a previous communication.

The helium employed was obtained by heating monazite sand. The gas was then successively exploded with oxygen, cooled with liquid air, compressed, and led over charcoal at the temperature of liquid air. It was then passed through a column of hot copper oxide, compressed over charcoal at the temperature of liquid air, and further led over charcoal under pressure at the temperature of liquid hydrogen, until the gas which had been absorbed in the charcoal and then separately collected no longer contained any appreciable impurity.

On the day before the final experiment, 75 litres of liquid air were prepared, and on the day itself, operations began with the preparation of 20 litres of liquid hydrogen. When the helium (200 litres) had been circulating in the liquefier for about three hours, more than 60 c.c. of liquid helium was obtained. In consequence of the extreme purity of the helium, and by virtue of the special contrivances adopted, the apparatus remained perfectly transparent during the whole experiment.

The liquid helium looks as if it was almost at its critical temperature, and its surface stands out like the edge of a knife against the glass. Evaporation under diminished pressure did not lead to solidification, and the triple point pressure is certainly below 1 cm. The temperature reached in this evaporation was probably about 3° absolute.

The boiling point was found to be 4·3° absolute, but a slight correction is suggested which would make it about 4·5°. The density of the liquid is 0·15; the ratio of the density of the vapour to that of the liquid is 1 : 11 at the boiling point, indicating that the critical temperature is not much higher than 5° absolute, and that the critical pressure is not much more than 2·3 atmospheres.

The value of a , the constant of van der Waals' equation, appears for helium to be about 0·00005, and the value of b is probably about double the value which was expected (0·0005). J. C. P.

Preparation of Colourless Alcoholic Potassium Hydroxide. ADOLF HALLA (*Chem. Zeit.*, 1908, 32, 890).—Thirty grams of pure stick potassium hydroxide are placed in a bottle with one litre of 95% alcohol, and left at atmospheric temperature until solution is effected, the bottle being shaken from time to time. The clear supernatant liquid is then carefully siphoned off into another bottle, which is stoppered and exposed to diffused daylight. The solution is thereby

bleached in the course of a few days, and remains colourless so long as it is kept in diffused daylight. P. H.

The Partition of Silver between Zinc and Lead. G. N. POTDAR (*J. Coll. Sci. Tōkyō*, 1908, 25, ix, 1—13. Compare Wright and Thompson, *Abstr.*, 1890, 336).—Silver-lead alloys were melted with zinc in an atmosphere of carbon dioxide, the temperature being maintained at 540° by means of a bath of boiling phosphoric sulphide. After stirring, the mass was allowed to remain fluid for five and a-half hours, rapidly cooled, and the silver in the two solidified layers estimated. The whole of the zinc layer has to be taken for analysis, as the distribution of zinc in it is far from uniform, owing perhaps to segregation during cooling. At 540°, silver is about 300 times more soluble in zinc than in lead, and this partition-coefficient is practically independent of the concentration of the silver.

In Parkes' process for the desilverisation of lead, the solid zinc scum is removed at 325—360°. Experiments at this temperature indicate that the removal of silver by the zinc is practically complete, the partition-coefficient at 358° varying in three trials from 1300 to 5700. C. H. D.

The Silver Hydrogel in Photographic Films. LÜPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 135—136).—The peculiarities of the silver deposits obtained with different developers, and with gelatin or collodion films, are explained by the more or less completely colloidal nature of the silver, and by adsorption of different substances from the developers (compare this vol., ii, 841). T. E.

Use of Metallic Deposits in Metallography. II. FEDERICO GIOLITTI (*Gazzetta*, 1908, 38, ii, 352—357).—The author has applied the method devised by him (*Abstr.*, 1906, ii, 759) to the qualitative study of alloys constituted of solid solutions. When a polished surface of a binary alloy containing mixed crystals either of two metals or of one of them and a compound of the two is immersed in a solution containing ions of the more electronegative or more noble of the two metals, differences of potential are established between the various portions of the surface. The cations of the solution will be deposited in the metallic state on the different parts of the section with a velocity increasing with the concentration of the more electronegative metal. By varying the concentration of the solution and the duration of immersion, or by observing the section under the microscope, the gradual and continuous variations of the metallic deposit on that part of the surface occupied by the mixed crystals can be followed. These variations, which correspond with differences in the concentration of the more noble metal in the mixed crystals, give an immediate indication that the constituent in question is a solid solution, and also permit the observer to judge the heterogeneity of concentration of this solid solution. Various bronzes have been studied in this way, microphotographs of the different sections after treatment with chromic oxide or with copper sulphate solution being given. T. H. P.

Magnesium Oxychloride Formed by Electrolysis of the Residual Solutions from the Manufacture of Potassium Chloride, and its Importance for the Preparation of Bromine by Kossuth and Mehns's Method. HANS HOF (*Chem. Zeit.*, 1908, 32, 993).—It has been found that the yield of free bromine, obtained by electrolysis of the residual solutions from the manufacture of potassium chloride, increases with the concentration of the solution electrolysed. On dilution with water, the electrolysed solution containing free bromine becomes gradually less yellow, and finally colourless, when the solution is found to contain only combined bromine; this may be again liberated by sulphuric acid. If the bromine is first removed by means of an organic solvent, the electrolysed solution, on dilution, becomes alkaline and opaque, in consequence of the separation of magnesium hydroxide. It is considered that magnesium hydroxide, formed during the electrolysis, remains dissolved in the concentrated magnesium chloride solution, forming a basic salt. This is decomposed by water with liberation of magnesium hydroxide, which then reacts with the free bromine. In agreement with this, analytical figures are given, showing that the proportion of bromine present as bromate to the free bromine increases with the dilution of the electrolysed solution.

By electrolysis of a concentrated solution of magnesium chloride, the author has obtained a neutral solution which does not react with bromine. When diluted, it becomes alkaline, and deposits magnesium hydroxide. The concentrated solution slowly deposits a white, amorphous mass, $\text{MgCl}_2 \cdot 5\text{MgO}$ (Bender, *Annalen*, 1871, 159, 341; Davis, *Chem News*, 1872, 25, 258), which is stable at 160° and yields magnesium chloride when treated with cold water, but is completely decomposed only by boiling water. G. Y.

Electrolytic Oxidation of Copper. F. SCHMIEDT (*Chem. Zentr.*, 1908, ii, 386; from *Elektrochem. Zeitsch.*, 1908, 15, 53—56).—The author has repeated the work of Müller and Spitzer (*Abstr.*, 1907, ii, 174), and finds that, besides cupric oxide and copper peroxide, there is also formed cuprous oxide, which, however, becomes decomposed by the hydrogen peroxide that is also produced. Copper peroxide is formed in largest quantities at the beginning of the electrolysis, when the temperature is low. J. V. E.

Alloys of Copper and Tin. FEDERICO GIOLITTI and G. TAVANTI (*Gazzetta*, 1908, 38, ii, 209—239).—The results obtained by the authors in studying the freezing points and microscopic appearance of the copper-tin alloys agree, in general, with those of Heycock and Neville (*Abstr.*, 1901, ii, 508; 1902, ii, 261). The freezing-point diagram of these alloys is divided clearly into two parts, the first comprising alloys containing from 0 to 38.34% of tin, and the second, those containing more than 38.34% of tin. Thus the diagram is a complex one, resulting from the combination of the equilibrium diagrams of $\text{Cu-Cu}_3\text{Sn}$ and $\text{Cu}_3\text{Sn-Sn}$. The diagram is discussed in detail. T. H. P.

Copper and Iron Salts in Presence of Alkalis and Acids. HERMANN FRISCHER (*Chem. Zeit.*, 1908, 32, 1005—1006).—Experiments are described to show that the action of sodium hydroxide on a mixture of ferrous and cupric sulphates takes place, contrary to Millberg's supposition (*Chem. Zeit.*, 1906, 30, 511; 1907, 31, 1143), according to the following equations: (1) $2\text{CuSO}_4 + 4\text{NaHO} = 2\text{Cu}(\text{OH})_2 + 2\text{Na}_2\text{SO}_4$, and (2) $2\text{FeSO}_4 + 2\text{Cu}(\text{OH})_2 = \text{Fe}_2(\text{OH})_4\text{SO}_4 + \text{Cu}_2\text{SO}$. The action of air on the resulting mixture leads to the formation of ferric hydroxide and cupric sulphate, the whole reaction being represented by the equation: $2\text{FeSO}_4 + 2\text{CuSO}_4 + 4\text{NaHO} + \text{H}_2\text{O} + \text{O} = 2\text{Fe}(\text{OH})_3 + 2\text{CuSO}_4 + 2\text{Na}_2\text{SO}_4$. Any further addition of alkali must result in precipitation of copper hydroxide. As the equation shows, the copper sulphate acts as the oxygen carrier; in agreement with this view, if potassium sodium tartrate and an excess of alkali are added to the mixture of ferrous and cupric salts, cuprous hydroxide is precipitated in the cold, and on heating is converted into the red anhydride, whilst the ferric salt remains in solution. If a sufficient excess of ferrous salt is present, the cuprous hydroxide is reduced to metallic copper. This reaction may be employed for the detection of ferrous salts.

If a ferrous salt is added to an ammoniacal solution of a cupric salt, ferric hydroxide is precipitated, whilst the blue colour of the solution gradually disappears; the cuprous salt remaining in solution is rapidly oxidised by air. In this case, also, the precipitation of the ferric hydroxide may be prevented by addition of a tartrate or a citrate.

The behaviour of copper and iron salts in presence of ammonia affords a ready means of preparing cuprous solutions for the absorption of carbon monoxide in gas analysis. It is evident, moreover, that, in the separation of iron and copper by means of ammonia, a preliminary oxidation of ferrous salts is unnecessary if the amount of copper present is equal to, or greater than, that of the iron. On the other hand, if the copper is to be estimated colorimetrically, the ferrous salts present must first be oxidised.

In acid solution, cuprous salts are oxidised at the expense of ferric salts, according to the equation: $\text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3 = 2\text{CuO} + 2\text{FeO}$.

G. Y.

Equilibrium in the Reaction between Lead Sulphide and Its Oxidation Products. III. RUDOLF SCHENCK and W. RASSBACH (*Ber.*, 1908, 41, 2917—2925).—Previous investigations (Abstr., 1907, ii, 546, 619) have shown that the metallurgically important reactions: (I) $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$; (II) $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2$, are reversible, the equilibrium being conditioned by a definite pressure of the sulphur dioxide, which is dependent on the temperature only. In addition to the two temperature-pressure curves so obtained, a third was indicated, the cause of which forms the main object of the present investigation. The result shows that a basic sulphate, $\text{PbSO}_4 \cdot \text{PbO}$, is formed, which, setting up its own reversible reaction, $2[\text{PbSO}_4 \cdot \text{PbO}] + \text{PbS} \rightleftharpoons 7\text{Pb} + 5\text{SO}_2$, accounts for the existence of the third temperature-pressure curve. These three curves divide the whole temperature-pressure diagram into four fields. The final product of all reactions in the first field is lead sulphate, in the second the basic sulphate, and in

the third lead oxide; these three stable phases do not evolve sulphur dioxide with lead sulphide. In the fourth field, no compound containing oxygen is stable with lead sulphide, an impure metal being obtained with evolution of sulphur dioxide. These conclusions are deduced from observations at temperatures below 820° ; above this temperature, complications are introduced, owing to the mutual solubility of lead oxide and lead sulphate.

The existence of the basic sulphate, $\text{PbSO}_4 \cdot \text{PbO}$, is proved as follows. Mixtures of lead sulphate and lead oxide in known proportions are heated to 1020° , and allowed to cool. The freezing-point curve, consisting of many branches, indicates the existence of many compounds of lead sulphate and lead oxide which do not form mixed crystals with one another or with either of the components. Distinct maxima are observed at two points: (966° , 40% PbO) and (951° , 61.5% PbO); the compositions of the mixture at these points correspond with the formulæ $\text{PbSO}_4 \cdot \text{PbO}$ and $\text{PbSO}_4 \cdot 2\text{PbO}$ respectively. The existence of a third basic sulphate, $\text{PbSO}_4 \cdot 3\text{PbO}$, is indicated by the curve, which, however, is only stable below 880° ; above this temperature, it passes into $\text{PbSO}_4 \cdot 2\text{PbO}$. The presence of these basic sulphates in the fused masses containing 40–70% lead oxide is indicated by the appearance of long, transparent needles. The only basic sulphate giving in the presence of lead sulphide and a little lead a well-defined temperature-pressure curve is $\text{PbSO}_4 \cdot \text{PbO}$, as already mentioned; the others react too slowly for any trustworthy data to be obtained.

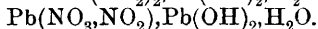
The following facts have been observed during the investigation. Lead sulphate does not melt below 1100° (compare Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, [v], 41, 360); an exact determination cannot be made, owing to dissociation into sulphur trioxide. Pure lead sulphate shows a transition point at 850° . Mixtures of lead oxide and sulphate, rich in the former, change in volume at the ordinary temperature, the original dense mass swelling up and crumbling to a coarse powder, in which scales of lead oxide can be detected. The force exerted during the expansion distorted the containing platinum crucible.

C. S.

Compounds of Lead with Nitrous Acid. ALBERTO CHILESOTTI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 173–183, 288–295. Compare this vol., ii, 845).—By measuring the *E.M.F.* of cells consisting of two lead electrodes, one immersed in a solution of a lead salt containing a known concentration of lead ions, and the other in a 0.1*N* lead nitrite solution, it is found that the concentration of the lead ions in the latter is very nearly equal to their concentration in a lead chloride solution of corresponding concentration (compare Abegg and Labenzinski, *Abstr.*, 1904, ii, 241). The lower conductivity of lead nitrite solutions, compared with those of lead chloride, is hence due, not to a less degree of dissociation (*loc. cit.*), but to a difference in the mobility of the complex ions.

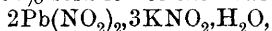
The conductivity of lead nitrite solutions undergoes a gradual increase, owing to decomposition of the nitrite according to the equation: $3\text{Pb}(\text{NO}_2)_2 + 2\text{H}_2\text{O} = \text{Pb}(\text{NO}_3)_2 + 2\text{Pb}(\text{OH})_2 + 4\text{NO}$; probably a small amount of secondary decomposition occurs with evolution of

nitrous oxide. The solutions examined, after boiling and cooling, deposit nacreous scales of $\text{Pb}(\text{NO}_2)_2, \text{Pb}(\text{OH})_2, \text{H}_2\text{O}$ or



Attempts to prepare a double nitrite of lead and potassium by mixing hot concentrated solutions of lead acetate and potassium nitrite in various proportions led, in all cases, to crystalline compounds, in which the ratio $\text{Pb} : \text{NO}_2$ lies between 1 : 3 and 1 : 4; the excess of lead oxide present is due probably to decomposition of the lead nitrite.

By the gradual addition of freshly precipitated and washed lead hydroxide to a boiling 30% solution of the double nitrite,



the author has prepared the basic lead nitrite, $\text{Pb}(\text{NO}_2)_2, \text{Pb}(\text{OH})_2, \text{H}_2\text{O}$, which can be obtained in the pure, non-hydrolysed condition by gently warming the impure product with a cold saturated, crude solution of the salt, and allowing to crystallise. Under certain conditions, this basic salt separates in the form $\text{Pb}(\text{NO}_2)_2, \text{Pb}(\text{OH})_2$. Study of the action of lead on a lead nitrate solution leads to the confirmation of the existence of the compound $4\text{PbO}, \text{N}_2\text{O}_3, \text{H}_2\text{O}$, prepared by Chevreul (*Ann. Chim.*, 1812, 83, 72) and others.

T. H. P.

Coagulation of Colloidal Aluminium Hydroxide by Electrolytes. SHIN-ICHI KAWAMURA (*J. Coll. Sci. Tōkyō*, 1908, 25, viii, 1—29).

—It has been found possible to determine the degree of coagulation of a colloidal solution of aluminium hydroxide, produced by various electrolytes, by measuring the viscosities of the solutions. The general relations found are not affected to any marked degree by the temperature, concentration of the colloidal solution, or duration of the experiment, and may be summarised as follows: (1) In those cases where coagulation occurs, the relative viscosity shows a marked rise only when the concentration of the electrolytes reaches certain values. From this point, the viscosity increases with the increasing concentration of the electrolyte to a certain limit, and then ceases to be influenced by the further addition of the electrolyte. In some cases, the degree of coagulation increases suddenly, and in others, more gradually, with the increasing concentration of the electrolyte. (2) The colloidal solution of aluminium hydroxide shows anodic cataphoresis; consequently, in accordance with Hardy's rule (compare Abstr., 1899, ii, 567; 1903, ii, 469; 1906, i, 121), only anions are found to exercise coagulating power. (3) With but few exceptions, the coagulating power of an electrolyte increases rapidly with the increasing valency of the anion; this is in agreement with Schulze's rule (compare Abstr., 1883, 295). (4) The highest degree of coagulation produced by various electrolytes differs considerably in different cases, and appears to be a characteristic of the electrolyte.

W. H. G.

Crystallised Iron from a Foundry at Teschen, Austria. FELIX CORNU (*Centr. Min.*, 1908, 545—546).—The crystals are about 3 mm. across, and have the form of distorted octahedra grouped along

the three cubic axes (similar to the well-known skeletal growths of magnetite). Anal. I of the crystals, and II of the ground mass of iron in which they are embedded.

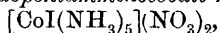
	Fe.	Si.	P.	S.	Cu.	Mn.	C.	O.
I.	95.32	0.22	0.16	—	—	1.24	1.80	1.26
II.	95.91	0.19	0.24	0.30	0.10	1.46	1.80	—

L. J. S.

Nature of the Pseudo-solutions of Ferric Hydroxide. III. FEDERICO GIOLITTI (*Gazzetta*, 1908, 38, ii, 252—258. Compare Abstr., 1906, ii, 857).—The typical or stable ferric hydrosol, prepared by treating washed precipitated ferric hydroxide with acetic acid after keeping it in contact with water for several months and dissolving in water the residue insoluble in acetic acid, is either a ferric hydroxide containing less water than the other hydrosols and the ordinary gelatinous hydroxide, or possibly anhydrous ferric oxide; the latter view is supported by the comparative difficulty with which this hydrosol is dissolved by acids. The hydrosol of Graham, prepared by dialysis, also changes gradually into the stable hydrosol.

T. H. P.

Iodopentamminecobalt Salts. ALFRED WERNER (*Ber.*, 1908, 41, 3007—3015).—The author finds that the substances obtained by Sand and Böckmann (this vol., ii, 44) by the action of iodine on the black nitrosopentamminecobalt salts, to which they ascribe the constitution of a complex metal ammonia containing cobalt atoms with co-ordination numbers 7 and 8, are, in reality, members of the hitherto unknown series of iodopentamminecobalt salts. For example, the product of the action of iodine on black nitrosopentamminecobalt nitrate is a mixture of *iodopentamminecobalt nitrate*,



with a little xantho-nitrate; the separation of the two is effected through the dichromates. By treatment with silver nitrate, the former yields aquopentamminecobalt nitrate, thus proving its constitution.

Members of the new series are readily obtained by heating aquopentamminecobalt iodide at 80°. Water is evolved, and the brown product, triturated with ammonium nitrate, yields iodopentamminecobalt nitrate. The *chloride*, *bromide*, *iodide*, and *dichromate* are described; they all have a green colour.

C. S.

Relationships between Nickel and Hydrogen. M. MAYER and V. ALTMAYER (*Ber.*, 1908, 41, 3062—3074).—The absorption of hydrogen by reduced nickel has been studied at temperatures between 360° and 560°, and at pressures between 1/15 and 4/5 of an atmosphere. The metal was obtained by the same method as was used by Sieverts (Abstr., 1907, ii, 741), but the conditions of absorption were different, as only small amounts (2.7 grams) of metal were used, and each experiment was allowed to proceed until equilibrium was attained. The amount of gas absorbed was much greater than in Sievert's experiments; thus at pressures between 1/15 and 4/5 of an

atmosphere, and a temperature of 360° , 1 vol. of the metal absorbs 5.5—50 volumes of gas. The isotherms representing the relationship between the pressure of the hydrogen and the relative number of atoms of hydrogen absorbed, are straight lines; thus indicating that Henry's law holds good, and that the system nickel-hydrogen is bivalent.

The rapidity with which equilibrium is established varies considerably with the amount of hydrogen present.

The solubility coefficient, that is, the ratio weight of absorbed hydrogen in 1 litre of nickel/weight of hydrogen in 1 litre of the gas volume, varies with the temperature.

	360° .	420° .	480° .	560° .
Ratio.....	297	302	306.4	299.1

J. J. S.

Decomposition of Chromic Acid by Hydrogen Peroxide

ERNST H. RIESENFELD and ALFRED WESCH (*Ber.*, 1908, **41**, 2826—2835. Compare Abstr., 1905, ii, 825).—The decomposition of chromic acid by hydrogen peroxide was measured in presence of a varying excess of chromic acid. In spite of an excess of from one to one hundred times the theoretical, the amount of oxygen evolved remained constant, averaging 1.94 atoms per molecule of hydrogen peroxide. Decomposition of chromic acid in presence of excess of hydrogen peroxide and increasing amounts of sulphuric acid showed that up to a certain point the reaction remained unchanged, 1 atom of chromium corresponding with about 4.7 atoms of oxygen. Above 2.5*N* acid, a strength known to react with hydrogen peroxide to form Caro's acid, more oxygen than 5 atoms is evolved, due to a decomposition of the Caro's acid in presence of chromic salts. When the same change is studied in presence of excess of chromic acid, it is found to be far less dependent on the amount of sulphuric acid. Above 2.5*N*, Caro's acid is formed as before, with the result that slightly less hydrogen peroxide is available, and accordingly less oxygen than 2 atoms is liberated. The concentration of the sulphuric acid when chromic acid solution is dropped into hydrogen peroxide is thus without influence, and perchromic acid, H_3CrO_8 , is formed; likewise, when hydrogen peroxide is dropped into excess of a mixture of potassium dichromate and sulphuric acid, the excess of chromic acid is without influence.

Spitalsky's views (Abstr., 1907, ii, 338, 942) are adversely criticised.

E. F. A.

Preparation of Uranium. FEDERICO GIOLITTI and G. TAVANTI

(*Gazzetta*, 1908, **38**, ii, 239—251).—The authors have investigated the various methods of preparing uranium.

The "pure uranyl acetate" of Kahlbaum or Merck is, in reality, a double sodium uranyl acetate, $\text{UO}_2(\text{OAc})_2 \cdot \text{NaOAc} \cdot 2\text{H}_2\text{O}$, which, on ignition, yields sodium pyrouranate, $\text{Na}_2\text{U}_2\text{O}_7$, as sole product; the latter is also obtained by igniting other uranyl salts of volatile acids containing salts of the alkali metals. When sodium pyrouranate is

heated to redness in a current of hydrogen, it is reduced according to the following equation: $\text{Na}_2\text{U}_2\text{O}_7 + 2\text{H}_2 = 2\text{NaOH} + 2\text{UO}_2 + \text{H}_2\text{O}$, but it is found to be impossible to remove the sodium hydroxide by washing with water.

The oxide, U_3O_8 , can be obtained pure as follows: A solution of sodium uranyl acetate (100 grams) in a mixture of water (4 litres) and hydrochloric acid (50 c.c.) is precipitated by means of concentrated ammonia solution (300 c.c.), the precipitate being washed ten times by decantation with 8–10 litres of 2% ammonium chloride solution. The precipitate is then re-dissolved in hydrochloric acid, precipitated by means of ammonia solution, and washed as before, these operations being afterwards repeated a third time. On calcining the final precipitate, pure U_3O_8 , free from alkali, is obtained.

When a mixture of this oxide with excess of powdered aluminium is thrown on to the surface of fused aluminium maintained at a vivid red heat, not alloys of aluminium and uranium, mixed with alumina as stated by Moissan (Abstr., 1906, ii, 601), but a mixture of uranous oxide, alumina, and aluminium are obtained. When, however, a mixture of ferric oxide with 10% of the oxide, U_3O_8 , is intimately mixed with more than sufficient aluminium filings to reduce both the oxides, and the reaction started by means of barium peroxide and aluminium, the oxide of uranium is reduced to metallic uranium.

T. H. P.

New Element in Thorianite. MASATAKA OGAWA (*J. Coll. Sci. Tôkyô*, 1908, 25, xv, 1–11).—A new element, which it is proposed to name *nipponium* (Np), has been isolated from thorianite, reinité, and molybdenite. Its equivalent weight is about 50 and atomic weight about 100, so that this element probably fills the gap between molybdenum and ruthenium. Two *oxides* of the element appear to exist; the higher oxide is an acidic oxide, and is reduced by zinc and hydrochloric acid to the basic oxide; the latter oxide, which in the ordinary course of analysis accompanies aluminium oxide, is separated from this by conversion into a difficultly volatile chloride by heating in a current of chlorine and carbon tetrachloride vapour. The anhydrous *chloride* so formed dissolves in water to a pale green solution, and gives a characteristic line, having a wave-length of 4882, together with two other feebler lines, in the greenish-blue part of the spectrum. The *hydroxide*, precipitated by ammonia in the presence of ammonium chloride, is almost white with a pale yellow tinge, and dissolves in alkalis; it becomes nearly black when dried at 100°. The ignited oxide is brown, and is insoluble in acids. The yellowish-green solution of the hydroxide in hydrochloric acid gives a brown precipitate when boiled with sodium thiosulphate, and a greenish-black precipitate with ammonium sulphide. A solution of the chloride acidified with acetic acid gives a yellowish-brown precipitate with potassium chromate. A brown precipitate is obtained by passing carbon dioxide into a solution of the green mass formed by fusing the oxide with sodium carbonate and potassium nitrate; it dissolves readily in dilute hydrochloric acid. The aqueous solution of the fused mass does not yield a precipitate with ammonia or ammonium

sulphide, but the addition of acid to the solution containing ammonium sulphide produces a brown precipitate.

W. H. G.

New Element Allied to Molybdenum. MASATAKA OGAWA (*J. Coll. Sci. Tōkyō*, 1908, 25, xvi, 1—13).—Both molybdenite and thorianite contain a new element, closely allied to molybdenum, which is probably identical with the new tin-group element recently described by Miss Evans (*Trans.*, 1908, 93, 666). The equivalent of the element is about 16.7. It appears to form two oxides; the higher oxide resembles molybdenum trioxide, and yields *barium*, *lead*, and *silver* salts similar to the corresponding molybdates; the *mercurous* salt, however, forms golden-yellow crystals; the hydrated lower oxide(?) has a graphitic appearance, and is insoluble in hot dilute hydrochloric acid. The oxides are reduced by hydrogen to the *metal*, which is non-fusible at a red heat; it burns brilliantly in the air, forming the higher oxide. The new element differs from molybdenum in that it is soluble in hot concentrated hydrochloric acid, and gives no colour reaction when its higher oxide is reduced with zinc and hydrochloric acid, either in the presence or absence of potassium thiocyanate.

Thorianite appears to contain, in addition to this new element and nipponium (compare preceding abstract), yet another new element, the oxide of which is radioactive, and dissolves in nitric acid to a bluish-green solution.

W. H. G.

A New Form of "Tin Plague." RUDOLF VON HASSLINGER (*Monatsh.*, 1908, 29, 787—790. Compare Cohen, *Abstr.*, 1900, ii, 212; this vol., ii, 858).—A tinned iron vessel, which had been for two years at 16—45°, showed a crystalline, brittle surface. Other masses of tin, inoculated with small portions of the crystalline tin, underwent the same change, the area affected increasing in diameter 3 to 5 mm. daily. No difference between experiments at 7°, 19°, and 37° could be noted. When tin-foil was inoculated, the change extended through the thickness of the foil. The crystalline tin preserves its appearance up to near the melting point, but becomes normal after melting and again solidifying.

C. H. D.

Reduction of Vanadic Acid by Potassium Iodide. T. WARZYNSKI and B. MDIVANI (*Chem. Zentr.*, 1908, ii, 763; from *Mon. Sci.*, 1908, 22, [ii], 527—528).—With the object of ascertaining whether the reducing power of potassium iodide in an acid medium is dependent on the electrolytic dissociation of the acid employed, comparable tests have been made, using acetic acid and mono-, di-, and tri-chloroacetic acids. It is found that reduction is effected most readily in the presence of trichloroacetic acid, and least readily in presence of acetic acid. With trichloroacetic acid, the reduction proceeds quantitatively to the tetroxide, and admits of the estimation of vanadic acid by this method.

J. V. E.

The Series Sodium Thioantimonate, Sodium Thiosulphate, and Water. A. D. DONK (*Chem. Weekblad*, 1908, 5, 767—771).—From mixtures of sodium thioantimonate and sodium thiosulphate in aqueous

solution at 0° and 30° , the following hydrated salts have been isolated :
 $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$; $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}, \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

A. J. W.

Passivity of Platinum. RUDOLF RUER (*Zeitsch. Elektrochem.*, 1908, 14, 633—634. Compare this vol., ii, 601).—Two platinum anodes in series were placed in 6% and 50% sulphuric acid respectively ; after twelve hours their positions were interchanged, and this was continued for seven days ; each anode lost 0.7 mg. When the anodes were not moved, they each lost 0.1 mg. In the first experiment, the cathode in the 50% acid gained 1.1 mg. ; hence the coating formed in the 6% acid dissolves in the strong acid. If an invisible skin of oxide forms on an anode in the strong acid, it is therefore not the same oxide as that produced in the weak acid.

T. E.

Mineralogical Chemistry.

Coloration of Minerals. KARL SIMON (*Jahrb. Min.*, 1908, *Beil.-Bd.*, 26, 249—295).—A review is given of the literature, and experiments made on the coloration of zircon, amethyst, smoky-quartz, tourmaline, and topaz. These minerals are all decolorised when strongly heated in an atmosphere of either hydrogen or oxygen, and the temperature at which the colour is lost depends to some extent on the size of the fragments. The colour is restored on exposing the mineral to sunlight, or to the emanations of radium. The colouring matter is in each case probably inorganic, but its exact nature is unknown.

L. J. S.

Relations between Quartz, Chalcedony, and Opal. HANS LEITMEIER (*Centr. Min.*, 1908, 632—638).—The following minerals, in a state of moderately fine powder, were heated with a 50% solution of potassium hydroxide at 80° for five hours; the residue was washed with a 50% solution of potassium hydroxide before being washed with water (otherwise some of the dissolved silica is re-precipitated), and the amount of silica in solution was determined:

	Sp. gr.	Water lost at 90°.	Water lost on ignition.	Silica dissolved.
Quartz from Rauris	2·613	—	(0·22 %)	7·23 %
Chalcedony from Weitendorf	2·608	—	1·50	76·02
" " " dehydrated	—	—	—	53·10
Chalcedony from Faroe.....	2·591	0·10 %	1·02	42·30
Cacholong "	2·370	0·25	1·35	54·49
Opal (hyalite) from Bohemia	2·177	0·34	3·04	56·68
Opal (precious), New South Wales	2·121	2·40	6·23	100·00
" " " dehydrated	—	—	—	82·34

Hot water acting for twelve hours on precious opal gelatinises the surface and dissolves 0·22%. It is concluded that chalcedony and

quartz are varieties of the same mineral species, and that chalcedony does not contain any admixed opal. L. J. S.

The Reversible Alteration of Cryolite. FELIX CORNU (*Centr. Min.*, 1908, 546—547).—R. Naeken (*Centr. Min.*, 1908, 38) has observed the change of monoclinic cryolite to a cubic modification at a temperature of 550—570°. The suggestion is made that this cubic modification ($\text{Na}_6\text{Al}_2\text{F}_{12}$) is isomorphous with cryolithionite ($\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$) (Abstr., 1904, ii, 347). L. J. S.

Origin of the Boric Acid in the Soffioni of Tuscany. GIOVANNI D'ACHIARDI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 238—239).—A reply to Nasini (compare this vol., ii, 862). T. H. P.

Manganese and Iron Minerals from the Crystalline Schists of Broșteni, Roumania. VASILE C. BUTUREANU (*Ann. Sci. Univ. Jassy*, 1908, 5, 87—108).—Fifteen analyses are given of "brostenite" (Abstr., 1901, ii, 26); they exhibit wide variations, indicating that the material is not homogeneous. Analyses are also given of wad, and a manganese and iron carbonate. L. J. S.

Vorobyevite and the Chemical Structure of Beryls. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. Petersburg*, 1908, 975—976).—The author describes a beryl containing caesium, to which he gives the name *vorobyevite*. From the best published analyses, the conclusion is drawn that the beryls constitute a class of minerals by themselves. Various members of this class are known, having the composition: $p\text{-GlAl}_2\text{SiO}_{12}qA$, where A is GlH_2SiO_4 , $\text{GlSiO}_3(?)$, Cs_2SiO_3 , Li_2SiO_3 , or Na_2SiO_3 . In beryls not containing alkali metals, the compound $2\text{GlAl}_2\text{Si}_4\text{O}_{12}(\text{GlSiO}_3)_4(\text{GlH}_2\text{SiO}_4)$ predominates. Vorobyevite contains 4.65—10.4% of a caesium compound of the type $\text{GlAl}_2\text{Si}_4\text{O}_{12}(\text{GlH}_3\text{SiO}_4)(\text{Cs}_2\text{SiO}_3)$. T. H. P.

Analysis of the Microcline from the Pegmatites of Mesvres. PHILIPPE BARBIER (*Bull. Soc. chim.*, 1908, [iv], 3, 821—822).—The pegmatites of the Mesvres valley contain a beautiful slightly translucent, laminated, milk-white, or pink microcline. The author has analysed specimens of this mineral collected at Mesvres, and obtained the following results. An analysis by Damour of specimens of the same microcline found at Broye is given for comparison:

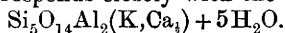
	SiO_2 .	Al_2O_3 .	K_2O .	Na_2O .	Total.
I. Mesvres . . .	66.12	19.11	10.54	4.12	99.93
II. „	66.13	19.09	10.62	4.12	99.96
III. Broye	64.80	19.90	12.11	2.10	98.91

E. H.

Analysis of the Christianite of Simiouse. PHILIPPE BARBIER (*Bull. Soc. chim.*, 1908, [iv], 3, 822—823).—The cavities in a basalt of Mt. Simiouse, near Montbrison, contain microscopic crystals of christianite and other minerals. The christianite gave on analysis:

SiO ₂ .	Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	BaO, MgO.	Loss on ignition.	Total.
52.10	18.33	4.96	6.89	1.12	traces	16.55	99.95

This mineral thus corresponds closely with the formula



E. H.

Aloisiite: a New Hydrosilicate from the Tufa of Fort Portal (Uganda). LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 233—238).—The silicate contained in the tufa of Fort Portal is of a type extremely poor in silica, and after deducting admixed calcium carbonate and gangue, has the following composition:

SiO ₂ .	FeO.	CaO.	MgO.	Na ₂ O.	H ₂ O.	Total.
24.52	20.56	26.50	11.08	9.96	6.95	99.57

These numbers correspond approximately with the formula (R'', R')SiO₆, where R'O is CaO, FeO, MgO, and R'₂O is Na₂O, H₂O. The author gives to this silicate the name *aloisiite*; it occurs also in an altered form in the tufa.

T. H. P.

Formation of Kaolin. OTTO HÄHNEL (*J. pr. Chem.*, 1908, [ii], 78, 280—294).—Analyses of a fresh (I), an effloresced (II), and a half-kaolinised porphyrite show that the processes of efflorescence and kaolinisation are not identical:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	
I.	72.9	15.4	2.89	—	0.41	4.40	5.11	0.5	per cent.
II.	70.98	15.50	3.21	traces	0.72	4.70	5.01	2.21	„ „
III.	75.0	18.72	1.2	—	0.2	2.31	2.78	1.03	„ „

On the other hand, the fresh decomposition products of a granite from under humus at Schierke closely resembles crude kaolin. The moors must, therefore, be credited with a kaolinising power. G. Y.

Calcium Sulphide (Oldhamite) in the Allegan Meteorite. WIRT TASSIN (*Proc. U.S. National Museum*, 1908, 34, 433—434).—Certain portions of this meteoric stone when treated with acid were noticed to evolve a considerable amount of hydrogen sulphide, and an analysis of the fine powder, freed from magnetic particles, showed the presence of 16.66% CaS in an olivine-enstatite mixture. This constituent could not be detected on a microscopical examination of the stone, and it appears to be present in a finely-divided state in the ground mass.

L. J. S.

Meteoric Chromites. WIRT TASSIN (*Proc. U.S. National Museum*, 1908, 34, 685—690).—Small quantities of chromite are present in

most meteorites ; in stones and stony irons rarely as much as 3%, and usually less than 1%, whilst in irons there is generally less than 0·01%. The following nine analyses were made on material isolated from the meteorites named, and eight earlier analyses of meteoric chromites are quoted.

	Cr ₂ O ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	SiO ₂ .
I. Admire.....	65·49	—	—	33·00	0·40	0·50
II. Mount Vernon	65·01	9·95	—	18·97	5·06	—
III. „	64·91	9·85	—	17·97	4·96	1·38
IV. Canyon Diablo	63·40	5·30	—	26·30	5·00	—
V. Marjalahti	61·39	1·96	—	30·46	6·70	—
VI. Hendersonville	56·73	2·98	—	29·64	2·42	—
VII. Allegan	56·70	12·38	—	27·60	4·00	— *
VIII. Admire	56·49	trace	10·20	29·92	trace	—
IX. Canyon Diablo	5·20	—	65·25	30·05	—	—

* Trace of TiO₂.

From the Admire pallasite, I was of small, non-magnetic, jet-black grains with a brilliant lustre; and VIII, of bluish-brown, magnetic particles with a dull lustre, isolated from the metallic portion of the meteorite. II, from the metallic portion of the Mount Vernon pallasite, had the form of relatively large (1 mm. across) octahedra with black colour and brilliant metallic lustre, D 4·49; whilst III had the form of minute, rounded grains, frequently enclosed in the olivine, and was brownish-black with a resinous lustre. IV, from the Canyon Diablo iron, had the form of small octahedra and rounded grains, was jet-black with brilliant lustre, and non-magnetic; IX, from the same iron, was in rounded grains, with bluish-black colour and dull lustre, and was strongly magnetic, being really a chromiferous magnetite.

Only the first of these analyses approximates to the typical chromite formula, FeO,Cr₂O₃; the others contain variable amounts of alumina and magnesia, but are of the type RO,R₂O₃.

L. J. S.

Physiological Chemistry.

The Total Sugar of the Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1908, 147, 226—228).—The total amount of the reducing sugar of the blood can be ascertained by hydrolysing the clot with hydrofluoric acid, and adding the amount of reducing substance thus obtained to that in the filtrate from the clot. S. B. S.

The Occurrence of Proteose in Blood and Urine. L. BORCHARDT (*Zeitsch. physiol. Chem.*, 1908, 57, 305—312).—If elastin is given in the food in fairly large amounts to dogs, a proteose (hemielastin) can be detected in the blood, and this is excreted by the kidneys and found in the urine. W. D. H.

Fatty Degeneration in the Blood. SAMUEL G. SHATTOCK and LEONARD S. DUDGEON (*Trans. Path. Soc. London*, 1907, 58, 227—255).—In preparations of blood corpuscles hardened in formaldehyde, and stained with Scarlet [Scarlet R], it is contended that stained particles in the leucocytes in various cases of disease indicate the occurrence of fatty degeneration. W. D. H.

Estimation of Catalases and Oxydases in Blood. II. WALTHER LÖB and PAUL MULZER (*Biochem. Zeitsch.*, 1908, 13, 475—495).—The rate of oxygen evolution was estimated both by the volume and pressure methods already described (this vol., ii, 999). The rate of reaction depends on the quantity of blood added. The curves representing the rate of gas evolution show with small quantities of blood a gradual rise. In the presence of larger quantities, the gradual rise is preceded by a sharper one. The velocity constant is not the same as that of the hæmase studied by Senter, and, from the complexity of the reaction, it is possible that more than one enzyme takes part in the reaction. The rate of action varies with the blood of different animals (rabbits). The action of various oxygen depolarisers was studied. Benzidine, formaldehyde, and salicylic acid are readily oxidised, but not alcohol. S. B. S.

The Regulation of the Physico-chemical Properties of the Blood after Injection of Different Solutions. GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1908, 13, 400—439).—Hypertonic, isotonic, and hypotonic saline and sucrose solutions were injected into dogs, and certain quantities of blood were withdrawn from the animals both before and at different intervals after the injections. Determinations were made of the conductivity and viscosity of the serum, the molecular concentration of the defibrinated blood (by lowering of freezing-point method), and the volume of the corpuscles (by the hæmatocrite). Injections of hypertonic sodium chloride solutions were found to increase the molecular concentration of the blood and conductivity of the serum over a relatively long period, whereas they caused only a very temporary dilution of the blood volume. The changes produced by hypertonic sucrose solutions were only of temporary character, and disappeared much more quickly than those produced by sodium chloride. Isotonic solutions produced but slight changes, and so also did strongly hypotonic solutions, when the volume of the injected liquid and the rate of injection were not great. If, however, the quantity of the fluid and the rate of injection is sufficiently great to produce marked changes in the blood elements, then the physico-chemical changes are demonstrable. S. B. S.

The Influence of Alkaline Ferro- and Ferri-cyanides on Blood-coagulation. J. LARGUIER DES BANCELS (*Compt. rend.*, 1908, 147, 266—268).—Both potassium ferro- and ferri-cyanides have a marked inhibitory action on the coagulation of the blood and of fibrinogen solutions, the latter acting more powerfully than the former, although it gives no precipitate with soluble calcium salts, whereas the

former does. It is suggested that multivalent negative ions inhibit the coagulation of negative colloids. S. B. S.

Hæmolytic Poisons, especially Bile Salts and Soaps. F. NEUFELD and HÄNDEL (*Chem. Zentr.*, 1908, ii, 891—892; from *Arb. Kais. Gesundh. Amt.*, 1908, 28, 572—584).—This is a study of the corpuscle-dissolving action of sodium taurocholate, soaps, and potassium hydroxide in comparison with other blood poisons, also of the action of hæmolytic agents on lipoids and proteins, so that their action on the cell-membrane and their destructive action on the whole corpuscle may be distinguished. Lecithin is soluble in a 10% solution of sodium taurocholate, but not in normal potassium hydroxide, or in a 1% solution of an oleate. Cholesterol crystals are soluble in none of these solutions, nor in sapotoxin. The taurocholate dissolves protein. In emulsions of olive oil in physiological salt solution, partly with lecithin and partly with egg-white, the addition of sodium taurocholate produces the liberation of fat, and the solution of lecithin and protein; the other materials used do not produce this effect.

In high concentrations, sodium taurocholate produces in the blood of sheep, goat, and ox an inhibition of hæmolysis, which in lower concentration rises as the concentration increases to an optimum. These three sorts of blood are peculiar in that they are refractory to pure cobra venom; the venom acts hæmolytically in the presence of lecithin. Other kinds of blood (guinea-pig, horse, hen) never show any inhibition unless physiological salt solution is replaced by an isotonic solution of sucrose.

Sodium taurocholate and a series of other hæmolytic agents are capable of uniting with complement, but this is not the case with all blood poisons; it depends on what constituent of the stroma or serum the poison is united to. In the case of sapotoxin, there is, for instance, no union with complement. The destruction of pneumococci by bile salts is also described, so also is "phagocytosis by emulsified fat droplets and the influence of specific anti-sera thereon."

W. D. H.

Hæmolysis. LEO VON LIEBERMANN (*Biochem. Zeitsch.*, 1908, 13, 363—364. Compare Abstr., 1907, ii, 973).—In order to produce hæmolysis of the corpuscles of pig's blood, 0.05 c.c. of pure oleic acid, and not oleic acid emulsion, as stated in the previous paper, should be added to 10 c.c. of pig's serum. There is also an error in the same place, as to the order in which different substances should be added to produce hæmolysis. S. B. S.

Bactericidal Action of Normal Serum. ROBERT MUIR and CARL HAMILTON BROWNING (*J. Pathol. Bacteriol.*, 1908, 13, 76—91).—A distinction is drawn between absorption of complement by bacteria and the bactericidal effect which may follow. Treatment of a normal serum with increasing amounts of a dead emulsion of a bacterium usually produces first a diminution of its bactericidal action on that bacterium, then for that on other bacteria, and finally a diminution of the hæmolytic complement. This shows there is in serum a substance

(bacteriophilic complement) with an affinity for bacteria in general. If the bactericidal action has been reduced as indicated above, it can be more than restored by adding a little of the homologous immune substance.

W. D. H.

Digestion of Fat. III. S. A. LEVITES (*Zeitsch. physiol. Chem.*, 1908, 57, 46—48. Compare Abstr., 1907, ii, 891).—The glycerol constituent of fat is rapidly absorbed. Absorption begins in the duodenum, and is completed in the neighbourhood of the cæcum. In the estimation of glycerol in the intestinal contents, the method of Shukoff and Schestakoff, which depends on the solubility of glycerol in acetone, gives results which are too high. Lewkowitsch's acetin method is better.

W. D. H.

Nutritive Value of Plant Amides. ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1908, 57, 67—73).—A critical review of the difference of opinion which has arisen between Lehmann, on the one hand, and Morgen and Henriques and Hansen, on the other, with reference to the nutritive value of asparagine and similar amides.

W. D. H.

Ferments of Nuclein Metabolism. ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1908, 57, 21—27. Compare Abstr., 1907, ii, 109, 564).—Previous work by the author (and by W. Jones) has shown that the formation of uric acid from nuclein is due to a succession of ferment actions. It is now shown that these ferments can be precipitated from organ-extracts by alcohol or by ammonium sulphate, and these ferments, when acting on pure guanine, resolve it quantitatively into uric acid; under favourable conditions, the time may be as short as one to two hours. Bacterial action, which some authors lay stress on, is not the cause of the change.

W. D. H.

Chemistry of Digestion. XXVI. The Behaviour of Different Proteins in the Stomach and Upper Duodenum of the Dog. E. S. LONDON and W. W. POLOWZOWA (*Zeitsch. physiol. Chem.*, 1908, 57, 113—130. Compare this vol., ii, 870).—Various proteins of animal and vegetable origin are not absorbed in the stomach. Proteins from serum and egg-white are difficult of digestion in the stomach, but most others are rendered soluble to the extent of 78%, the proportion between proteoses, peptones, and residual substances being 59.3, 32.9, 7.8. The juices in the first part of the duodenum act immediately on the soluble products of gastric digestion, resolving them into ultimate cleavage products, whereas the undissolved substances in the chyme are not attacked for some time. The first 6 or 7 centimetres of the duodenum absorb about 6% of the protein.

W. D. H.

Absorption of Protein. KORNÉL VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1908, 57, 267—287).—The view is advanced that the cleavage products of protein digestion cannot be detected in the circulating blood; the percentage of protein in the blood is, however, increased, although whether protein synthesis occurs in the intestinal wall or in

the blood itself is unsettled. The non-coagulable nitrogen in the blood is not increased, as stated by Cathcart and Leathes. W. D. H.

Muscular Activity and Protein Metabolism. PHILIP A. SHAFFER (*Amer. J. Physiol.*, 1908, 22, 445—455).—The experiments made on two men, and given with full details, showed a rise of total nitrogen excreted in one, and a fall in the other, with muscular work. Work within physiological limits has *per se* no effect on protein metabolism as indicated by the nitrogen and sulphur of the urine. The excretion of uric acid, urea, ammonia, and creatinine is wholly unaffected. W. D. H.

The Value of Protein Cleavage Products in the Animal Organism. VII. EMIL ABDERHALDEN and JOSEF OLINGER (*Zeitsch. physiol. Chem.*, 1908, 57, 74—79. Compare this vol., ii, 51).—The present experiments on a dog fed with the final cleavage products of casein and meat, confirm results recorded previously that such substances are capable of maintaining weight and nitrogenous equilibrium. W. D. H.

The Influence of Nitrogen-free Sources of Energy on the Rate of Protein Decomposition by the Organism. W. FALTA and A. GIGON (*Biochem. Zeitsch.*, 1908, 13, 267—273).—Dogs of similar size were fed on a standard diet for a time, and then allowed to fast for various periods. They were then given diets consisting, in one set of experiments, of meat alone; in another, of a mixture of meat and lævulose; in another, of meat and inosite, and in a fourth set, of meat and alcohol. It was found that the longer the period of fasting before administration of the meal the more rapid the protein decomposition (as estimated by the nitrogen excreted), and the less the protein-sparing action of the carbohydrate when this formed part of the food. The addition of inosite only slows the rate of protein decomposition during the first twelve hours. The time of the fast before the meal has no influence on the action of inosite. Alcohol accelerates the rate of protein decomposition. There is a tendency in the organism to replenish the glycogen stores which had become depleted by fasting, and this is done by obtaining the carbohydrate entirely from the protein when no other glycogen-former is ingested; hence, after fasting, the rapid degradation of protein. The carbohydrate store in the organism has therefore great influence on the time of decomposition. Experiments were also carried out on the effect of superposing various extra diets on a standard diet. It was found that the composition of the standard diet exerts considerable influence on the time of decomposition of the superposed diets. S. B. S.

The Influence of Nitrogen-free Sources of Energy on the Rate of Protein Decomposition by the Organism. G. A. PARI (*Biochem. Zeitsch.*, 1908, 13, 274—280).—The experiments were similar in character to those of Falta and Gigon (see preceding abstract). The effects of the addition of carbohydrates other than

lævulose and of fat, on the rate of protein decomposition after a fast, were investigated. It was found that after a long fast, sucrose no longer has the power of slowing the rate of protein decomposition. Fat and β -hydroxybutyric acid, which are not glycogen formers, do not lose, however, their power to retard the rate of decomposition. S. B. S.

The Influence of the Thyroid Gland on the Rate of Decomposition. G. A. PARI (*Biochem. Zeitsch.*, 1908, 13, 281—284).—Eppinger, Falta, and Rudinger have shown that in dogs without thyroid glands, the protein metabolised during fasting is less, and can be but little diminished by carbohydrates or fat, in contrast to what happens in the normal starving animal. The latter fact is attributed, from other factors discovered, to the depression of carbohydrate metabolism in animals deprived of the thyroid. To throw further light on this matter, experiments similar to those recorded in the preceding abstracts were carried out with animals deprived of the thyroid, which received meals of meat, with or without addition of other food-stuffs, after a period of fasting, and the rate of protein decomposition was determined by estimating the rate of nitrogen excretion. In the normal animal, the influence of carbohydrates on the retardation of the decomposition of protein is diminished by longer periods of fasting. In thyroid-ectomised animals, long periods of fasting do not diminish this delaying influence to anything like the same extent. S. B. S.

Influence of Thyroidectomy and Thyroid Feeding on Intermediary Metabolism. FRANK P. UNDERHILL and TADASU SAIKI (*J. Biol. Chem.*, 1908, 5, 225—242).—After complete thyroidectomy and parathyroidectomy in dogs, the urinary ammonia is increased beyond what is observed in inanition. The nitrogen in the form of creatinine, purine, and allantoin is unaltered, but creatine is found in the urine. These dogs are incapable of utilising dextrose introduced subcutaneously to anything like the same degree as normal dogs can. The loss of the glands may thus cause a change in gaseous metabolism similar to that seen in cretinism. If normal dogs are fed on thyroid, the urinary nitrogen is increased; there is also a larger output of purine-nitrogen, and a low output of phosphorus. There is, however, but little change in the inter-relation of the urinary nitrogenous constituents.

There is no choline in the blood after thyroidectomy. W. D. H.

The Utilisation of the Energy of Provender as Influenced by the Temperature of the Surroundings, and the Nutritional Condition of Rabbits. W. USTJANZEFF and G. BOGAJEWSKY (*Biochem. Zeitsch.*, 1908, 13, 365—399).—Rabbits were fed for a preliminary period on a given diet which was insufficient for the energy needs of the organism. The carbon and nitrogen content, and also the calorific value of this diet and of the excreta, were estimated, and from these data, the loss from the body of fat and protein calculated, and also the calorific value of this loss. The same animal was then given the like diet with the addition of hay, and

the same data obtained as in the preliminary period. From the two sets of data, the physiological food value of the hay was calculated. Experiments were carried out with animals in varying conditions of nutrition, and with the surrounding atmosphere at varying temperatures (0° , 20° , and 30°). It was found that Rübner's law of isodynamic replacement holds good if hay is used as provender, when the physiologically available energy of the latter is only about half of the total energy needs of the animal, and when the animal is kept in an atmosphere of low temperature.

S. B. S.

Secretin. OTTO VON FÜRTH and CARL SCHWARZ (*Pflüger's Archiv*, 1908, 124, 427—446).—Extracts of intestinal mucous membrane, prepared according to the method of Bayliss and Starling, contain choline. Choline stimulates pancreatic activity, and this action is antagonised by atropine. The secretin of Bayliss and Starling is a mixture of several substances, among which choline occurs. The effect of secretin is not abolished, but only lessened, by atropine.

W. D. H.

Oxidation Processes in Echinoderm Eggs. OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1908, 57, 1—16).—The research deals with the respiratory process, measured by the amount of oxygen used, in the eggs of *Arbacia pustulosa*. The figures given show (1) that the amount of oxygen used is from six to seven times greater in fertilised than in unfertilised eggs; (2) this is not mainly used in nuclear division, for at the stage when thirty-two cells are present, the use of oxygen is not proportionately increased from the stage when eight cells are present; (3) moreover, if the continuance of cell division is hindered by hypertonic sea-water, the amount of oxygen used is not markedly altered; (4) an egg-cell breathes 500 (± 100) times more vigorously than a sperm cell; (5) hypertonic solutions increase the use of oxygen in unfertilised eggs ten-fold; (6) a transference from hypertonic to normal sea-water also leads to an increase, but not such a marked one; (7) the temperature-coefficient shows the process to be a chemical one.

W. D. H.

A Mono-amino-diphosphatide in Egg-Yolk. HUGH MACLEAN (*Zeitsch. physiol. Chem.*, 1908, 57, 304).—A mono-amino-diphosphatide (P : N = 2 : 1) analogous to Erlandsen's cuorin, which he separated from heart muscle, can be separated from egg-yolk.

W. D. H.

A Globulin from the Egg-Yolk of *Squalus acanthias*. CARL L. ALSBERG and E. D. CLARK (*J. Biol. Chem.*, 1908, 5, 243—246).—The egg-yolk of the spiny dogfish contains no vitellin, but in its place, a globulin (or a mixture of globulins) which does not contain phosphorus, and, probably, iron is also absent.

W. D. H.

The Assimilation of Phosphorus and Calcium during the Embryonic Life of the Chick. EM. CARPIAUX (*Bull. Acad. roy. Belg.* 1908, 283—295).—Analyses were made of the inorganic and lecithin-phosphorus and of the calcium in eggs in different stages of develop-

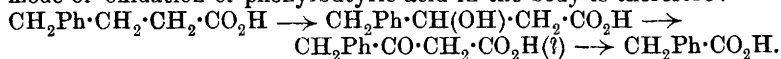
ment. It was found that the chick during embryonic life uses chiefly the phosphorus in the egg itself, and if it utilises that of the shell at all, it does so only to a very limited extent. The shell furnishes four-fifths of the calcium necessary for the formation of the chick, and towards the end of the incubation period considerable use is made of this calcium. At this period, destruction of the lecithin takes place, which proceeds *pari passu* with the utilisation of the lime. S. B. S.

The Peroxydases of Animal Tissues. FR. BATTELLI and MILE. L. STERN (*Biochem. Zeitsch.*, 1908, 13, 44—88).—Tissue extracts possess the capacity of increasing the rate of oxidation of hydriodic acid by means of hydrogen peroxide. The reaction is manifested when carried out in the presence of starch. In the cases of most tissues, the reaction is masked by the presence of a catalase, which causes a too rapid destruction of the peroxide. If, however, ethyl hydroperoxide is employed instead of hydrogen peroxide, the reaction can, in most cases, be demonstrated, for the catalase of the tissue does not act on this substance, which possesses a similar peroxydase reaction to hydrogen peroxide. Even when the former peroxide is employed, the results are uncertain, and this fact is probably due to the presence of the substances in the tissues, which react chemically with iodine and thus mask the iodine-starch reaction. A more suitable method of investigating the peroxide reaction of the tissues consists in estimating the amount of carbon dioxide evolved when tissue extracts are treated with ethyl hydroperoxide or hydrogen peroxide and formic acid. The oxidation which then takes place, can occur in acid solutions, under which condition the catalase action on hydrogen peroxide is considerably depressed. The following tissues were investigated, and are enumerated in order of the magnitude of their peroxydase content: liver, kidneys, spleen, lungs, pancreas, lymph glands, ox-muscle, brain, testicles, dog-muscle, thymus, suprarenals, thyroid, rabbits muscle. Blood is also rich in peroxydase. The optimum temperature of reaction in most cases is 38—40°, and the ferment is destroyed at 66° in neutral media and at 55° in acid or alkaline media. In the case of the blood, however, the reaction is much more energetic at 55—60°, and is in other respects anomalous. It is stated to contain a so-called pseudo-peroxydase in the pigment. The formaldehyde is also oxidised under the same conditions as formic acid, but not so energetically. Higher fatty acids, which *in vivo* are readily oxidised, do not cause evolution of carbon dioxide under the same conditions as formic acid does. For this reason, it is not yet possible to determine the exact biological functions of peroxydases. S. B. S.

Mode of Oxidation of Phenyl Derivatives of Fatty Acids in the Animal Organism. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 5, 173—186).—The subcutaneous injection of sodium phenylbutyrate results in the excretion of phenaceturic acid and a small quantity of β -hydroxy- γ -phenylbutyric acid. No phenylacetone or phenylacetoacetic acid could be found.

If β -hydroxy- γ -phenylbutyric acid is given in the same way, phenaceturic acid is again excreted, and phenylacetone could not be detected.

Administration of phenylacetone results in the excretion of hippuric acid, phenylaceturic acid not being formed. The probable mode of oxidation of phenylbutyric acid in the body is therefore:



Phenylacetic acid is excreted as phenaceturic acid. The intermediate formation of ketones is probably confined to phenylbutyric and phenylpropionic acids, and is not a general reaction. In normal metabolism, probably only part of the butyric and phenylpropionic acids passes through the stage of acetone and acetophenone respectively.

Phenylisocrotonic acid is excreted as phenaceturic acid.

β -Dihydroxyphenylbutyric acid is excreted as hippuric acid and a little β -hydroxyphenylbutyrolactone. Mandelic acid is not formed. Dihydroxyphenylbutyric acid therefore does not undergo β -oxidation, but oxidation takes place at the γ -carbon atom. Dihydroxyphenylbutyric acid is not a product of the catabolism of phenylbutyric acid.

Phenylacetone is readily identified by conversion into its *p*-nitrophenylhydrazone, which crystallises from alcohol or pyridine in sparingly soluble rosettes of platelets, melting at 145—145.5°.

W. D. H.

Chemistry of the Brains of Birds and Fishes. ALFRED ARGIRIS (*Zeitsch. physiol. Chem.*, 1908, 57, 288—295).—Cerebrin from human brain yields 21.83% of galactose; that from birds' brain, 21.75%. A crystalline substance corresponding with Thudichum's sphingosin was also obtained. The birds employed were hens and ducks. Fishes' (cod) brain yielded cholesterol, lecithin, jecorin, and so-called protagan.

W. D. H.

The Chemical Composition of Peripheral Nerves. FRITZ FALK (*Biochem. Zeitsch.*, 1908, 13, 153—172).—Both medullated and non-medullated nerves were investigated (sciatic of man, and splenic nerves of ox). The dried medullated nerves were extracted consecutively with benzene, acetone, and ether; the ether-soluble fraction was treated with alcohol, and to the filtrate from the precipitate thus produced, ammoniacal lead acetate in alcohol was added and, after separation of the precipitate and excess of precipitant, alcoholic cadmium chloride solution. By means of the various solvents and precipitants, a series of fractions was obtained, which were partly identified with known substances. The benzene-soluble fraction consisted chiefly of ordinary fats; the acetone extract contained chiefly cholesterol (m. p. 145°); from the ethereal extract a cerebroside separated, and by the precipitation of this extract with alcohol, the cephalins. Ammoniacal lead acetate precipitated another product belonging to the group of cephalins (m. p. 174°). The cerebroside was identical with the cerebrone of Thierfelder (m. p. 209°). The cephalin (m. p. 174°) had the chemical composition of a mono-amino-monophosphatide; it could not be identified with the cephalins already described and obtained from the brain. Only a

small quantity of cadmium chloride precipitate soluble in cold benzene was obtained, and the amount of lecithin appeared therefore to be small and to be accompanied by other phosphatides, which have not yet been identified. A quantitative separation of the various constituents of medullated and non-medullated nerves showed that the former contained 25% cholesterol, 12.4% cephalins, 18.2% cerebrosides, and 2.9% lecithin, whereas the latter contained 47% cholesterol, 23.7% cephalins, 6% cerebrosides, and 9.8% lecithin.

S. B. S.

Weigert's Method of Staining Medullated Nerve Fibres. J. LORRAIN SMITH, W. MAIR, and JOCELYN F. THORPE (*J. Pathol. Bacteriol.*, 1908, 13, 14—27).—Weigert's method of hæmatoxylin staining, after treatment with potassium dichromate, depends, as osmic acid staining does, on the presence of an unsaturated grouping in the fatty matter present. Cholesterol by itself gives a negative result, although it contains an unsaturated grouping, but it forms myelin figures in contact with soap. These and the crystals described in tissues by C. P. White (composed of cholesterol and fatty acid) stain slowly by the Weigert method. Some results obtained with lecithin are attributed to cholesterol as an impurity in the lecithin used.

W. D. H.

Action of Curare and Physostigmine [Eserine] on Nerve-endings. Action of Barium Chloride on Bird's Muscle. CHARLES WALLIS EDMUND and GEORGE B. ROTH (*Amer. J. Physiol.*, 1908, 23, 28—45, 46—47).—The tonic contraction produced by nicotine in muscles is counteracted by curare; this antagonism is less marked if the nerves are cut, and, as a rule, this lessening of the antagonism coincides in data with the degeneration of the nerve-ending. This may be because denervated muscle has an increased sensitiveness towards nicotine, so that curare is unable to displace it. This view is upheld, and so curare is considered to act, not on the nerve-ending as usually taught, but on the muscle, or on some substance in the muscle of the nature of Langley's receptive substance. As a support to this view, experiments with eserine are recorded. This alkaloid acts in the same way as nicotine, only more slowly. It acts more quickly on denervated muscle, which, therefore, has an increased sensitiveness to it. Curare neutralises the effect whether the muscles are denervated or not. The tonic contraction produced by barium chloride is, however, not antagonised by curare under any circumstances.

W. D. H.

Chemico-physical Investigation of the Crystalline Lens. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 153—159).—The aqueous humour of the eye contains normally a very small proportion of protein, which is coagulable by heat, but has not the characters of the lenticular protein, and probably has its origin in the blood or lymph. The vitreous body resembles a sponge, the net-work of which consists of protein substances coagulable by heat, and contracts during coagulation, expressing the liquid contained

in the alveoli. This liquid contains a small quantity of a substance precipitable by acetic acid and insoluble in excess of the acid, and is possibly identical with the coagulable protein found in the aqueous humour. Neglecting these small amounts of proteins, the ocular liquids may be regarded as aqueous solutions of crystalloids, mainly of sodium chloride. With regard to their chemical reaction, the ocular liquids behave like a solution of sodium hydrogen carbonate containing sufficient carbon dioxide to render it neutral to phenolphthalein. Excess of carbon dioxide in the ocular liquids renders them acid to phenolphthalein, and may result in the precipitation of the protein as alkali-protein and in the production of superficial opacity of the crystalline lens.

T. H. P.

Amount of Choline in the Lecithin of Heart Muscle. HUGH MACLEAN (*Zeitsch. physiol. Chem.*, 1908, 57, 296—303).—The lecithin of heart muscle when decomposed in aqueous or alcoholic solution yields, on the average, not more than 52% of its nitrogen in the form of choline. Whether a second nitrogenous product is also present is to be investigated.

W. D. H.

Hydrolysis of Chicken Flesh. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 22, 433—439).—The entire muscle was used, the substances soluble in water, alcohol, and ether having been removed. The result of hydrolysis shows that the amino-acids occur in different proportions from those given previously by Abderhalden and Sasaki and by Hart in relation to the syntonin of ox flesh. It is, however, doubtful whether the analyses can be fairly compared, especially as the sum total of the products in one case is 60%, and in the other 47%, of the material employed. The most striking feature in the hydrolysis of chicken muscle is the high yield of lysine.

W. D. H.

The Degradation of Acetoacetic Acid in the Animal Body. II. GUSTAV EMBDEN and LOUIS MICHAUD (*Biochem. Zeitsch.*, 1908, 13, 262—266).—It has been already shown that the liver tissue possesses the property of destroying acetoacetic acid. As the latter is excreted in cases of diabetes, experiments were carried out to determine whether this is due to increased production, or to the loss of capacity of the liver in diabetic individuals to destroy the acid, which is probably a normal intermediary metabolism product. For this purpose, experiments were made with the liver of dogs which had been rendered diabetic by the extirpation of the pancreas. Control experiments were carried out with the liver tissue of similar normal animals. It was found that the capacity for destroying acetoacetic acid was the same in the liver of the diabetic as in that of normal animals. The muscular tissue of diabetic animals also retained its property of destroying the acid.

S. B. S.

The Behaviour of Creatine in Autolysis. A. ROTHMANN (*Zeitsch. physiol. Chem.*, 1908, 57, 131—142. Compare Stangassinger, this vol., ii, 515).—According to Gottlieb and Stangassinger (*Abstr.*,

1907, ii, 637), creatine and creatinine are destroyed or altered by ferment action during autolysis. Mellanby (this vol., ii, 308) finds, on the other hand, that this is not the case if bacteria are excluded. The present experiments undertaken with aseptic and antiseptic precautions confirm the results of the first-named authors.

W. D. H.

The Action of Arsenic on Autolysis. LEO HESS and PAUL SAXL (*Chem. Zentr.*, 1908, ii, 338; from *Zeitsch. exp. Path. Ther.*, 1908, 5, 89—93).—The action of arsenic, even when highly dilute, is inhibitory towards the autolytic changes in organs (liver). This is designated negative catalysis.

W. D. H.

The Occurrence of Choline in Thymus, Spleen, and Lymph Glands. CARL SCHWARZ and R. LEDERER (*Pflüger's Archiv*, 1908, 124, 353—360).—The occurrence of choline in extracts of thymus, spleen, and lymph glands is proved by chemical and physiological tests. The effect that extracts of these organs have in lowering blood pressure is attributed mainly to choline. Other depressor substances present were not chemically identified, but the suggestion is made that they may belong to the group of histones.

W. D. H.

The Depressor Substance in the Thyroid. OTTO VON FÜRTH and CARL SCHWARZ (*Pflüger's Archiv*, 1908, 124, 361—368).—The substance present in thyroid extracts which depresses arterial pressure is identified as choline.

W. D. H.

The Chemistry of Amyloid Degeneration. OLAV HANSSEN (*Biochem. Zeitsch.*, 1908, 13, 185—197).—The amyloid tissue (the "sago granules" of the spleen) was separated from the surrounding tissue by a mechanical method. The product obtained in this way was, when dried, a yellow or brown powder, which gave the usual blue coloration with iodine after addition of sulphuric acid, and the ordinary protein reactions. The C : N ratio in three different preparations was constant (approximately 4); these contained no oxidised sulphur, and consequently no conjugated sulphuric acid, and the observation of previous observers, who noted the presence of chondroitin-sulphuric acid, appears to be incorrect. The amyloid tissue is, in general, very resistant to the action of proteolytic ferments; it is changed, however, by the action of pepsin and hydrochloric acid into a product which is soluble in dilute ammonia, but which no longer gives the iodine reaction. The capacity to give this reaction is also lost on treatment of the tissue with alkalis.

Although the mechanically separated amyloid tissue itself contained no oxidised sulphur, the organs from which it had been obtained did. It seems probable that the chondroitinsulphuric acid or a similar substance is formed at the same time as the amyloid tissue. No other marked differences between amyloid and normal tissue were ascertained.

S. B. S.

So-called Fatty Degeneration of the Suprarenal. CHARLES POWELL WHITE (*J. Pathol. Bacteriol.*, 1908, 13, 11—13).—The

presence of fats and lipoids in the suprarenal cortex is a physiological condition. The cortex is believed to be engaged in the secretion of cholesterol, lecithin, and fats, and this has some connexion with the regulation of growth and development. W. D. H.

Silicic Acid in Whartonian Jelly. FRANZ FRAUENBERGER (*Zeitsch. physiol. Chem.*, 1908, 57, 17—20).—The amount of silicic acid in the Whartonian jelly of the human umbilical cord is less than Schulz stated it to be. According to Schulz, the ash contains 0.6% of the acid; the figure should be 0.028. W. D. H.

The Action of Electrolytes on the Rhythmic Movements of Medusæ. I. Action of the Salts of Sea-water. ALBRECHT BETHE (*Pflüger's Archiv.*, 1908, 124, 541—578).—An investigation of the various salts, alone and in combination, on the movements of jelly fish was carried out on the lines of the well-known work of Loeb and others. The relative importance of the various ions is discussed. Thus sodium chloride by itself first stimulates and then paralyses the movements; this action is reversible; potassium stimulates the rhythm; magnesium paralyses it; the paralysing action of calcium only occurs when it is highly concentrated. W. D. H.

The Circulation of the Bile. GUSTAV BAYER (*Biochem. Zeitsch.*, 1908, 13, 215—233).—Although the bile salts are strongly toxic to individual organs, they are being continually resorbed from the intestine and entering the circulation. They then exert no toxic effect, even in cases of jaundice. This is due to the fact that the salts are changed in some manner by the serum proteins, and are thereby deprived of their toxic character. This was confirmed by investigating the toxic action of bile salts, when alone and when mixed with serum, on muscular tissue, the central nervous system, the circulation, and also the hæmolytic action. The change effected by serum on the bile salts which deprives them of their toxic character is probably of a physical nature ("colloidal envelopment"). Serum which has been previously warmed acts more efficiently in this respect than unwarmed serum. This action between serum proteins and bile salts produces a disappearance of the complement, a fact which was ascertained by allowing red blood corpuscles to act on amboceptor and complement containing sera in the presence of bile salts which had themselves been deprived of their hæmolytic action by means of an inactive serum. The change in the bile salt molecule wrought by the serum renders excretion difficult, and a bile salt thus changed will not readily dialyse. The liver cells exert a great affinity for the bile salts, and the fixation of cholates by these cells can be demonstrated *in vitro*. S. B. S.

Bile Hæmolysis. III. The Reasons of the Increased Rate of Bile Hæmolysis in Concentrated Salt Solutions. GUSTAV BAYER (*Biochem. Zeitsch.*, 1908, 13, 234—242).—It was shown that bile salts diminish the surface tension of salt solutions to a greater extent than they do that of pure water. Substances which lower the surface

tension of a solution tend to concentrate on the surface. The bile salts tend in emulsions of blood corpuscles to collect round the erythrocytes, and the more rapidly the more concentrated the salt solution used as their solvent. In concentrated salt solutions, there is a more rapid entry therefore of the bile salts (which bring about hæmolysis by their action on the lipoids) than in water. S. B. S.

The Influence of Tolylene-2:4-diamine on the Secretion of Cholesterol in the Bile. CHASOBURŌ KUSUMOTO (*Biochem. Zeitsch.*, 1908, 13, 354—362).—The polycholia, following administration of tolylene-2:4-diamine, is stated to be due to the destruction of blood-corpuscles; thus supplying material for bile pigment which is derived from hæmoglobin. As the corpuscles also contain cholesterol, it might be expected, therefore, that administration of tolylene-2:4-diamine would also lead to an increased elimination of this substance in the bile. This the author has experimentally shown to be the case. The experiments were carried out on dogs with biliary fistulæ. S. B. S.

Hæmolytic Factors in Milk. JANET E. LANE-CLAYPON (*J. Pathol. Bacteriol.*, 1908, 13, 34—37).—Milk, when fresh, contains both complement and amboceptor in about 1/10 the strength of that in serum. In order to obtain hæmolysis, "ox-colloid" must be added; this confirms Bordet's views. "Ox-colloid" is prepared by heating ox-serum to 56% for thirty minutes, and then removing the amboceptor by adding about twice the amount of corpuscles which it can sensitise. The mixture is incubated for one hour, and centrifuged; the supernatant fluid is "ox-colloid."

On adding blood-corpuscles to milk, the cream picks them up and carries them to the top. This red plug does not occur if the milk has been previously heated for a few minutes to 70%, and this circumstance may be used to detect heated or pasteurised milk. W. D. H.

The Degree of Acidity of Urine. ADOLF JOLLES (*Biochem. Zeitsch.*, 1908, 13, 177—184).—The concentration of the hydrogen ions was estimated by determining the rate of hydrolysis of sucrose caused by it at various temperatures. At higher temperatures, for example, at 90°, the results were complicated by the decomposition of the urea and the formation of ammonium carbonate. For this reason, the urea was estimated in the urine both before and after the process of inversion, as also the acidity (by titration) and the mono- and di-phosphates. The results indicated that the concentration of hydrogen ions is very small, and corresponds very closely with that due to monosodium phosphate present in the urine. Owing to the decomposition of urea, trustworthy results by sugar catalysis are only obtainable when the temperature of the experiment does not exceed 37°. S. B. S.

The Rate of Elimination of Chloroform. D. NOËL PATON (*Proc. Roy. Soc. Edinburgh*, 1908, 28, 472—496); D. NOËL PATON and DOROTHY E. LINDSAY (*ibid.*, 497—502).—The experiments were performed on dogs and rabbits; the blood and tissues, as well as the excreta,

were examined, and the analytical results given in detail. It was found that when chloroform is given by the respiratory passages, it is first dissolved in the blood, and thus acts on the nerve-centres, excess being rapidly eliminated. If it is subcutaneously administered, and still more if given by the stomach, the assumption is slow, more stable compounds are formed, and elimination is consequently delayed. The drug has thus more time to produce a slow toxic effect upon the protoplasm of the tissues. The onset of late chloroform poisoning after anaesthesia is due to delayed elimination brought about by unusually firm fixation or by respiratory deficiency.] W. D. H.

Excretion of Creatinine in Man. C. J. C. VAN HOOGENHUYZE and H. VERPLOEGH (*Zeitsch. physiol. Chem.*, 1908, 57, 161—266. Compare Abstr., 1906, ii, 186).—An extensive series of estimations of creatinine are recorded in health and disease, which confirm, in the main, the conclusions drawn by Folin and other workers. Mellanby's view, that creatinine is converted into creatine in the liver, is confirmed, as is also the statement of Gottlieb and Stangassinger that substances (probably ferments) occur in the liver and other organs which transform creatine into creatinine. If the liver is largely destroyed (for instance, by cancer), large amounts of creatine instead of creatinine pass into the urine. The lowering of hepatic activity will explain the presence of creatine in the urine in fever and hunger. In the healthy tissues and blood, creatinine is never found, as it is removed so quickly by the kidneys. W. D. H.

Excretion of Creatine and Creatinine in Health and Disease. PHILIP SHAFFER (*Amer. J. Physiol.*, 1908, 23, 1—22).—Normally, from 7 to 11 mg. of creatinine nitrogen are excreted per kilo of body-weight. This is constant from day to day and from hour to hour; it is not influenced by the volume of the urine, or by the total nitrogen excreted. This creatinine coefficient is parallel to the muscular efficiency of the individual, and in many diseases it is lowered. Creatinine is not an index of total endogenous protein catabolism, but of some special process of normal muscular metabolism. Mellanby's view that the liver is the seat of its formation, whence it reaches the muscle, is dissented from. The creatinine excretion is slightly increased in acute fevers; here it is not parallel to muscular efficiency. Unless creatine occurs in the food, it is absent from normal urine; it may be excreted in acute fevers, in the acute stages of exophthalmic goitre, by women during involution of the uterus, and in other conditions in which there is a rapid loss of muscle protein. W. D. H.

Cystinuria with Diamines. FRANCIS H. THIELE (*Trans. Path. Soc.*, 1907, 58, 255—263).—A case of cystinuria is recorded; tyrosine and other mono-amino-acids were absent from the urine. The urine contained cystine, and, in addition, excess of neutral sulphur, and also cadaverine; putrescine was present in the faeces. All the cystine was apparently derived from tissue catabolism, since starvation, changes of diet, and administration of cystine made no difference in the amount

excreted. The conclusion is drawn that the tissues were deficient in a ferment which normally removes sulphur from thio-amino-compounds.

W. D. H.

Diuresis. XV. Excretion of Sodium Chloride in Phloridzin Diabetes. JOH. BIBERFELD (*Pflüger's Archiv*, 1908, 124, 532—540. Compare Abstr., 1906, ii, 564).—Polemical. A reply to Loewi and Neubauer on their criticisms of the author's previous work.

W. D. H.

Morphine Diabetes. W. SPITTA (*Chem. Zentr.*, 1908, ii, 343; from *Zeitsch. exp. Path. Ther.*, 1908, 5, 94—104).—The reducing substance often found in the urine of those dosed with morphine is probably lævulose, although it is stated to be optically inactive. Dextrose, glycuronic acid, and pentose are absent.

W. D. H.

Gout. HEINRICH KIONKA (*Chem. Zentr.*, 1908, ii, 342; from *Zeitsch. exp. Path. Ther.*, 1908, 5, 131—141, 142—146).—After the administration of uric urid, glycine can be detected in the blood. A crystalline derivative of it, naphthalenesulphonylglycine, was prepared, which showed all the crystallographic constants of the same substance prepared synthetically. A crystallographic description is also given of the corresponding derivatives of other amino-acids (leucine, alanine, &c.).

Feebly alkaline solutions of glycine, alanine, leucine, and allantoin catalytically accelerate the precipitation of acid urates from solutions of uric acid. The presence of such substances in gout is therefore harmful.

W. D. H.

High Temperatures and Heat Stroke. HARVEY SUTTON (*J. Pathol. Bacteriol.*, 1908, 13, 62—73).—In the human subject, the rise of internal temperature, due to exposure to high external temperature, is accompanied by a marked rise in total respiratory exchange and a rise in the respiratory quotient; this probably points to a greatly increased combustion of carbohydrates.

W. D. H.

Crystals in Tumours. CHARLES POWELL WHITE (*J. Pathol. Bacteriol.*, 1908, 13, 3—11).—Crystals consisting of a loose combination of cholesterol with fatty acids, lecithin, or other substances occur in or among the cells of malignant tumours and in some other conditions. These crystals appear to be associated with cell proliferation rather than with degeneration. In degenerated areas, the crystals formed are mostly either cholesterol, fatty acids, or fats. It is suggested that cholesterol is associated with the regulations of cell proliferation.

W. D. H.

Peptonisation in Raw and Pasteurised Milk. RACHEL H. COLWELL and HENRY C. SHERMAN (*J. Biol. Chem.*, 1908, 5, 247—252).—The conclusion is drawn that pasteurisation is not an ideal process as a safeguard against infectious disease. Heating may destroy acid-producing organisms, but leaves intact putrefactive, ammonia-forming, and peptonising organisms. Pasteurisation at high temperatures (75—90°)

has less restraining effect on peptonisation and development of offensive odours than heating to 60°. The amount of ammonia does not always run parallel with intensity of the putrid odour. The determinations of intensity of odour, and also of peptone by the biuret reaction are admittedly rough, and, although conclusions are drawn in reference to infectious disease, no experiments or observations on pathogenic organisms appear to have been made.

W. H. D.

Action of Wines and of Alcohols on the Frog. VITTORIO NAZARI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 166—172).—In small doses, alcohols have no apparent physiological action on frogs, but in larger doses they produce narcosis or complete muscular relaxation, which lasts a longer or shorter time according to the concentration of the alcohol employed and to the size of the frog. Complete recovery takes place from this narcosis, but larger doses of the alcohols cause death. In the following list, the alcohols examined are arranged in the order of increasing narcotic power: ethyl, methyl, propyl, *isobutyl*, *isoamyl*, amyl. The alcoholic content of a wine can be determined roughly by ascertaining at what dilution it just causes or fails to cause narcosis, 1 c.c. of 4% ethyl alcohol having no narcotic influence even on small frogs; in this connexion, the presence in the wines of small proportions of highly narcotic higher alcohols must be borne in mind.

T. H. P.

The Mechanism of the Action of Arsenic Preparations on Trypanosomes in the Animal Organism. II. MARTIN JACOBY and ALBERT SCHÜTZE (*Biochem. Zeitsch.*, 1908, 13, 285—298).—Mice received injections of atoxyl, or of arsenious acid, and were then inoculated with *Nagana* trypanosomes. The trypanosomes from these animals were then inoculated into other animals similarly treated. This process of transference from animal to animal which had been injected with atoxyl or arsenious acid was repeated several times, and the sensitiveness of the trypanosomes obtained after many animals had been thus inoculated towards both arsenious acid and atoxyl was investigated, the experiments being carried out *in vitro*. No marked difference in this respect between these and normal trypanosomes could be ascertained.

S. B. S.

The Behaviour of Iron Arseno-paranucleate and of Arsenious Acid in the Organism. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1908, 13, 321—338).—The arseno-paranucleate was obtained by precipitating an arsenical peptic digestion product of caseinogen by ferric ammonium sulphate. There is evidence that the product obtained in this way is a definite compound, and not a mixture of ferric arsenate and paranucleate. Its behaviour in the organism was investigated by examining the urine after its administration, and determining the rate and the form of the arsenic excretion. It was found that if alcohol is added to alkaline urine, the arsenic in inorganic form is precipitated, whereas that in organic combination dissolves in alcohol. Iron arseno-paranucleate is readily resorbed from the digestive tract, a fact which confirms the assumption that the arseno-paranucleate is a definite

compound, for arsenate of iron is not readily resorbed. The arsenic excreted is chiefly in the form of an organic compound, although small quantities of inorganic arsenic can be detected in the urine in the first days after the administration. The arseno-paranucleate is also resorbed after subcutaneous injection. After administration of arsenious acid, both organic and inorganic arsenic is excreted, the former being in excess of the latter. Of ingested arsenious acid, at least 62% is excreted in the urine after six days. In some experiments, arsenic was detected in the urine of animals to which no arsenic compound had been directly administered; this is due to the small arsenic content of certain vegetables which served as food.

S. B. S.

Physiological Action of Choline. GEORG MODRAKOWSKI (*Pflüger's Archiv*, 1908, 124, 601—632).—This alkaloid appears to be less toxic than is usually considered to be the case. Many of the physiological effects, including the lowering of blood-pressure, usually attributed to it occur only in commercial specimens, but not in the pure substance. The action of the impurity is antagonised by atropine; hence it is that commercial choline produces, after atropinisation, a rise of blood-pressure, which is always the result if the pure alkaloid is employed. Pure specimens rapidly develop the impurity. The experiments were made with choline synthetically prepared.

W. D. H.

The Behaviour of the Brain towards Strychnine. TORATA SANO (*Pflüger's Archiv*, 1908, 124, 369—380).—The grey cortex of the human brain neutralises the toxic action of strychnine; this is especially marked in the motor areas, and the action is attributed in the main to the giant pyramid cells.

W. D. H.

Action of Strychnine and Caffeine. TORATA SANO (*Pflüger's Archiv*, 1908, 124, 381—391).—From experiments on frogs, the conclusion is drawn that strychnine has an anæsthetic as well as a stimulating action; the former manifests itself mainly on the pain receptive elements of the central nervous system, and the latter on the tactile elements; the stimulating action outlasts the anæsthetic, and is slower of development. Similar conclusions are drawn regarding the action of caffeine.

W. D. H.

The Liver in Chloroform Necrosis (Delayed Chloroform Poisoning). H. GIDEON WELLS (*J. Biol. Chem.*, 1908, 5, 129—146).—Rapid autolysis of the liver cells; sometimes follows chloroform anaesthesia in man. A third or more of the solids may disappear in a few days, and the liver contains proteoses, purine bases, polypeptides, and amino-acids. The sulphur in insoluble form is unaltered, but, in spite of loss of nuclear structure, the insoluble phosphorus is increased. The distribution of nitrogen in mono- and di-amino-acids in the coagulated liver proteins does not differ from the normal. Fatty metamorphosis is present in moderate degree; the increase in ether extractives is due to infiltration with simple fats; the lecithin is

slightly decreased, and the amount of cholesterol unaltered. There is less replacement of proteins by water, and more fatty infiltration than in acute yellow atrophy.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Chemical Changes Involved in the Assimilation of Free Nitrogen by *Azotobacter* and *Radiobacter*. JULIUS STOKLASA [with ADOLF ERNEST, FRANZ STRAÑÁK and EUGEN VÍTEK] (*Centr. Bakt. Par.*, 1908, 21, ii, 620. Compare this vol., ii, 880).—The activity of the culture decreases as it ages, doubtless because of the accumulation of acid. Quantitative experiments made to trace the fate of the dextrose were only partly successful; starting with 15.9 grams of dextrose, 7.9 were converted into carbon dioxide, 0.3 into ethyl alcohol, 0.2 into formic acid, 0.7 into acetic acid, 0.2 into lactic acid, leaving a balance of 6.5 unaccounted for, part of which, however, is assimilated into the cell wall of the organisms.

Contrary to the statements of Severin and Krzemieniewski, hydrogen is invariably liberated, and, if sodium nitrate has been added, a certain amount of nitrite and of ammonia is produced.

The author has made an analysis of the bacterial mass and found N 11.3% and ash 8.6%; the latter contained P_2O_5 4.9, and K_2O 2.4, these two substances forming practically the whole of the ash.

E. J. R.

Fixation of Atmospheric Nitrogen by Pure Cultures of *Azotobacter*. Distribution of the Organism. MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 67—74. Compare Stoklasa, this vol., ii, 880).—The author supposed previously that the active agent in nitrogen fixation is not *Azotobacter*, but *Bacillus radiobacter*, almost invariably found with it. His subsequent experiments have demonstrated the incorrectness of this view, and it is now clear that *Azotobacter* fixes nitrogen. The present paper deals with an improvement in technique, whereby it is possible to obtain a better idea than formerly of the distribution of the organism.

It is customary to use a sugar as the source of carbon in culture solutions, but the author finds that calcium malate is better; his solution was 100 tap water, 2 calcium malate, 0.05 K_2HPO_4 . Plates can be made if 1 to 2 parts of agar agar are also added; on these, a larger number of organisms develop into colonies than on any other plates, so that a more exact estimate of the number of *Azotobacter* present in a sample of soil can now be made. Instead of calcium malate, the lactate, acetate, or propionate can also be used, but in these media the organisms soon lose their power of growth, and re-inoculation to obtain pure cultures cannot be continued for long. Growth is also slow when calcium citrate, tartrate, or succinate is used, and there is no growth when calcium glycollate is supplied.

The amount of nitrogen fixed per gram of calcium salt oxidised was 4.9 mg. with the propionate, 2.8 mg. with the acetate, 2.6 mg. with the malate, and 1.8 mg. with the lactate. About 7 mg. are fixed for each gram of sugar oxidised when sugar is used as the source of carbon.

When calcium malate plate cultures are made of soil extracts, it is not usual to find colonies of *Azotobacter*, because only a small proportion survive and develop on plates, but when soil adhering to the roots of leguminous plants is examined, a number of colonies are produced, showing that a distinct relationship exists between the distribution of *Azotobacter* and the *Leguminosae*. E. J. R.

Variation of the Rate of Disinfection with Change in the Concentration of the Disinfectant. HERBERT EDMESTON WATSON (*J. Hygiene*, 1908, 8, 536—542).—Miss Chick's results on the laws of disinfection, in which she showed that the disinfection is strictly analogous to a chemical reaction in which individual bacteria play the part of molecules, can be expressed by a mathematical formula, the use of which is illustrated by one of the problems worked out as follows: A solution of phenol containing 10 parts per 1000 disinfects a culture of *Bacillus paratyphosus* in twenty-five minutes; another solution takes thirty-five minutes. What is the strength of the second solution? Let the strength of the second solution be x ; for phenol, $n=5.5$. Therefore $5.5 \log 10 + \log 25 = \text{constant} = 5.5 \log x + \log 35$. From this $x=9.4$. W. D. H.

Protein Formation in Ripening Seeds. N. WASSILIEF (*Ber. deut. bot. Ges.*, 1908, 26a, 454—467. Compare Abstr., 1901, ii, 185, and Nedokutschaeff, Abstr., 1902, ii, 281; 1903, ii, 508; Zaleski, 1905, ii, 549).—A continuation of work on the source and method of formation of protein in ripening seeds. As the result of a series of determinations, the amounts of nitrogen present in various forms, for example, as protein, asparagine, amino-acids, substances precipitated by phosphotungstic acid, &c., in (1) seeds at various stages of ripeness, (2) whole fruits, (3) husks of fruits, (4) whole leaves, (5) laminae, and (6) petioles, of *Lupinus albus*, the following principal conclusions are drawn.

After the removal of fruits from the plants, protein formation takes place in the former whether they are kept in the dark or in the light, and at the expense of asparagine, present in the fruit as plucked. The amino-acids at first increase slightly in amount, especially if the fruits are kept in the dark, doubtless as the result of protein decomposition, but eventually they are also used up, being probably transformed into asparagine, and then into protein. Organic bases play much the same rôle as amino-acids.

In the foregoing changes, the seeds become gradually richer in nitrogenous material, due to movement of nitrogenous substances from the husks of the fruits to the seeds. At the same time, the seeds become enriched with protein at the expense of the husks, so that the protein of the ripe seeds is, in part, derived from amino-compounds initially present in them when the fruits are plucked, and,

in part, from amino-compounds subsequently formed in the husks. Seeds separated from the husks, and kept either dry or damp, form some protein from asparagine and other amino-compounds originally present in them. T. A. H.

The Rapid Change in Composition of Certain Tropical Fruits during Ripening. H. C. PRINSEN GEERLIGS (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 74—84).—The fruits investigated are commonly gathered in an immature state; within a few days they become tender and palatable; a few days later, however, they become over-ripe, and change to a soft, unpalatable mass. Experiments with bananas (*Musa*) showed that during the ripening process there is an evolution of carbon dioxide and water, and a considerable conversion of starch into sugar. The composition at the various stages is as follows:

	April 17, unripe.	April 19.	April 20.	April 22.	April 23, ripe.	April 24, over-ripe.
Dry matter, per cent...	41.76	40.79	40.52	40.14	39.02	38.88
Starch	30.98	24.98	20.52	13.80	9.59	7.68
Sucrose	0.86	4.43	6.53	10.50	13.68	10.36
Dextrose.....	0.25	0.96	1.80	3.18	4.72	6.1
Lævulose		0.90	1.53	2.70	3.61	4.8

Quite similar results were obtained with the mango (*Mangifera*) and the tamarind (*Tamarindus*).

Oxygen is necessary for the ripening process; bananas will keep their starch intact if surrounded with an atmosphere of nitrogen. The author, therefore, considers sugar production to be a vital process, although he succeeded in demonstrating the presence of an enzyme capable of decomposing starch.

Sapodilla (*Achras sapota*) does not fall into line with the above-mentioned fruits; the amount of sugar before and after ripening remains unaltered, and the change appears to be mainly a softening of the hard pectin, and a deposition of tannin and gutta-percha from the juice as insoluble substances. E. J. R.

Vegetable Phosphatides. ERNST SCHULZE (*Chem. Zeit.*, 1908, 32, 981—983. Compare this vol., i, 385).—Phosphatides were determined in a number of seeds (without husks), and the following results obtained (percentages in dry matter):

	Phosphorus.		Phosphatides
	Total per cent.	Per cent. in ether-alcohol.	as lecithin.
Yellow lupins	—	0.082	2.14
Blue „	1.53	0.084	2.19
Garden beans	1.32	0.049	1.27
<i>Phaseolus multiflora</i>	—	0.035	0.90
Sunflower	—	0.017	0.44
<i>Pepo cucurbita</i>	2.10	0.021	0.55
<i>Ricinus</i>	1.14	0.011	0.29
Beech	—	0.011	0.30
Chestnut	—	0.026	0.67
Horse chestnut	—	0.026	0.67
<i>Pinus cembra</i>	1.16	0.038	0.99
<i>Pinus maritima</i>	2.60	0.033	0.86

The phosphatide represents only a small percentage of the total phosphorus (in the case of *Ricinus*, only 1%), and, since the seeds contain very little inorganic phosphorus, it is evident that some other organic phosphorus compounds must be present in much larger quantity than the phosphatides. The substance known as phytin, which yields inositol as a cleavage product, is one of these substances, and is presumably of greater importance to plants than the phosphatides.

N. H. J. M.

Water-soluble Polysaccharides of Barley and Malt.

HORACE T. BROWN (*Bied. Zentr.*, 1908, 37, 675—676; from *Zeitsch. ges. Brauwesen*, 1907, 30, 286).—Finely-crushed barley (1 kilo.) was stirred with boiling water (7 litres), cooled to 70°, and, after adding 15 c.c. of malt extract, boiled for a long time. A further amount (250 c.c.) of malt extract was then added, and the whole digested for one hour at 50—55° and again boiled. It was then filtered, the residue well washed with hot water, and the filtrate evaporated to 4 litres under reduced pressure. The resulting liquid, D. 1·060, containing 15% of dry matter, was treated with 80% alcohol; on cooling, white flakes of crude amylan separated. The latter, after being thoroughly washed with 60—70% alcohol, was treated with 500 c.c. of water, and again precipitated with alcohol.

The soluble constituents of barley are as follows: ash, 0·75; proteins, 0·75; sugar, 4·10; starch, 56·20, and amylan, 9·65%. The amylan yields, when hydrolysed with 2·5% oxalic acid, chiefly dextrose along with galactose, mannose, arabinose, and xylose.

Crude amylan from malt dissolves readily in cold water, is strongly dextrorotatory, and has slightly reducing properties. When hydrolysed, it yields dextrose and arabinose.

N. H. J. M.

Fruits of *Caulophyllum thalictroides* and *Cornus sericea*.

EDITH STOCKTON and C. G. ELDREDGE (*Chem. News*, 1908, 98, 190—191).—The pulp of the fruit of *Caulophyllum thalictroides* contains lævulose and small quantities of citric, tartaric, and tannic acids. The crushed nuts yield to ether about 3% of oil, calculated on the whole fruits, of which a portion is volatile and the remainder belongs either to the laurin or olein group.

The pulp of the fruit of *Cornus sericea* contains potassium hydrogen tartrate, potassium hydrogen oxalate, calcium oxalate, gum, tannic, gallic, and malic acids, and a sugar, possibly lævulose. The nuts yield to ether a pale amber-coloured oil, which deposits some solid matter, perhaps palmitin, on standing.

T. A. H.

Constituents of the Rhizome of *Imperatoria ostruthium*.

JOHANNES HERZOG (*Arch. Pharm.*, 1908, 246, 414—417).—The author has applied the method devised for the preparation of pimpinellin (this vol., i, 905), namely, extraction with benzene and treatment of the concentrated extract with light petroleum, to this rhizome, and has isolated thereby oxypeucedanin, identical with that prepared by Erdmann and by Bothe from the root of *Peucedanum*

officinale. Gorup-Besanez (Abstr., 1874, 907; 1877, 717) obtained ostruthin as the principal constituent of the young rhizome of *Imperatoria ostruthium*, although Heut subsequently (this Journ., 1875, 772) detected oxypeucedanin in the rhizome. It remains to be seen whether ostruthin and oxypeucedanin both occur always in the rhizome, or whether the former is replaced by the latter as the rhizome ages or is collected and stored.

T. A. H.

Constituents of Saffron. BALTHASAR PFYL and W. SCHEITZ (*Zeitsch. Nahr. Genussm.*, 1908, 16, 337—346. Compare Hilger, Abstr., 1900, i, 682).—With the object of devising a process for the detection of inferior saffron (this vol., ii, 997), attempts were made, following lines suggested by the results of previous investigators, to obtain data regarding the properties of the chief constituents of the drug.

The methods suggested by Quadrat (*J. pr. Chem.*, 1852, 56, 68) and Weiss (*ibid.*, 1867, 101, 65), involving the extraction of the saffron, previously freed from fat, &c., by means of ether or light petroleum, with water, and precipitation of the colouring matter (polychroit or crocin) from the aqueous extract by lead acetate or alcohol, do not yield a pure preparation, and the same is true of Kayser's process, depending on the use of animal charcoal for the extraction of the colouring matter (Abstr., 1885, 59). Only amorphous, impure preparations of crocin could be obtained, and these, on hydrolysis with acids, furnished dextrose (compare Kayser, *loc. cit.*; Schunck and Marchlewski, Abstr., 1894, i, 340).

Similarly, Kayser's crocetin (*loc. cit.*) could only be obtained as an amorphous, red mass, which, however, yielded crystalline salts with metals and certain organic bases (compare Decker, Abstr., 1906, i, 686).

Kayser's picrocrocin (*loc. cit.*) could not be prepared, although by using his process for its isolation a small amount of a white, crystalline substance, m. p. 67°, which did not reduce Fehling's solution, was obtained.

From a chloroformic extract of saffron, three substances were isolated: (1) a colourless, crystalline product, m. p. 280°, which did not reduce Fehling's solution; (2) a yellow, crystalline substance, m. p. 164°, readily soluble in water or alcohol, which when boiled with acid developed the odour of saffron oil and yielded a reducing sugar, probably lævulose, and (3) a crystalline hydrocarbon, m. p. 118° (compare Schüler, *Inaug. Diss. Munich*, 1899, and Hilger, *loc. cit.*), apparently similar to the hydrocarbons found in marigold petals, arnica flowers, &c. The second of these products somewhat resembles the picrocrocin described by Kayser.

An alcoholic extract of saffron contains, in addition to colouring matter, a sugar (? lævulose) and a glucoside, which, on hydrolysis yields saffron oil and lævulose (?). The sugar provisionally regarded as lævulose is lævorotatory, reduces Fehling's solution, yields phenylglucosazone, and gives the Seliwanoff reaction (Abstr., 1903, ii, 616).

T. A. H.

Have Manganese Salts, Employed as Stimulants, a Favourable Influence on Vegetation? SIGURD RHODIN (*Bied. Zentr.*, 1908, 37, 667—668; from *K. Landtbr. Akad. Handl. Tidskr. Stockholm*, 1908, 30—33).—Field experiments with oats grown on peaty soil and with potatoes on rich garden soil. Manganese peroxide (1 kilo. per are), manganese acetate, and benzoate (30 grams per 100 square metres) reduced the yield of oats. In the potato experiment, manganese sulphate (6 kilos. per hectare) was employed. One variety of potatoes showed an increase of 1% of starch on the manganese plot; the total starch was, however, considerably less than without manganese, owing to the smaller yield of tubers. N. H. J. M.

Manurial Experiments with Nitrogen in 1907. HENRIK G. SÖDERBAUM (*Bied. Zentr.*, 1908, 37, 657—659; from *K. Landtbr. Akad. Handl. Tidskr. Stockholm*, 1908, 104—110).—Oats were grown in sandy soil (25 kilos. per pot), and manured with 0.25, 0.5, and 0.75 gram of nitrogen in different forms, in addition to minerals. The relative manurial effects of the nitrogen compounds varied according to the amounts employed. With the smallest amounts, sodium nitrate gave the highest yields. When 0.5 gram of nitrogen was applied, ammonium sulphate gave the best results; then Polzeniusz's, Carlson's, and Frank's calcium cyanamide preparations; the next best were sodium nitrate and albumin (about equal), and last, calcium nitrate. With the largest amounts of nitrogen, ammonium sulphate was again the best; then Carlson's and Polzeniusz's calcium cyanamide; Frank's cyanamide gave considerably less produce, whilst calcium nitrate was again the least satisfactory.

The total divergence of the results from those of the previous year is attributed to the unusually low temperature in 1907, and the consequent more prolonged vegetative period. N. H. J. M.

Field Experiments with Ammonium Sulphate. HERMANN BACHMANN (*Bied. Zentr.*, 1908, 37, 664—665; from *Fühling's Landw. Zeit.*, 1907, 530).—Experiments with rye, oats, barley, and mangolds grown on sandy soil and on loam showed that ammonium sulphate produced considerably greater yields than sodium nitrate.

N. H. J. M.

Utilisation of Nitrogen in the Form of Ammonium Nitrate. THEODOR PFEIFFER, A. HEPNER, and L. FRANK (*Bied. Zentr.*, 1908, 37, 663—664; from *Mitt. Landw. Inst. K. Univ. Breslau*, 1908, 5, 341).—The plants were grown in sand, and manured with ammonium nitrate and sulphate and sodium nitrate respectively. The position of ammonium nitrate as a manure is between sodium nitrate and ammonium sulphate; it may, however, under certain conditions, equal sodium nitrate. Addition of sodium chloride had no appreciable effect. The favourable results obtained by Wagner with sodium chloride in conjunction with ammonium sulphate may have been due to the presence of zeolites in the soil.

Addition of phosphorite along with ammonium nitrate increased the yield and also the amount of nitrogen taken up. N. H. J. M.

Manurial Trials with Sodium Nitrate and Ammonium Sulphate. H. CLAUSEN (*Bied. Zentr.*, 1908, 37, 585; from *Illustr. landw. Zeit.*, 1907, 27, 842).—Ammonium sulphate proved more effective than sodium nitrate on potatoes, rye, and oats growing on sandy soils. The superiority may be accounted for in several ways; there are indications that the potato plant can directly assimilate ammonia, so that nitrification becomes unnecessary; it is also known that sodium nitrate washes into the sub-soil, and is therefore lost more readily than ammonium sulphate. On the soils in question, Wagner's generalisation, that ammonium sulphate is only 75% as effective as sodium nitrate, clearly does not hold, and the author is of opinion that results similar to his own would commonly be obtained elsewhere.

E. J. R.

Plot Experiments on the New Nitrogenous Manures. HJALMAR VON FEILITZEN (*Bied. Zentr.*, 1908, 37, 659—663; from *Svenska Mosskulturförening. Tidskr.*, 1908, 91—108).—Calcium nitrate produced higher yields of potatoes and of starch than potassium nitrate both on incompletely humified *Sphagnum* soil deficient in nitrogen, and on peat soil rich in nitrogen. Similar experiments with oats grown in sandy peat gave similar results.

Experiments in which different varieties of potatoes were grown in sandy soil, and manured respectively with sodium nitrate and two calcium cyanamide preparations, showed that, whilst the plants manured with cyanamide developed somewhat better than those on the nitrate plots, the final yields both of potatoes and starch were highest where nitrate had been supplied.

N. H. J. M.

Analytical Chemistry.

A Shortened Burette. F. TSCHAPLOWITZ (*Zeitsch. anal. Chem.*, 1908, 47, 697—698).—The apparatus consists of two 25 c.c. burettes connected at their lower end with a single tap. When the contents of one of the burettes has been run off through the tap, a half-turn of the latter enables the contents of the second burette to be used.

W. P. S.

Combined Wash-bottle and Pipette. J. W. HOGARTH (*J. Roy. Soc., New South Wales*, 1905, 38, 418—420).—A modified wash-bottle by means of which it is possible to deliver an exactly measured volume of liquid.

P. H.

Destruction of Organic Substances. M. KERBOSCH (*Pharm. Weekblad*, 1908, 45, 1210—1213).—The author emphasises the importance of the absence of organic matter in testing for metallic

poisons, and describes a method for destroying it by heating the material with a mixture of sulphuric acid and nitric acid. The method has been applied to milk, peas, meat, and sardines.

A. J. W.

The Use of Nitrous Acid, Nitrites, and Aqua Regia in the Estimation of the Mineral Constituents of Urine. JOSEPH H. KASTLE (*Amer. J. Physiol.*, 1908, 22, 411—422).—The difficulty of incinerating urine completely is well known. If, however, the urea is first got rid of by heating with sodium nitrite, nitrous acid, or aqua regia, incineration is rapidly accomplished, and the inorganic constituents of the ash can be estimated accurately. Each of the three reagents mentioned has special advantages in certain cases.

W. D. H.

Action of Thiosulphate on Permanganate in Alkaline Solution. HEINRICH KILIANI (*Chem. Zeit.*, 1908, 32, 1018).—Reinige proposed to estimate alkali iodides by titration with permanganate (conversion into iodate), and to estimate the excess by means of thiosulphate, when tetrathionate was supposed to be formed. The author, having received a private communication from Herms, has had the matter investigated, and now states that in the oxidation of thiosulphate in alkaline solution, sulphate is formed. Hence, when using Reinige's process, it must be remembered that 8 mols. of potassium permanganate do not require 24, but only 3, mols. of sodium thiosulphate for decolorisation.

L. DE K.

Estimation of [Organic] Sulphur by Carius' Method. ERWIN RUPP (*Chem. Zeit.*, 1908, 32, 984).—It is recommended to add barium chloride when oxidising the substance with nitric acid instead of adding it when the oxidation is finished. The barium sulphate thus obtained is of a coarse structure, and consequently readily washed and collected. It must be remembered that it always contains barium nitrate, from which it may be freed by boiling with 150—200 c.c. of water, any large particles being broken up with a glass rod.

L. DE K.

Volumetric Estimation of Sulphuric Acid. THOMAS COOKSEY (*J. Roy. Soc., New South Wales*, 1907, 41, 215—217).—The author has improved the titration of barium and calcium salts by means of *N/10* sodium carbonate and phenolphthalein as indicator, by adding alcohol in such quantity that, after the experiment is finished, the liquid will contain about half its bulk of it. Before titrating, the liquid must, if necessary, be rendered neutral to phenolphthalein with potassium hydroxide. The barium or calcium carbonate is immediately precipitated, and the end reaction becomes very distinct.

Sulphates (if necessary, freed from metals other than alkalis) are estimated conveniently by adding to the carefully-neutralised solution a definite amount of barium chloride, the excess of which is then estimated by the above process.

L. DE K.

Modification of Hüfner's Method for the Volumetric Estimation of Nitrogen. VICTOR VON CORDIER (*Zeitsch. anal. Chem.*, 1908, 47, 682—687).—The apparatus used consists of a cylindrical bulb with a long neck, which is provided with a side-tube, the whole being similar to a Victor Meyer's vapour density apparatus. The bulb has a capacity of about 100 c.c., and is fitted with a stoppered tubulure for introducing the sodium hypobromite solution. A second bulb is also provided, and serves as a reservoir for a further quantity of the solution; it is attached to the main bulb by a tapped tube, which enters the shoulder of the main bulb, and also at its top by a second tapped tube, which is connected with the neck of the apparatus. About 50 c.c. of Knop's (sodium hypobromite) solution are placed in the main bulb, and about 40 c.c. in the reserve bulb. When required, this portion of the solution is allowed to enter the main bulb by opening both the taps. The use of the apparatus enables a larger quantity of substance to be taken for the estimation, and results of experiments are given showing that the method may be used for the estimation of nitrogen in guanidine picrate, urea nitrate, acetylurea, ammonium platinichloride, &c.

W. P. S.

Estimation of Ammonia in Urine. A. RONCHÈSE (*Bull. Soc. chim.*, 1908, [iv], 3, 840. Compare Abstr., 1907, ii, 651).—A claim for priority against Malfatti (this vol., ii, 531).

E. H.

Presence of Nitrite and Ammonia in Well-water and Its Signification. J. VAN EYK (*Pharm. Weekblad*, 1908, 45, 1162—1165).—At the ordinary temperature, zinc reduces nitrates in aqueous solution to nitrites, and then to ammonia. The author considers that nitrates in well-water may be reduced to nitrites by the zinc employed to galvanise the iron pipes of water pumps.

A. J. W.

Estimation of Phosphorus, Sulphur, and Silicon in Acetylene. ADOLF FRAENCKEL (*Chem. Zentr.*, 1908, ii, 643—644; from *J. Gasbeleuchtung*, 1908, 51, 431—435).—The acetylene generated from a known weight of calcium carbide is burnt in a special apparatus, and the products of combustion are drawn through sodium hypobromite solution.

On evaporating to dryness with addition of hydrochloric acid, the silica is obtained; in the filtrate from this, the phosphoric acid is estimated as usual with magnesia mixture. Sulphur is estimated similarly by passing the products of combustion through sodium hypobromite and estimating the sulphuric acid formed as usual.

L. DE K.

Estimation of Phosphoric Acid by Lorenz's Method. OTTOKAR FALLADA (*Chem. Zentr.*, 1908, ii, 827—828; from *Osterr.-ung. Zeitsch. Zucker.-Ind. Landw.*, 1908, 37, 333—336).—Lorenz's method (direct weighing of the yellow precipitate) is recommended, and will be found useful for the estimation of citrate-soluble phosphoric acid.

L. DE K.

Estimation of Arsenic in Iron Ores. MARCEL GUEDRAS (*Chem. Zentr.*, 1908, ii, 444; from *Rev. gener. Chim. pure appl.*, 1908, 11, 251—253).—One gram of the finely-powdered ore is boiled in a 500 c.c. flask with 150 c.c. of hydrochloric acid and 5 grams of stannous chloride, and the distillate is collected in a graduated 100 c.c. receiver containing 50 c.c. of water.

When 40 c.c. have passed over, the distillate is nearly neutralised, a few grams of sodium hydrogen carbonate are added, and the arsenic is titrated as usual with standard iodine. L. DE K.

Apparatus for the Estimation of Carbon in Iron. MAX WIDEMANN (*Chem. Zentr.*, 1908, ii, 724—725; from *Zeitsch. Chem. Apparatenkunde*, 1908, 3, 296).—An improved flask and condensation arrangement. The essential improvement consists in the condensing tube being fitted with 5 bulbs. The gaseous products escape through a side-tube. The tube carrying off the water is fitted with a funnel, in which the water rises in case of sudden pressure, thus preventing the tube from cracking. L. DE K.

Simultaneous Estimation of Carbon, Hydrogen, and Nitrogen, &c., in Organic Compounds by the Method of Simplified Elementary Analysis. MAX DENNSTEDT and F. HASSLER (*Ber.*, 1908, 41, 2778—2782).—Oxygen, prepared by heating potassium permanganate, passes through a sulphuric acid tube, through one limb of a T-piece, and through a soda-lime-calcium chloride tube into the bifurcated entry-tube of the combustion apparatus. Through the other limb of the T-piece, oxygen is driven into a weighted rubber bag (15 kilo. per 300 sq. cm.) which acts as a reservoir, by which the current of oxygen during the combustion can be adjusted to a nicety. The combustion tube and absorption apparatus are arranged as usual. To absorb oxygen, a 1 litre Erlenmeyer flask is provided with a two-holed stopper, through which one tube, passing to the bottom of the flask, is connected with an ordinary pressure-adjusting bulb, whilst a capillary T-piece, passing just through the other hole, is connected by one limb with the combustion apparatus, a safety bottle being inserted to prevent back-suction; the other limb of the T-piece, provided with rubber tubing and a pinch-cock, serves as a gas-exit.

The best absorbent of oxygen is cuprous chloride in hydrochloric acid containing pieces of copper gauze. The solution is prepared best from copper sulphate and an excess of hydrochloric acid, as the presence of sulphuric acid increases the rate of absorption of the oxygen. The solution is efficient so long as copper gauze remains undissolved.

The expulsion of air from the whole apparatus requires one to one and a-half hours. At the completion of the combustion the nitrogen is swept into the Erlenmeyer flask for about twenty minutes; after standing overnight, the nitrogen is measured in a Hempel burette. Any nitrogen retained as lead nitrate by the lead peroxide must be extracted by 33% alcohol, the solution evaporated, and the residue of lead nitrate weighed. Sulphur and the halogens are estimated as described in previous communications.

The method is most suitable for the analysis of costly substances, difficult to obtain pure. C. S.

Volumetric Estimation of Sodium Hydroxide in the Presence of Sodium Carbonate. A. C. ANDERSEN (*J. Pharm. Chim.*, 1908, 28, 370—371; from *Tidskr. Kem. Farm. Terapi*, 1908, 11, 161).—This estimation is generally carried out by adding barium chloride, which precipitates the carbonate and leaves the hydroxide; the latter is then titrated with standard acid and phenolphthalein as indicator. But in order to obtain trustworthy results, the author proposes the following slight modification.

After operating in the manner described, another portion of the solution is taken, and sufficient standard acid is added to neutralise the greater part of the hydroxide. The liquid is then heated to boiling, and a slight excess of barium chloride solution is added. When the liquid has cooled (the flask being closed), the titration is continued with phenolphthalein as indicator. L. DE K.

Ready Means of Comparing Sodium Carbonate and Oxalic Acid Solutions. A. TIAN (*Chem. Zentr.*, 1908, ii, 636; from *Rev. gen. Chim. pure appl.*, 1908, 11, 208).—The process is based on the fact that oxalic acid liberates the mineral acid from a calcium salt. A measured amount of the oxalic acid solution to be tested is mixed with an excess of calcium chloride, and the turbid liquid titrated with sodium carbonate solution, using helianthin as indicator.

L. DE K.

Estimation of Small Amounts of Barium in Rocks. RALPH W. LANGLEY (*Amer. J. Sci.*, 1908, [iv], 26, 123—124).—The author estimates small amounts of barium in rocks by precipitation with sulphuric acid immediately after the separation of silica. It is necessary to re-dissolve the barium sulphate in concentrated sulphuric acid, and to precipitate it with water, in order to free it from ferric and other sulphates. If barium is not removed as sulphate, it is precipitated as phosphate, and introduces an error in the estimation of magnesium.

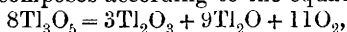
R. J. C.

Separation of the Metals which are Precipitated by Hydrogen Sulphide. H. BOLLENBACH (*Zeitsch. anal. Chem.*, 1908, 47, 690—693).—The metals which are precipitated by hydrogen sulphide, and are insoluble in ammonium sulphide, namely, mercury, lead, bismuth, cadmium, and copper, may be separated from each other by the following method. The precipitated sulphides are treated with nitric acid, when all but the mercury goes into solution. Ammonium persulphate is added to the solution, then a considerable excess of ammonia, and the mixture is boiled. Lead and bismuth are precipitated and removed by filtration. The precipitate is dissolved in concentrated hydrochloric acid; one portion of the solution is rendered ammoniacal, then acidified with acetic acid, and tested with potassium dichromate, a yellow precipitate denoting the presence of lead (bismuth chromate is readily soluble in acetic acid).

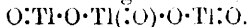
A second portion of the hydrochloric acid solution is treated with stannous chloride, and sufficient sodium hydroxide is added to redissolve the stannous hydroxide. A black precipitate shows that bismuth is present. The filtrate from the lead and bismuth peroxides is boiled with hydrochloric acid to decompose the ammonium persulphate, and then rendered ammoniacal. A blue coloration denotes the presence of copper. The blue solution is then treated with potassium cyanide and hydrogen sulphide, when a yellow precipitate is obtained if cadmium is present. W. P. S.

Electrolytic Estimation of Thallium and Probable Existence of a New Oxide of this Metal. GINO GALLO and G. CENNI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 276—284).—When a solution of thallous sulphate, slightly acidified with sulphuric acid, is electrolysed, the whole of the thallium is deposited on the anode in the form of an oxide, generally supposed to be the sesquioxide. It was found, however, by Heiberg (*Abstr.*, 1903, ii, 614) that, when the deposit of oxide is heated in order to dry it, its weight at first diminishes and subsequently increases, this increase being supposed by him to be due mainly to the action on the oxide of sulphur dioxide from the gas heating the oven, whilst Werther (*J. pr. Chem.*, 1864, 91, 385) regarded it as being caused by the absorption of carbon dioxide. The authors find that the minimum weight of the deposit is greater than that of the sesquioxide corresponding with the amount of thallium employed, their results indicating that the sesquioxide is converted into an oxide of the composition Tl_3O_5 . The oxide Tl_2O_3 is probably transformed partly into TlO_2 , which, with Tl_2O_3 , gives the compound Tl_3O_5 . The formation of such an oxide is not surprising, considering the position of thallium between mercury and lead in the periodic system, and also the existence of mercury peroxide (compare Antropoff, *Zeitsch. Elektrochem.*, 1906, 12, 585; Pellini, *Gazzetta*, 1908, 38, i, 71).

The best procedure for the quantitative, anodic deposition of thallium as oxide is to dissolve thallous sulphate in about 100 c.c. of water in a Classen capsule, the solution being acidified by the addition of about 0.1 gram of oxalic acid, and electrolysed at the ordinary temperature with a platinum disk rotating at 800 revs. per minute as negative electrode; the voltage should be 3—4, and the current density, 0.15—0.20 ampere. The end of the electrolysis is ascertained by adding a little water so as to raise the level of the liquid in the capsule; no deposit should appear on the clean platinum surface thus freshly brought into contact with the solution. The weight of the deposit, after drying at 160—200°, corresponds with the formula Tl_3O_5 , and, when dissolved in hydrochloric acid, the oxide causes evolution of chlorine and forms the chloride, $TlCl_3 \cdot 3TlCl$. The oxide hence decomposes according to the equation:



and the authors regard it as having the structure



T. H. P.

Analysis of a Mineral containing Copper, Bismuth, Lead, Silver, Calcium, Iron, and Quartz. AUGUST CHWALA and V. MACRI (*Chem. Zentr.* 1908, ii, 261; from *Mon. Sci.*, 1908, [iv], 22, 372).—The mineral is decomposed by means of nitric acid and potassium chlorate, and a solution of ammonium nitrate is added to keep lead and calcium sulphates in solution. The siliceous matter is then collected and washed, first with a hot acid and then with a hot ammoniacal solution of ammonium nitrate. After removing any silver from the filtrate by means of hydrochloric acid, sulphuric acid is added, and then excess of ammonia, which precipitates the iron only; this is washed first with an acid and then with an ammoniacal solution of ammonium nitrate. The bismuth is then precipitated with ammonium carbonate, and, finally, the copper and lead are separated as usual.
L. DE K.

Solubility of Rare Earth Oxalates in Solutions containing Uranyl Salts. OTTO HAUSER (*Zeitsch. anal. Chem.*, 1908, 47, 677—680).—It is pointed out that uranyl salts have a considerable solvent action on cerium and lanthanum oxalates, and, unless a considerable excess of oxalic acid is added, the results obtained in the usual method of precipitating these earths as oxalates are untrustworthy, if uranyl salts are present.
W. P. S.

Separation of the Metals of the Ammonium Sulphide Group. ERICH EBLER (*Zeitsch. anal. Chem.*, 1908, 47, 665—677).—The following process of separating the metals precipitated by ammonium sulphide is recommended. The precipitate, consisting of iron, manganese, nickel, cobalt, and zinc sulphides, and aluminium and chromium hydroxides, is boiled with hydrochloric acid until all the hydrogen sulphide has been expelled, then oxidised with nitric acid, and treated with hydrogen peroxide and sodium hydroxide. The precipitate, which contains the iron, manganese, nickel, and cobalt, is separated by filtration, dissolved in hydrochloric acid, hydrogen peroxide is added, and the iron and manganese are precipitated with ammonia; these two metals are separated from their hydrochloric acid solution by the addition of ammonium chloride, hydroxylamine hydrochloride, and ammonia, the iron being precipitated, whilst the manganese remains in solution. The nickel and cobalt are separated by adding dicyanodiamide and potassium hydroxide to the filtrate containing them; the nickel is precipitated as a crystalline compound. The filtrate containing the aluminium, chromium, and zinc is boiled, and ammonium chloride is added repeatedly until ammonia ceases to be given off; the aluminium hydroxide thus precipitated is removed by filtration, and the filtrate is treated with sulphurous acid after acidifying with hydrochloric acid. The addition of ammonia to the hot solution precipitates the chromium, leaving the zinc in solution.
W. P. S.

Estimation of Iron, Alumina, and Phosphoric Acid in Presence of Each Other. THOMAS COOKSEY (*J. Roy. Soc., New South Wales*, 1907, 41, 163—171).—The acid solution is mixed with a definite

amount of a standard solution of sodium dihydrogen phosphate, and potassium hydroxide solution is added until the liquid is neutral to methyl-orange. The whole is diluted to 80—90 c.c., and heated on the water-bath until the precipitate has settled. To the filtrate is added an excess of calcium chloride, the liquid is acidified slightly with *N*/10 acid, boiled to expel carbon dioxide, and the free phosphoric acid is titrated with *N*/10 potassium hydroxide, using phenolphthalein as indicator, as soon as the liquid is neutral to methyl-orange; 1 c.c. = 0.00355 gram of P_2O_5 .

The iron oxide is determined iodometrically, and calculated to ferric phosphate. This deducted from the weight of the first precipitate gives the aluminium phosphate, which is then calculated to alumina. From the total phosphoric acid found, is then deducted the amount purposely added.

L. DE K.

Separation of Iron from Nickel and Cobalt by Lead Oxide.

T. H. LABY (*J. Roy. Soc., New South Wales*, 1904, 37, 157).—After trying the separation by means of ammonium hydroxide and chloride, ammonium carbonate, the basic acetate process, the phosphate method, the electrolytical separation, and the ether extraction process, the author finally calls attention to a process given by Field (*Chem. News*, 1859, 1, 5), which he finds is also suitable for the separation of iron from cobalt.

In this process the iron is precipitated as hydroxide by evaporating the nitrate solution with excess of lead oxide; the lead is separated readily from the filtrate with sulphuric acid. The nickel or cobalt is then estimated electrolytically in ammoniacal solution.

L. DE K.

Detection of Cobalt in the Presence of Large Quantities of Nickel. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1908, 13, 390—391).—Supposing the amount of nickel to be about 1000 times that of the cobalt, the solution containing about 10 grams of the nitrates is concentrated to 25—50 c.c. and mixed while hot with 50 grams of ammonium molybdate dissolved in a little boiling water. When cold, the liquid is filtered from the nickel precipitate, and the rose colour of the cobalt becomes visible. On boiling with excess of sodium hydroxide and a little hydrogen peroxide, the cobalt is obtained as a brown oxide, which may then be identified by means of the borax bead.

L. DE K.

Approximate Colorimetric Estimation of Cobalt and Nickel in the Presence of Each Other. R. W. CHALLINOR (*J. Roy. Soc., New South Wales*, 1905, 38, 406—417).—The two metals are estimated jointly by electrolysis, and then dissolved in dilute nitric acid (1 : 1). After evaporating nearly to dryness, the mass is dissolved in water and diluted to a known volume. If the liquid is green, more than 76% of nickel is present; an aliquot portion of the liquid, containing 0.04—0.05 gram of the mixed metals, is taken, and a standard solution of cobalt is run in until the colour (after diluting to the 50 c.c. mark) is equal to that of a standard solution containing the nearest weight of the mixed metals. If, however, the solution is pink, showing

the presence of more than 24% of cobalt, standard nickel is run in, any excess of which may be again checked with cobalt.

After allowing for nickel added, the amount of nickel in the mixture is readily calculated.

L. DE K.

Iodometric Estimation of Chromic and Vanadic Acids in the Presence of Each Other. GRAHAM EDGAR (*Amer. J. Sci.*, 1908, [iv], 26, 333—336).—The mixed acids (about 0.2 gram) are boiled with 15 c.c. of hydrochloric acid and 2 grams of potassium bromide in a Voit flask, a slow current of hydrogen is passed, and the bromine evolved, owing to the reduction of 2CrO_4 to Cr_2O_3 and V_2O_5 to V_2O_4 , is absorbed in an alkaline solution of potassium iodide contained in a Drexel bottle connected with a Will and Varrentrap trap, also containing the same solution. After the operation is over, the potassium iodide solution is acidified with hydrochloric acid, and the iodine set free titrated as usual. The Drexel bottle is then filled with fresh potassium iodide solution.

To the contents of the Voit flask are now added 2 grams of potassium iodide, 15 c.c. of hydrochloric acid, and 3 c.c. of syrupy phosphoric acid, and the distillation is repeated as before in a current of hydrogen. The hydriodic acid acts on the V_2O_4 , reducing this to V_2O_3 with liberation of iodine, which is absorbed in the Drexel bottle and titrated as usual. The second titration therefore gives the vanadic acid only, and the difference between the first and second gives the necessary data for the calculation of the chromic acid.

L. DE K.

Tin. DAVID B. DOTT (*Pharm. J.*, 1908, [iv], 27, 486).—Contrary to general belief, metastannic acid, formed by the action of nitric acid on tin, is soluble in hydrochloric acid. All quantitative processes based on the separation of silica from tin by evaporation to dryness are untrustworthy, as a large proportion of the tin volatilises as chloride. The author proposes the following method for the estimation of tin in the presence of antimony.

The solution is divided into two equal portions. In one of these, both metals are precipitated with hydrogen sulphide, and the precipitate is then converted in the usual manner into a mixture of tin and antimony dioxides. The other portion is saturated with oxalic acid, heated, and treated with hydrogen sulphide, which now precipitates the antimony only; this is then converted into dioxide and deducted from the joint weight.

Low's modification of Pearce's method for the estimation of tin in ores, by fusing with sodium hydroxide, dissolving in hydrochloric acid, reducing by boiling with iron wire, and, after filtering into a flask filled with carbon dioxide, rapidly titrating with standard iodine, gives good results.

L. DE K.

Analysis of Oxidised Antimony and Lead Sulphide Compounds. FELIX JACOBSON (*Chem. Zeit.*, 1908, 32, 984—985).—The article is mainly devoted to the assay of commercial Sulphur antimonii auratum (this vol., ii, 540).

The process is also applicable to lead sulphide. For the estimation of free sulphur, the use of boiling chloroform is recommended.

L. DE K.

Volumetric Estimation of Bismuth. PIERRE BALAVOINE (*Zeitsch. anal. Chem.*, 1908, 47, 681).—The author mentions that previous to the publication of the results of Moser's investigation (Abstr., 1907, ii, 433) on the volumetric estimation of bismuth, he had recorded the results of experiments showing that the method was untrustworthy.

W. P. S.

Analysis of Organic Mixtures with the Aid of the Refractometer. ERNST E. SUNDWICK (*Pharm. Zentr.-h.*, 1908, 49, 783—787).—Some remarks on the process of Beythien and Hennicke (this vol., ii, 72).

The author's own process is based on the following equations: (1) $V:V_1=C_1-B:C-B$, in which V and V_1 represent two volumes containing the same amount of dissolved matter, C the refraction of the joint solution, and B the refraction of the solvent (water, alcohol, chloroform, acetone, toluene, &c.); (2) $V(C-B)=\text{constant}$, and (3) $P(C-B)/d=\text{constant}$.

L. DE K.

Methyl Alcohol and its Impurities. FRANZ FRIEDRICHS (*Chem. Zeit.*, 1908, 32, 890—891).—In examining methyl alcohol for impurities, the carbylamine test for chloroform should not be omitted, in view of the fact that methyl alcohol is sometimes treated with bleaching powder in order to remove acetone, which is thereby converted into chloroform.

P. H.

Gravimetric Alcoholometry. BLONDEAU (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 26, 148—160).—Tables are given showing the weight of alcohol per hectolitre of mixtures of alcohol and water. The values are given for each reading of the Gay-Lussac alcoholometer between 1 and 100 at temperatures from 0° to 30° (compare Abstr., 1908, ii, 738).

W. P. S.

New Differential Reactions of the Naphthols. VOLCY-BOUCHER (*Ann. Chim. anal.*, 1908, 13, 335—338).—The following reagents are used: Alcohol of 95° (French), a 10% solution of copper sulphate, and a 10% solution of potassium cyanide prepared just before use.

Identification of the Naphthols.—0.5 Gram of the substance is placed in a test-tube, and dissolved in the smallest possible quantity of alcohol, added drop by drop. Two c.c. of the copper solution are added, and, after thorough shaking, 4 c.c. of the cyanide. With α -naphthol an abundant, violet-red precipitate is obtained; β -naphthol yields a yellow precipitate. If now just sufficient alcohol is added to dissolve the precipitate, a rose-coloured liquid showing a violet reflection will be obtained with the α -compound, but a golden-yellow solution in the case of β -naphthol.

Identification of the Camphorated Naphthols.—A thread of the

substance is placed in a test-tube, and 2 c.c. of copper solution are added. The substance, which floats on the surface, is dissolved by cautious addition of alcohol, and 4 c.c. of the cyanide are then added. The result is the same as with the ordinary naphthols.

The same process serves for the detection of small proportions of α -naphthol in the β -compound. Benzonaphthol does not give the reaction.

L. DE K.

Estimation of Lactose by Ammoniacal Copper Salt Solutions. YOSHITAKA SHIMIDZU (*Biochem. Zeitsch.*, 1908, 13, 243—261).—Lactose can be estimated by means of the Kumagawa-Suto modification of Pavy's method, if it is first hydrolysed into dextrose and galactose. For the latter purpose, 10% sulphuric acid, or 5% hydrochloric acid, are suitable, and inversion is complete within one hour if 100 c.c. of acid is used for 0.25 to 1 gram of the sugar. The method is applicable to the estimation of sugar in milk. S. B. S.

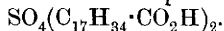
Precipitation of Lævulose by Basic Lead Acetate. H. C. PRINSEN-GEERLIGS (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 932—936).—The results of the experiments recorded show that, whilst basic lead acetate does not precipitate lævulose from its solution when the latter contains nothing but the sugar, an appreciable quantity of the sugar is precipitated if other substances which yield insoluble lead compounds are also present. As all syrups and crude sugars give such solutions, these, when clarified with basic lead acetate, furnish filtrates containing less lævulose than the original solution. The reducing sugar precipitated is shown to be actually lævulose. W. P. S.

Detection of Formic Acid in Honey. TH. MERL (*Zeitsch. Nahr. Genussm.*, 1908, 16, 385—389).—Formic acid is best detected in honey by heating the sodium formate, obtained on evaporating the neutralised distillate of the honey, with concentrated sulphuric acid. The carbon monoxide produced is collected over potassium hydroxide solution, and, if its volume is measured, the quantity of formic acid present may be calculated. Lactic acid, which may also be present in the distillate, yields carbon monoxide on treatment with sulphuric acid, and a portion of the distillate should therefore be oxidised with permanganate and the resulting oxalic acid estimated. The quantity of carbon monoxide due to the lactic acid is then deducted from the total volume of gas found. The calomel formed by the action of formic acid on mercuric chloride may also be employed as a measure of the amount of formic acid present, but it is pointed out that other substances present in honey distillates reduce mercuric chloride.

W. P. S.

Acidification and Distillation of Fatty Acids; Distilled Oleic Acid. HUGO DUBOVITZ (*Chem. Zentr.*, 1908, ii, 545; from *Seifensieder Zeit.*, 1908, 35, 728—729).—The acidification of the fatty acids yields, according to Benedikt, sulphostearic acid, which on boiling with water yields hydroxystearic acid. The author, however, obtained about twice the

quantity of hydroxystearic acid than would be expected, and has therefore altered Benedikt's formula for sulphostearic acid into



The presence of small quantities of neutral fat in commercial oleic acid ("distillation olein") is difficult to confirm, owing to the possible presence of anhydrides and lactones. Owing to the presence of volatile fatty acids, the estimation of water in the oleic acid should be effected in a vacuum over calcium chloride.

L. DE K.

Estimation of β -Hydroxybutyric Acid in Urine. PHILIP A. SHAFFER (*J. Biol. Chem.*, 1908, 5, 211—224).—Previous methods for the estimation of this acid are criticised. The method proposed is to distil with sulphuric acid and potassium dichromate, when under suitable conditions, the acid is converted quantitatively into acetone, which is then determined by standard iodine and thiosulphate solutions. A number of precautions, especially in estimations in urine, have to be taken.

W. D. H.

Detection and Estimation of β -Hydroxybutyric Acid in Urine. OTIS F. BLACK (*J. Biol. Chem.*, 1908, 5, 207—210).—Acetoacetic acid is recognised by the red colour produced by ferric chloride. If β -hydroxybutyric acid is tested in the same way in the presence of hydrogen peroxide, the same colour reaction is obtained. In applying the test to urine, evaporation at a gentle heat gets rid of acetoacetic acid; the residue is acidified with hydrochloric acid, and made into a paste with plaster of Paris. This is broken up and extracted with ether, the ether is evaporated, and the test applied to the residue. For quantitative purposes, the residue is extracted with water and examined with a polarimeter.

W. D. H.

Natural and Added Free Tartaric Acid in Natural Wines. H. ASTRUC and J. MAHOUX (*Bull. Soc. chim.*, 1908, [iv], 3, 840—845; *Ann. Chim. anal.*, 1908, 13, 307—315).—The method of estimating the total tartaric acid and the total potassium in a wine, and deducing therefrom the amount of free tartaric acid, gives too low a value for the latter, since the amount of potassium combined with other acids is neglected. In this manner, excessive (added) quantities of free tartaric acid in natural wines are overlooked.

The authors have estimated the total tartaric acid and potassium by the official methods, and the added tartaric acid and total potassium by other methods, in three natural wines prepared by the authors, both when untreated and after addition of variable known quantities of tartaric acid and potassium, and draw the following conclusions from their results. The official methods are liable to large errors in opposite directions, the other methods (Pasteur, Reboul, Magnier de la Source, &c.) are more trustworthy, and should therefore be preferred; it is also more accurate to ignore the estimation of total potassium, and to evaporate in the presence of potassium bromide, in order to estimate free tartaric acid. It is impossible to distinguish natural from added tartaric acid in potable wines.

The authors' results contradict the statement that natural wines from ripe grapes are necessarily always free from tartaric acid.

E. H.

Method of Estimating Succinic Acid in Fermented Liquids containing Other Fixed and Volatile Acids. M. EMMANUEL Pozzi-Escot (*Compt. rend.*, 1908, 147, 600—601; *Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 185—186 *).—The following method is stated to be trustworthy for the separation and estimation of succinic acid in solutions containing colouring matters, tannin, proteins, and fixed and volatile acids. A portion of the solution is treated with a small quantity of gelatin, neutralised with ammonia, and then rendered distinctly acid with acetic acid. Barium chloride is next added, and the precipitate, consisting of proteins, tannin, barium oxalate, barium sulphate, &c., is removed by filtration. The filtrate is boiled and treated with a considerable excess of lead acetate, which precipitates any remaining protein and tannin, and phosphoric, tartaric, and citric acids. The precipitate is collected on a filter and washed with very dilute acetic acid. The filtrate is treated with hydrogen sulphide to remove the excess of lead, and the solution is then acidified with sulphuric acid, boiled, and the malic acid is oxidised by the addition of an excess of potassium permanganate. This excess is decomposed by means of potassium hydrogen sulphite, and the sulphuric acid is removed by treatment with barium chloride. The solution is then concentrated, rendered slightly ammoniacal, and the succinic acid is precipitated by the addition of an alcoholic solution of barium bromide, a quantity of alcohol equal to three times the volume of the total solution being also added. The barium succinate is collected on a filter, washed with 60% alcohol, and ignited. The amount of succinic acid is calculated from the weight of barium carbonate obtained (compare this vol., ii, 904).

W. P. S.

Naphtharesorcinol as a Reagent for Certain Aldehyde and Keto-acids. JOHN A. MANDEL and CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 13, 148—151).—The reaction described by B. Tollens for glycuronic acid (heating with naphtharesorcinol and hydrochloric acid, and subsequent extraction with ether) is applicable to several other substances, especially those containing certain combinations of carboxyl and carbonyl groups in the molecule. Also, certain more complex substances, such as glucothionic acid, ovomucoid, chondroitinsulphuric acid, and various nucleo-proteins, give the reaction.

S. B. S.

Separation of Benzoic Acid and Cinnamic Acid. ANNE W. K. DE JONG (*Pharm. Weekblad*, 1908, 45, 1115—1116).—Scheringa's process (separation of the bulk of the cinnamic acid as calcium cinnamate and oxidation of the remainder with permanganate: *Abstr.*, 1907, ii, 823) is, in the author's opinion, unsuitable for quantitative purposes, owing to the formation of benzoic acid.

L. DE K.

* and *Ann. Chim. anal.*, 1908, 13, 439—440.

Süchting's Method for Estimating Acidity of Soils. BR. TACKE and H. SÜCHTING (*J. pr. Chem.*, 1908, [ii], 78, 139—142).—Mainly polemical. A reply to van Schermbeck (this vol., ii, 743).
J. J. S.

Humic Acid. A. J. VAN SCHERMBECK (*J. pr. Chem.*, 1908, [ii], 78, 285—288. Compare this vol., ii, 743).—A reply to Tacke and Süchting (preceding abstract), and a further criticism of these authors' methods.
G. Y.

Colour Reactions of Sesamé Oil with (a) Aromatic Aldehydes and (b) Various Sugars. The Similar Reactions with Biliary Acids. C. FLEIG (*Bull. Soc. chim.*, 1908, [iv], 3, 984—991, 992—999).—The suggestion has been made (Mylius, *Abstr.*, 1887, 1149) and denied (Ville, *Abstr.*, 1907, ii, 913) that the red or violet colorations formed in the Pettenkofer test for biliary acids, and in the Camoin-Baudouin test for sesamé oil, depend on the formation of furfuraldehyde by the action of the sulphuric or hydrochloric acid on the sucrose used. The author has therefore tried to obtain definite data on this point by using (1) various aromatic aldehydes and (2) polyhydric alcohols and sugars in place of sucrose, and the results, on the whole, support Mylius' contention. It is suggested that the differences in colour produced in using furfuraldehyde instead of sucrose, as noted by Ville, may be due to secondary influences exerted by other hydrolytic products formed when sucrose is used.

Of the thirteen aldehydes tried, *p*-hydroxybenzaldehyde, anisaldehyde, protocatechualdehyde, vanillin, piperonal, and cinnamaldehyde give colours as intense as those yielded by furfuraldehyde, whilst benzaldehyde, salicylaldehyde, *o*-nitrobenzaldehyde, and *p*-dimethylaminobenzaldehyde yield less intense tints, and *m*- and *p*-nitrobenzaldehyde and cuminaldehyde are still less satisfactory.

The polyhydric alcohols and sugars tried as substitutes for sucrose in the Camoin-Baudouin reaction fall into the following five groups, in order of decreasing intensity of colour produced : (a) *lævulose*, invert sugar, sucrose, sorbose; (b) raffinose; (c) xylose, arabinose; (d) galactose, mannose, mannitol, dextrose; (e) *isodulcitol*, erythritol, sorbitol, dulcitol, lactose, maltose, glycerol. All the sugars in this list, except arabinose, were also tried in the Pettenkofer test, and gave similar results.

In both tests the production of colour is expedited by warming the mixture slightly; hydrochloric acid may be used in place of sulphuric acid or vice versa, but in some cases the former acid is advantageous. In the tests for sesamé oil, an alcoholic extract of the oil may be used in place of the oil itself. Full details are given in the two papers as to the exact methods employed in making the tests. The second paper concludes with a summary of the literature dealing with the constituent of sesamé oil to which the production of the colour is due, and the conclusion is drawn that this coloration may be due to the presence of a number of different substances.
T. A. H.

Formation of Formaldehyde in Solutions of Sugar. A. ALEXANDER RAMSAY (*J. Roy. Soc., New South Wales*, 1907, 41, 172—175).—Attention is called to the fact, noticed amongst others by the

author, that small quantities of formaldehyde are formed during the heating or distillation of saccharine liquids (jams, for instance); thus upsetting the value of some tests recommended for the detection of added formalin. L. DE K.

Identification of Thujone in Liqueurs. LOUIS DUPARC and A. MONNIER (*Ann. chim. anal.*, 1908, 13, 378—382).—The liqueur is submitted to distillation, and 10 c.c. of the distillate (which should be of 60° alcoholic strength) is mixed with 2 c.c. of 10% zinc sulphate, 0.5 c.c. of 10% sodium nitroprusside, and then with 4 c.c. of 5% sodium hydroxide free from carbonate. After the lapse of one minute, 2 to 3 c.c. of glacial acetic acid are added, when, after a few minutes, a very characteristic, dark red precipitate forms if thujone is present.

The author has examined altogether fifty-four different essences (2 parts dissolved in 1000 parts of alcohol), and, with the exception of thujone, they yielded white or yellow precipitates; those which contained citral, however, gave an orange-red deposit. L. DE K.

Analysis of Scammony Resins. P. GUIGUES (*Bull. Soc. chim.*, 1908, [iv], 3, 872—878).—The ether assay of scammony resin advocated by the *Codex Medicamentarius* is unsound, since (1) the resin of jalap is partly soluble in ether, whilst some resins from scammony are incompletely soluble in this solvent; (2) it permits the substitution of fusiform jalap resin, soluble in ether, for the true scammony resin; (3) it prevents the recognition of foreign resins, particularly colophony, soluble in ether; and (4) it is subject to numerous errors, and does not give constant results.

The solubility of scammony resin is not appreciably altered by boiling with water or with 10% hydrochloric acid for several hours. Assay of the resin by turpentine instead of ether is no more successful. The author proposes to detect adulteration by determination of the rotatory power. The following are the values obtained for the optical activities of resins: Commercial Tampico jalap, $-34^{\circ}20'$; true Orizaba jalap, $-24^{\circ}45'$; officinal jalap, -36° ; officinal turbith, $-30^{\circ}10'$ to $31^{\circ}35'$; ordinary colophony, $+6^{\circ}$ to $+7^{\circ}$; sandarac from the Arabic bazaar, $+46^{\circ}20'$; pure sandarac, $+31^{\circ}$ to $+34^{\circ}$; recent mastic, $+29^{\circ}30'$; second quality mastic, $+21^{\circ}50'$; guaiacum, -17° . For scammony, the author obtained $-24^{\circ}30'$ as a maximum from the resin extracted from the gum-resin, and $-18^{\circ}30'$ to $-23^{\circ}30'$ for resins extracted from the roots. The rotatory power is independent of the solubility in ether. These values show that only the Orizaba jalap (fusiform) resin and guaiacum resin can be used as adulterants. Since only the scammony resins extracted from the gum resin, which are at least twice as expensive as that extracted from the root, have rotatory powers as high as $-24^{\circ}30'$, a resin having α_D higher than $-23^{\circ}30'$ is most probably fusiform jalap resin. Guaiacum resin should be readily detected by its chemical characteristics. E. H.

Detection of Arbutin in Plants. Mlle. A. FICHTENHOLZ (*J. Pharm. Chim.*, 1908, [vi], 27, 255—262).—In applying Bourquelot's method (*Abstr.*, 1902, ii, 55) to the detection of glucosides in plants,

it is necessary to allow the emulsin to act on the plant extract during several days, as the action of the ferment is frequently slow, owing to the presence of tannic or gallic acids, which retard its activity. In the case of such glucosides as arbutin, which has a high levorotation, it is advantageous to defecate the plant extract with lead acetate before adding emulsin. Bearberry leaves contain at least 1.66% of arbutin.

T. A. H.

Volumetric Estimation of Potassium Ferrocyanide. H. BOLLENBACH (*Zeitsch. anal. Chem.*, 1908, 47, 687—690).—The following modification of de Haën's process was found to give trustworthy results. The potassium ferrocyanide solution is acidified with sulphuric acid, and an excess of *N*/10 permanganate solution is added. After the addition of a few drops of ferric sulphate solution, the excess of permanganate is titrated with *N*/10 ferrocyanide solution. Each drop of the latter added produces a greenish-blue precipitate, which disappears on shaking, as long as any permanganate remains.

W. P. S.

Detection and Estimation of Hexamethylenamine in Pharmaceutical Mixtures. WILLIAM A. PUCKNER and W. S. HILPERT (*J. Amer. Chem. Soc.*, 1908, 30, 1471—1474).—The process is based on the fact that hexamethylenamine does not suffer decomposition on boiling with aqueous potassium hydroxide, but that it is converted into formaldehyde and ammonium sulphate on boiling with dilute sulphuric acid. The ammonia formed is then readily estimated, any ammonia pre-existing in the sample under examination being removed by the preliminary alkaline treatment.

The reactions with mercuric chloride and with bromine are also useful in the identification of hexamethylenamine. Advantage may also be taken of its solubility in chloroform.

L. DE K.

Estimation of the Total Alkaloids in Cinchona Barks. N. H. COHEN (*Pharm. Weekblad*, 1908, 45, 1089—1098).—A modification of Florence's method (*Abstr.*, 1907, ii, 317). Five grams of the very fine powder are placed in a small corked flask, 125 grams of ether and 5 c.c. of 15% sodium hydroxide are added, and the whole is weighed. After shaking vigorously every five minutes for an hour, the flask is fitted to a vertical condenser, and the contents are boiled for half an hour. When cold, ether is added to restore the original weight, 5 c.c. of water are introduced, and, after thorough shaking, the ether is transferred to a 250 c.c. flask. Twenty c.c. of lime water are added, the flask is closed, preferably with the same cork, and the whole thoroughly shaken. One hundred c.c. of the ether are now drawn through a plug of cottonwool into a weighed 200 c.c. flask, the ether is distilled off, and the residual alkaloids dried for one and a-half hours at 100° and weighed. The weight $\times 25$ = percentage of alkaloids, about 0.5 of which consists of impurities. These may be estimated by dissolving the alkaloids in 10 c.c. of 2% sulphuric acid and shaking the solution with ether, which is then evaporated in a weighed flask.

Florence's estimation of the quinine by means of *N*/10 ethereal oxalic acid cannot be recommended.
L. DE K.

The Quantitative Relations of the Thalleoquinine Reactions. JOS. VONDRASEK (*Chem. Zentr.*, 1908, ii, 833—834; from *Pharm. Post*, 1908, 41, 605—607).—The author recommends that the test for quinine should be carried out as follows: 0.01 gram of the quinine salt is dissolved in a mixture of 1 c.c. of *N* hydrochloric acid and 2 c.c. of *N*/10 potassium bromate, and boiled until the liquid turns orange-yellow. When cold, 1—2 c.c. of ammonia are added, and a dark green solution is obtained. Quinidine also gives the test. In this reaction, three atoms of chlorine are taken up by 1 mol. of quinine. The test may be also carried out in the cold, when addition of ammonia will give a dark green precipitate and a dark green liquid. On adding alcohol, a solution is obtained which is suitable for the colorimetric estimation of quinine.

Quinine and quinidine may be distinguished from cinchonine and cinchonidine by heating the aqueous solutions with excess of potassium bromate, which yields a blue liquid. The colour is destroyed on adding acid.
L. DE K.

Assay of Coca. ANNE W. K. DE JONG (*Chem. Weekblad*, 1908, 5, 645—647).—A reply to M. Greshoff (this vol., ii, 441). The author gives experimental results in support of the contention that Greshoff's method of estimating coca is untrustworthy, and attributes this to decomposition caused by heating the alkaloid salts in aqueous solution (compare Abstr., 1905, ii, 778; this vol., ii, 440).

A. J. W.

Assay of Coca. MAURITS GRESHOFF (*Chem. Weekblad*, 1908, 5, 705—706. Compare this vol., ii, 441).—Polemical. A final reply to de Jong (preceding abstract).
L. DE K.

Detection of Vegetable Poisons in Decomposed Animal Bodies. THEODOR PANZER (*Zeitsch. anal. Chem.*, 1908, 47, 572—590).—Corpses which have undergone a considerable amount of decomposition may contain substances which yield general reactions similar to those given by the alkaloids. These substances, which are chiefly found in the brain, and to a less extent in the liver and kidneys, do not give the characteristic reactions of the separate alkaloids. If a residue is obtained from the ethereal extract of the alkaline solution obtained in the usual way (Stas-Otto method) from the organs under examination, which residue gives general alkaloidal reactions, the solution of the residue should be rendered acid with hydrochloric acid and extracted with ether; this treatment removes the substances, and the aqueous solution is then examined for alkaloids. If possible, it is preferable not to mix the brains with the other organs of the body under examination.
W. P. S.

Process for the Valuation of Saffron. BALTHASAR PFYLL and W. SCHEITZ (*Zeitsch. Nahr. Genussm.*, 1908, 16, 347—352).—The

process depends upon the estimation of the amount of sugar formed by the hydrolysis of the glucoside soluble in chloroform, which the authors have shown occurs in saffron (this vol., ii, 979). Saffron is dried, powdered, and re-dried, and 5 grams of the preparation extracted in a Soxhlet apparatus with light petroleum and, after drying, re-extracted with dry chloroform. The solvent is evaporated from the chloroformic extract, and the residue dissolved as far as possible in acetone. The latter is evaporated, and the glucoside in the residue hydrolysed by adding 5 c.c. of *N*-hydrochloric acid and heating during fifteen minutes, water being added as required to bring the total amount of liquid up to 25 c.c. The filtrate from this is neutralised with *N*-alkali, and the sugar estimated by Allihn's method.

The best quality of commercial saffron, consisting only of the stigmas of the saffron crocus, yields in this way 0.1996 to 0.2090 gram of metallic copper, and samples yielding less than this may be regarded as having an unduly large proportion of styles included, or as containing constituents foreign to the saffron crocus. The quantity of adulterant present is not directly proportional to the diminution in the amount of copper obtained, since the latter is, in part, dependent on the concentration of sugar solution used, and a table is supplied in the original from which, by a method of interpolation, the quantity of "real saffron" present in a sample can be calculated from determinations made by the above process. Trials with the usual adulterants of saffron, namely, saffron crocus styles, logwood, red poppy petals, red peony petals, honey, marigold petals, safflower, Cape saffron, and Spanish thistle flowers, show that each of these products, when subjected to this process, yields practically no reducing substance, and that with turmeric and red sandalwood very much smaller quantities of copper are obtained than with real saffron.

T. A. H.

Detection of Proteins by means of Formaldehyde. LEO VON LIEBERMANN (*Zeitsch. Nahr. Genussm.*, 1908, 16, 231).—Five c.c. of the solution to be tested are treated with one drop of 40% formaldehyde solution and one drop of very dilute ferric chloride solution. The mixture is then allowed to flow over the surface of 5 c.c. of concentrated sulphuric acid. If protein (albumin or albumose) is present in the solution, a violet ring is observed at the junction of the two liquids.

W. P. S.

A New Reaction for Bile Acids. ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1908, 57, 30—34; *Ber.*, 1908, 41, 2766).—If a few drops of a 5% solution of rhamnose are warmed with a similar amount of a 0.1% solution of taurocholate or glycocholate, and a few drops of concentrated hydrochloric or sulphuric acid, a momentary red coloration is obtained, which passes in a short time into a green fluorescence. This test is given also by cholic acid, but not by glycine or taurine. The delicacy of the test is very considerable. In employing it to detect bile acids in urine, the fluid is first mixed with a solution of caseinogen, and the latter is precipitated by careful

addition of sulphuric acid and filtered off. The precipitate is digested with absolute alcohol at room temperature for an hour, filtered, and the reaction tried with the filtrate. Cholesterol, albumin, urea, carbohydrates, higher hydrocarbons, and acids of the fatty and benzene series do not give the test. W. D. H.

A Colour Reaction of Bile Acids with Vanillin and Sulphuric Acid. KATSUJI INOUE and HIIZU ITO (*Zeitsch. physiol. Chem.*, 1908, 57, 313—314).—If vanillin is added to an aqueous solution of bile acids, and then concentrated sulphuric acid, a red ring appears at the junction of the two liquids; on shaking up the mixture, it becomes red, then brown or yellow, and finally violet. On diluting this with glacial acetic acid, a wide absorption band at *D*, reaching to *C* on one side and *E* on the other, is seen. Tables are given showing the delicacy of the test with cholic, glycocholic, and taurocholic acids. W. D. H.

The Lecithin-content of Milk. JOSEPH NERKING and E. HAENSEL (*Biochem. Zeitsch.*, 1908, 13, 348—353).—For estimation of lecithin, 100 c.c. of milk were precipitated with 200 c.c. of alcohol. The precipitate was extracted with chloroform in a Soxhlet apparatus. The alcoholic filtrate was evaporated at 50—60°, and the residue also extracted with chloroform. The two chloroform extracts were united, and the residue, after evaporating off the solvent, incinerated with fusion mixture. The amount of phosphoric acid in the ash was estimated, and from the results, the lecithin-content calculated. The amount of lecithin from several species of animals varied (as a mean of several analyses in each case) between 0.0109 and 0.0833%.

S. B. S.

Detection of Indican in Urine. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, 57, 519—521).—The urine is mixed with copper sulphate solution and hydrochloric acid, and then chloroform added; the chloroform is coloured blue if indican is present. This method is described with full details, as to procedure and the precautions to be observed.

Gautier's statement that the urine of rabbits fed on cabbage does not contain indican is incorrect. W. D. H.

The Guaiacum Reaction. CARL L. ALSBERG (*Arch. exp. Path. Pharm., Suppl.*, 1908, 39—53).—Various points in relation to this test for blood are discussed, and its unsatisfactory nature pointed out. The blood of many invertebrates gives the reaction, and particular attention has been paid to blood which contains hæmocyanin. This blood gives the test even after it is boiled. Hæmocyanin itself, other copper compounds, certain manganese compounds, and other salts give the test. W. D. H.

Estimation of Catalases and Oxydases in Blood. I. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, 13, 339—347).—A preliminary account is given of the apparatus employed for the estimation of the amount of oxygen evolved when a hydrogen peroxide solution is treated with blood. The gas evolved was measured both by a "volume method"

and a "pressure method." In the former case, the vessel containing the peroxide was connected with a Hempel burette, and in the latter, with a manometer. The blood in both cases was contained in a small capsule resting on a plate which was fixed on to a ground stopper inserted into the side of the peroxide containing vessel above the level of the liquid. By turning the stopper through 180° , the capsule could be dropped into the peroxide solution. This was only done when the apparatus was in connexion with the burette or manometer, and had reached the constant temperature at which the experiment was carried out.

S. B. S.

Diazo-reaction of Atoxyl. ERCOLE COVELLI (*Chem. Zeit.*, 1908, 32, 1006).—Solutions of atoxyl give the following reactions: (1) with a hypochlorite, a yellow precipitate or coloration; (2) with a hypochlorite, phenol, and ammonia, a blue coloration, which can be observed even in a dilution of 1 : 100,000; (3) with reducing agents, such as zinc and sulphuric acid in the cold, or stannous chloride or hypophosphorous acid in hot hydrochloric acid, a yellow precipitate; and (4) with a fatty aldehyde and a hot mineral acid, a yellow coloration.

More delicate and characteristic reactions are given by arsenodiazobenzene, which is formed when atoxyl is treated with a few drops of a 1/2% solution of sodium nitrite and a few drops of sulphuric acid. The resulting solution gives: (a) with α -naphthylamine hydrochloride, a purplish-red coloration. This extremely delicate reaction is recommended for the detection of unchanged atoxyl, for example, in urine. Carbamide and the amino-acids, which react with nitrous acid, do not interfere with the test. The reaction may be employed also for the colorimetric estimation of atoxyl; (b) with a few drops of acet-aldehyde and potassium hydroxide, added drop by drop, a carmine-red coloration, changing to yellow, and finally becoming colourless. The carmine-red is stable in presence of an excess of alkali; and (3) with phenols, such as β -naphthol, abrastol, resorcinol, morphine, or dionine, a purplish-red coloration. Towards biliverdin and pathological urines, which give Ehrlich's diazo-reaction, arsenodiazobenzene behaves in the same manner as sulphodiazobenzene.

G. Y.

General and Physical Chemistry.

Refractive Indices of Solutions. FREDERICK H. GETMAN and F. B. WILSON (*Amer. Chem. J.*, 1908, 40, 468—484).—The specific refraction of various salts, acids, and non-electrolytes in water, calculated on the assumption that the refractive powers of solvent and solute are uninfluenced by the act of solution, have been compared with their specific refractions calculated from atomic refractions.

The lack of agreement in most of the cases studied is supposed to indicate the presence of hydrates in solution, but it has not been found possible to calculate the degree of hydration from the results.

R. J. C.

Refractometric Studies of some Methane Derivatives in which Two or Three Atoms of Hydrogen are Replaced by Negative Radicles. II. Sodium Salts. ALBIN HALLER and PAUL TH. MULLER (*Ann. Chim. Phys.*, 1908, [viii], 15, 289—296).—Mainly a résumé of work already published (*Abstr.*, 1905, i, 112); the difference between the values of M_p for free acid and sodium salt in the case of ethyl cyanoacetoacetate is 3.74; the acid therefore is a *pseudo-acid*. The possible constitutional formulæ of the sodium salts of the *pseudo-acids* are discussed.

M. A. W.

Atomic Decomposition and Spectral Series. AUGUST L. BERNOULLI (*Physikal. Zeitsch.*, 1908, 9, 745—749; *Ber. deut. physikal. Ges.*, 1908, 6, 636—642).—The author supposes that the molecules of a gas are not alike, but that the molecular and atomic weights represent average values. On the assumption that every chemical element in the gaseous condition represents a conglomeration of polymerised forms of a primordial matter in equilibrium, and that the gas mixtures obey Rayleigh's radiation law, a formula is deduced from which the atomic weights of the elements can be calculated. The formula is written

$$A = 1.0104 \left(\frac{-1 - \sqrt{3}}{2} \right)^p \cdot \left(\frac{-1 + \sqrt{3}}{2} \right)^q,$$

p and q being integral numbers. Using different values of p and q , atomic weight numbers in very good agreement with the experimental values are obtained.

Similar assumptions to the above have led the author to a formula which gives the lines and bands in the spectra of the elements with considerable accuracy.

H. M. D.

Flame Spectrum of Cupric Chloride. PETER KIEN (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 337—358).—The first part of the paper contains an historical review of previous investigations on the spectrum of cupric chloride; in the second, new experiments are described, the object of which was to determine the intensity and the structure of the bands.

The cupric chloride was introduced into the flame of a blow-pipe

fed with coal-gas and air, or oxygen, by means of a roll of filter paper moistened with a solution of the salt. By means of a spring and clockwork mechanism, the filter paper roll was moved up into the flame at a definite rate, and a steady supply of cupric chloride thereby obtained.

The intensity of the spectrum is not greatly influenced by the temperature, but depends very much on the amount of cupric chloride in the flame. As already pointed out by Lecoq de Boisbaudran, four stages of the spectrum, depending on the amount of salt in the flame, can be distinguished. The author's observations agree very well with those of Boisbaudran, except in the fourth stage, when an extremely small amount of salt is present; in these circumstances the only remaining band of any considerable strength reaches from $\lambda = 5100$ to $\lambda = 5800$, and has a maximum at $\lambda = 5400$ — 5600 .

The four characteristic double bands which are seen in the second stage: α ($\lambda = 4259$ — 4279), β ($\lambda = 4333$ — 4353), λ (4412 — 4433), and δ (4493 — 4515), are found with great dispersion to consist of groups of bands in which series of lines can be recognised.

Attention is called to the sensitiveness of the cupric chloride spectrum. Photographic registration of the "sodium chloride" spectrum in coal or coke fires has confirmed Salet's conclusion that this is due to traces of cupric chloride.

H. M. D.

Spectrum of Neo-erbium Oxide and Kirchhoff's Law. KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1908, 41, 3783—3789. Compare Hofmann and Burger, this vol., ii, 189).—The reflection spectrum of neo-erbium oxide illuminated by an electric arc light is far more characteristic than the absorption spectrum of a 10% solution of the nitrate, and, in agreement with Kirchhoff's law, it is found that the lines of maximum absorption in the former spectrum correspond with the bright lines in the emission spectrum of the oxide heated with a hydrogen flame. The bands of maximum absorption of the nitrate solution do not exactly correspond with the lines of the oxide spectrum, but are somewhat displaced; thus, the maxima of emission of the oxide are: $\lambda = 661.3$, 653.0 , 563.4 , 540.2 , 522.6 , 493.0 , 489.1 , 463.0 , and 447.0 ; the maxima of absorption of the oxide are: $\lambda = 661.7$, 652.4 , 563.8 , 540.4 , 522.4 , 491.5 , 489.5 , 462.5 , and 446.5 ; and of the nitrate solution, $\lambda = 667$, 654 , 541 , 523 , 519 , 492 , 487 , 450 , and 442 . Both the oxalate and fluoride in a solid state give absorption spectra very similar in character to the absorption spectra of solutions of the nitrate and sulphate, although the intensities and positions of the bands vary slightly in each case. Sharp lines as well as bands appear in the absorption spectrum of the solid sulphate, so that a transition of the band spectrum of a salt to the line spectrum of the oxide appears probable.

W. H. G.

Spectroscopic Behaviour of Hydrocarbons with Conjugate Ethylene Linkings. JULIUS W. BRÜHL (*Ber.*, 1908, 41, 3712—3720. Compare *Trans.*, 1907, 91, 115).—Reif's results (this vol., i, 847) confirm the author's previous conclusions. The values for the refractive dispersions $\Delta^{\beta\beta}$ -hexenol and $\Delta^{\beta\beta}$ -hexadiene have been re-determined and Reif's results confirmed.

In the latter compound, the values indicate exaltations of +1.49, +1.71, and +0.52 units in the values for $(n_a^2 - 1)/(n_a^2 + 2) \times P/d$, $(n_b^2 - 1)/(n_b^2 + 2) \times P/d$, and $M_\gamma - M_\alpha$ respectively.

Using the formula $(n^2 - 1)/n^2 + 2 \times P/d$, the following values have been calculated for $\Delta^{4\gamma\epsilon}$ -hexatriene from W. H. Perkin's numbers :

H_α	D.	$M_\gamma - M_\alpha$
30.59	31.03	2.22

which indicate exaltations of 2.07, 2.49, and 1.01 units respectively. These results are striking when compared with the normal optical behaviour of benzene, $\Delta^{1,3,5}$ -cyclohexatriene, which shows practically no exaltation. Harries and Majima's $\Delta^{1,3}$ -dihydrocymene (this vol., i, 733) also exhibits characteristic exaltations, due to conjugated ethylene linkings.

It is pointed out that the intermediate product described by Auwers and Hessenland (this vol., i, 551) in the preparation of $\Delta^{1,3}$ -dihydro-*p*-xylene, and stated to be the corresponding acid, cannot have this constitution, as its methyl ester exhibits no exaltation, but is optically normal. It is suggested that the ethylene linkings in the acid are not in conjugate positions.

Zelinsky and Gorsky (this vol., i, 619) claim to have prepared dihydrobenzenes which give normal molecular refractions and dispersions, although they contain conjugated ethyl linkings. It is pointed out that these authors have not conclusively proved the constitution of their compounds by the examination of decomposition products. J. J. S.

Water of Crystallisation as Affected by Light. RALPH H. MCKEE and ELVIN J. BERKHEISER (*Amer. Chem. J.*, 1908, 40, 303—305).—Aniline-*p*-sulphonic acid has been found to lose its water of crystallisation more readily when exposed to light than when kept under exactly similar conditions in the dark. Careful observations showed that, although the temperature of the specimens exposed to direct sunlight was 2.86° lower than those screened from such light by black paper, yet the former lost more than 98% of their water of crystallisation during ten winter days' exposure, whilst the latter only lost 35% during the same period. From determinations of the solubility of the product, no evidence was obtained of any transformation having taken place into the ortho- or meta-compound. When hydrated sulph-anilic acid or the product obtained after exposure to sunlight was crystallised from water above 80°, it was found to be in an anhydrous state, whilst from water at 40° the crystals obtained had again 2H₂O. J. V. E.

Violet Coloration Produced in Glass by the Influence of Light. J. G. MASCHHAUPT (*Chem. Weekblad*, 1908, 5, 807—808).—The author attributes the violet colour sometimes developed in the glass of old mirrors to the action of sunlight, and describes experiments in support of his contention. A. J. W.

Some Reflections on Radiology. ALBERT REYCHLER (*Bull. Soc. chim.*, 1908, [iv], 3, 1009—1012).—Rutherford and Soddy's theory that radioactive substances consist of unstable, large accumulations of particles of a primordial matter, which are liable to internal

changes and decompositions, tending towards closer and more stable arrangements of the particles, does not in the author's view account for all the facts observed, and particularly for (a) the large amounts of energy disengaged and (b) the conversion of an atom of uranium into several atoms of helium (?) and one atom of radium, which is more voluminous and more active than that of the parent substance.

These difficulties disappear if the ether is taken as the primordial matter, and is regarded as existing in elementary atoms in two forms, namely, condensed, as nodules, an accumulation of which forms the atom, and also in the free state. If the intra-atomic transpositions may then be regarded as involving also the condensation of the free ether, the changes which occur can be represented thus: radium + ether = α -particles + β -particles + emanation. This view would explain the discrepancy between Ramsay and Rutherford's estimates of the length of "life" of a radium atom, that of the former being too short. It implies, however, that radioactive matter enclosed in a glass tube should gain in weight, since the ether would have free access and only β -rays could escape. The β -rays it is suggested, however, may be in part an inflow of electropositive ether.

T. A. H.

Extraordinary Radioactivity of Water from a Spring at Valdemorillo. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 398—400).—Samples of water from a spring at Valdemorillo were found to have radioactivities varying from 27,000 to 51,687 volts per hour-litre. The latter value is remarkably high, and much exceeds that found with the waters from Lerez (10,000—12,000 volts per hour-litre: compare Abstr., 1907, ii, 218; this vol., ii, 750).

W. A. D.

Radioactivity of Three Springs at Oña (Burgos). JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 400—402).—The following table shows the character of the rock through which the springs percolate, and the radioactivity of the water and mud therefrom in volts per hour-litre:

	Rock.	Activity of water.	Activity of mud.
Spring <i>A</i>	Argillaceous limestone.....	34.8	23.6
„ <i>B</i>	Cretaceous „	30.0	99.3
„ <i>C</i>	Argillaceous „	12.8	30.2

Spring *B* is one of considerable volume feeding the river Oca. All three springs come to the surface within a radius of 200 metres from one another. It is probable that all three springs arise from a common source; the difference between the values for the mud of *B* and that from *A* and *C* is probably due merely to the muds being of different consistency.

W. A. D.

Radioactivity of the Gases of the Thermal Spring of Uriage (Isère). GUSTAVE MASSOL (*Compt. rend.*, 1908, 147, 844—846).—During the passage of the water through a siphon to the reservoir, very variable quantities of gas are evolved; determina-

tions in two successive half-hours (when a considerable volume of water was flowing) gave 538 litres and 724 litres respectively. Of this gas, 7% is soluble in potassium hydroxide solution (carbon dioxide and hydrogen sulphide), whilst the remainder consists of nitrogen and allied gases. The radioactivity of the gas, as measured by a Curie electroscope (as modified by Chéneveau and Laborde), was 0.150 and 0.144 per 10 litres of gas (at 20° and 745 mm.), the radioactivity of the emanation per minute from 1 mg. of radium being taken as the unit. These results are not strictly comparable with Besson's (following abstract), since the latter refer to the gas dissolved in the water, of which 64.6% is insoluble in potassium hydroxide solution (Lefort found that 1 litre of the water of Uriage contains 3.2 c.c. CO₂, 7.44 c.c. H₂S, and 19.5 c.c. N₂). For the radioactivity of the gas remaining dissolved in the water, the author obtains the value 0.500 per 10 litres. The saline residue left on evaporating the water, the deposit formed in the reservoir, and the rock from which the water flows are all quite inactive. E. H.

Radioactivity of the Waters of Uriage-les-Bains (Isere). PAUL BESSON (*Compt. rend.*, 1908, 147, 848—850. Compare preceding abstract).—Three litres of the water were boiled for one hour, the gases evolved being collected over mercury and dried by means of potassium hydroxide and phosphoric acid. After keeping for three hours, the radioactivity of the gas was measured by means of the Chéneveau and Laborde modification of the Curie electroscope. For the gas from 10 litres of water, the values 0.012, 0.015, and 0.018 in mg.-minute units were obtained at pressures of 745 mm., 740 mm., and 735 mm. respectively. Thus the value seems to increase as the atmospheric pressure decreases. This observation of radioactivity in a mineral water containing 6.0567 grams of sodium chloride and 3.311 grams of calcium, magnesium, and sodium sulphates is in accordance with Kofler's work on the solubility of the emanation in saline solutions. The period of half-decay according to Curie's law is four days. The residue left on evaporation is inactive.

The ferruginous water has the very low radioactivity 0.003 mg.-minutes. E. H.

Absorption of the Radioactive Emanations by Charcoal. R. W. BOYLE (*J. Physical Chem.*, 1908, 12, 484—506).—Experiments have been made to determine how the absorbing power of charcoal for the emanations of radium and thorium depends on the conditions.

The absorbing power of charcoal for radium emanation at the ordinary temperature is considerable, but the rate of absorption soon falls off, owing to saturation of the upper layer and the comparatively slow rate of diffusion to the lower layers.

The majority of the experiments were made with thorium emanation. As the rate of decay of the emanation is so great, the observations were made by leading the latter, mixed with air, through tubes containing various absorbing or non-absorbing materials, and estimating its activity by measuring the ionisation of air produced. The results are given in the form of tables and curves, the latter being

obtained by plotting the ionisation current against the speed of the air current.

The degree of absorption of the emanation depends: (1) on the speed of the air current, being diminished by increasing the speed; (2) on the nature of the charcoal, being greatest for cocoanut, intermediate for animal, and least for wood, charcoal; (3) on the extent of absorbing surface exposed, being greatest for the most finely-divided charcoal, and (4) is greater the lower the temperature. G. S.

Action of the Radium Emanation on Water. ERNEST RUTHERFORD and T. ROYDS (*Phil. Mag.*, 1908, [vi], 16, 812—818. Compare Cameron and Ramsay, *Trans.*, 1908, 93, 992).—Preliminary experiments are described, the object of which was to ascertain the minimum amount of neon which can be detected spectroscopically. Small quantities of air were subjected to the action of cocoanut charcoal, cooled by liquid air, and the residual gas introduced into a small spectrum tube, 7 cm. long and 1 mm. in diameter, and examined for neon. Operating on 1/15 c.c. of air, the yellow line of neon is readily observed; with 2/15 c.c. of air, the red lines of neon are clearly visible, and with 1/5 c.c. of air, a brilliant neon spectrum showing most of the lines is obtained. Since, according to Ramsay, one volume of neon is contained in about 100,000 volumes of air, these experiments show that less than one-millionth of a c.c. of neon can be detected spectroscopically.

The gases formed by the action on water of a quantity of emanation, corresponding with the equilibrium amount from 150 mg. of radium, were then examined in a similar manner, after the hydrogen and oxygen had been removed by explosion. A complete and brilliant spectrum of helium was found, but there was no trace of a neon spectrum. In all, five experiments were made; neon was only observed in one case, and was found to be due to a small air leak. The gases obtained from the aqueous solution of the radium salt, from which the emanation had been pumped off, also showed no trace of neon when examined in the same way.

The positive results obtained by Cameron and Ramsay in similar experiments are attributed to the leakage of air into the apparatus used. H. M. D.

Nature of the Positive Rays. WILHELM WIEN (*Sitzungsber. K. Akad. wiss., München*, 1908, 55—65).—Experiments are described the object of which was to find an explanation for the well-known fact that the canal rays are unequally deviated under the influence of a magnetic field. The results indicate that this lack of uniformity cannot be due to the ions having different masses, but is a consequence of differences in the lengths of the paths which they traverse in the charged condition. The nature of the canal rays is determined by a condition of equilibrium, in which the ratio of the charged to the uncharged particles has a constant value. Under the influence of a magnetic field, some of the charged particles are removed, but the condition corresponding with the equilibrium ratio is immediately restored by dissociation of the atoms. H. M. D.

β -Rays of Actinium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1908, 9, 697—702).—The β -rays emitted by actinium are not absorbed by aluminium according to an exponential formula. With gradually increasing thicknesses of aluminium, the absorption is at first more rapid than that required by such a formula; in the second stage, the absorption is exponential, whilst in the third, a more rapid rate of absorption is again found. It is found that the increase in the absorption in the third stage is dependent on the experimental arrangements.

The large value of the absorption coefficient for small thicknesses of the absorbing layer is found to be due to the emission of easily absorbed β -rays by radio-actinium. This was separated from the other products of disintegration, and its β -ray activity examined. In addition to β -rays, which are absorbed to the extent of 50% by 0.04 mm. of aluminium, it emits a much more penetrating type of radiation, which consists either of hard β -rays or soft γ -rays.

β -Rays are also emitted by actinium *A* and actinium *C*. The former are absorbed even more readily than the soft β -rays of radio-actinium; the latter are absorbed to the extent of 50% by 0.24 mm. of aluminium.

The view that homogeneous products emit homogeneous β -radiation is confirmed by the results of this investigation. H. M. D.

Influence of Pressure on Ionisation Produced in Gases by the *X*-Rays. The Saturation Current. E. ROTHÉ (*Compt. rend.*, 1908, 147, 785—788).—A method is described for studying the influence of pressure on ionisation phenomena in general, and details are given of the precautions necessary to secure regular working of the Crookes' tube. The author shows that the intensity of the saturation current is proportional to pressure from 0.1 to 5 atmospheres. W. O. W.

Volatilisation Produced by Canal Rays. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1908, 14, 752—756).—The canal rays consist of charged or uncharged atoms or molecules projected with great velocity. When such particles strike a metal, they impart their velocity to one or more atoms of the metal, which may rebound with sufficient violence to pass away from the surface of the metal. The consequences of this idea are followed out, and the author thinks that the cathodic volatilisation of metals is better explained in this way than by Kohlschütter's chemical theory (this vol., ii, 457). T. E.

Electromotive Force of Iodine Concentration Cells in Water and Alcohol. ARTHUR P. LAURIE (*Proc. Roy. Soc. Edin.*, 1908, 28, 382—393; *Zeitsch. physikal. Chem.*, 1908, 64, 615—628).—Measurements are recorded of the *E.M.F.* of concentration cells consisting of platinum wires immersed in differently concentrated solutions of iodine in aqueous and alcoholic potassium iodide.

For aqueous solutions in which the iodine concentration is small, the observed values of the *E.M.F.* of the concentration cell are in good agreement with those calculated from Nernst's equation when

the free iodine concentrations are determined from the equilibrium constant corresponding with the dissociation equation: $\text{KI}_3 \rightleftharpoons \text{KI} + \text{I}_2$. For more concentrated solutions, the observed values differ sensibly from those obtained by calculation.

Similar relationships between the two series of numbers are found in the case of alcoholic solutions, and the conclusion is drawn that Nernst's equation also applies to these solutions and that they contain potassium tri-iodide like the aqueous solutions.

Measurements in aqueous alcoholic solutions show that the *E.M.F.* of a given concentration cell increases as the proportion of alcohol in the mixture increases.

When solutions containing equal quantities of iodine and potassium iodide in water and alcohol respectively are opposed to one another, a considerable *E.M.F.* is obtained. The action of the cell involves the transference of iodine from the aqueous to the alcoholic solution, and the transference of potassium iodide in the reverse direction. In both cases the transference is towards the solvent in which the substances dissolve more readily.

H. M. D.

Explanation of Supertension. III and IV. FELIX KAUFER (*Zeitsch. Elektrochem.*, 1908, 14, 737—741, 749—752).—In consequence of Müller's criticism (this vol., ii, 802), the author has made measurements of the difference of potential between lead or smooth platinum cathodes and a solution of acetophenone or benzophenone in aqueous alcohol containing potassium acetate during electrolysis. These show that, under the same conditions, the fall of potential between the solution and the cathode is greater with lead than with platinum.

The resistance of a cell with a mercury cathode and an anode of platinum or of lead in which the electrolyte is sulphuric acid of maximum conductivity is measured during the passage of a current. With a low current density (under 0.05 ampere per sq. cm.) the attainment of a steady condition is extremely slow. The resistance of the cell is much larger than that observed with no current flowing; it is greatest with small current density, and is not dependent on the nature of the anode. Stirring the mercury does not change the resistance. As in the case of lead previously investigated (this vol., ii, 558), the author assumes the existence of a film of a hydride of high resistance on the surface of the mercury. The product of film resistance and current, which is the supertension due to the transition resistance at the surface of the cathode, is approximately independent of the current density and varies from 0.05 to 0.1 volt.

T. E.

Influence of the Velocity of Ionic Reactions on the Current-Potential Curve. ARNOLD EUCKEN (*Zeitsch. physikal. Chem.*, 1908, 64, 562—580).—The relation of current and potential has been studied in the double cyanides of potassium with silver, gold, copper, and mercury, but only the first of these allows of the production of a limiting current independent of the potential. The velocity of dissociation, $\text{Ag}(\text{CN})_2' \rightarrow \text{Ag}' + 2(\text{CN})'$, is very great. The finite

velocity observed by Caspari (Abstr., 1900, ii, 7) is due to a secondary reaction. The smaller the velocity of the ionic reaction the smaller is the limiting current.

The velocity of dissociation of acetic, lactic, and benzoic acids has been calculated from the results of previous observers. C. H. D.

Ionisation Constants of the Secondary Hydrogen Ion of Dibasic Acids. RUDOLF WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1908, 14, 740—741).—A claim of priority against Chandler (this vol., ii, 467). T. E.

Specific Charge of the Ions Emitted by Hot Substances. OWEN W. RICHARDSON (*Phil. Mag.*, 1908, [vi], 16, 740—767).—The ratio of the electric charge to the mass of the positive ions emitted by hot substances has been determined by measurements of the deflexion of the path, due to the action of a transverse magnetic field on the ions when moving in a uniform electric field.

The experimental data indicate that the ratio of the mass to that of the hydrogen atom is the same for the ions from carbon and platinum, and this is very nearly equal to the corresponding quantity determined by J. J. Thomson for the ions from iron. The values are respectively: for platinum, 25.7; for carbon, 27.6; and for iron, about 24.

These numbers show that the positive ions cannot be atoms of the metal or atoms of absorbed hydrogen; neither can they be regarded as identical with the positive electrons found by Thomson in the canal rays.

The emitted ions appear to be quite homogeneous, and experiments carried out between 750° and 1200° indicate that the ratio of charge to mass does not depend on the temperature of the hot substance in any simple way.

The mass ratios in terms of hydrogen are not very different from the molecular weights of nitrogen, carbon monoxide, and oxygen, but there is no evidence that the different substances evolve one or other of these gases when heated. The author, on the other hand, thinks it possible that the positive ionisation is due to a real constituent which is common to the different elements examined. In this case it is necessary to assume that the ions carry a charge which is smaller than the generally recognised fundamental electronic charge. H. M. D.

Determination of the Hydration of Ions by Transference. **Experiments in the Presence of a Non-electrolyte.** EDWARD W. WASHBURN (*Tech. Quart.*, 1908, 21, 288—320).—Experiments have been made to determine the transference of water which accompanies the migration of ions in aqueous solution by the measurement of transport numbers in presence of a third constituent, or reference substance, which remains stationary during the passage of the current. By referring the changes in concentration of the water and of the electrolyte to this third substance, the amounts of each transferred are calculated, and from these "true" transference numbers have been obtained.

Sucrose, raffinose, and arsenious acid were used as reference substances, the first two substances being estimated polarimetrically, the third by means of an iodine solution. The behaviour of arsenious acid is uncertain, on account of its ready oxidisability. A description of the transport apparatus has been previously given (this vol., ii, 805).

The experimental data show that the electrolysis of solutions of potassium, sodium, or lithium chloride containing one of the above reference substances is attended by an increase in the ratio of the quantity of non-electrolyte to that of water at the anode, and by a corresponding decrease at the cathode. It is shown that this is due chiefly, if not wholly, to a transfer of water from the anode to the cathode. From the measured changes, the relative degrees of hydration of the chlorine, lithium, sodium, and potassium ions have been calculated. On the assumption that the chlorine ion is not hydrated, the minimum hydration values of the cations have been calculated; these correspond with the formulæ: $K(H_2O)_{1.3}$, $Na(H_2O)_{2.0}$, and $Li(H_2O)_{4.7}$. From Buchböck's data for hydrochloric acid solutions, the minimum hydration value for the hydrogen ion corresponds with $H(H_2O)_{0.3}$. Absolute values for the hydration cannot be obtained until the hydration value of some one ion has been determined by some other method.

On account of this transference of water during electrolysis, the transport numbers hitherto obtained for more concentrated solutions of the alkali metal chlorides are erroneous. The true transference numbers are found to vary with the concentration much less than the apparent values obtained by the ordinary Hittorf method.

The true values are also given by the method of moving boundaries, and the author's data are found to agree very well with the results of Denison and Steele obtained by this method.

H. M. D.

Variation of the Degree of Dissociation of Certain Electrolytes with Temperature. ADOLFO CAMPETTI (*Atti R. Accad. Sci. Torino*, 1908, 43, 1071—1094).—The author has determined the conductivities, the temperature-coefficients of conductivity, and the degrees of dissociation of solutions of zinc and magnesium sulphates and of sulphuric acid for temperatures varying from 10° to 90° and for concentrations 3.0—0.001*N*.

The variation of the dissociation with the temperature is, as far as its sign is concerned, in agreement with van't Hoff's law. For an interval of concentration which is not too great, the degree of dissociation is best expressed as a function of the concentration by van't Hoff's formula: $K = \alpha^{3/2} c^{1/2} / (1 - \alpha)$, the expression given by Rudolphi, $K = \alpha^2 c^{1/2} / (1 - \alpha)$, yielding somewhat less concordant results.

Integration of van't Hoff's formula, $q = -RT^2/K.dK/dT$, assuming that the heat of dissociation, q , per gram-molecule is constant for the temperature interval, $T_2 - T_1$, leads to the expression $q(T_1 - T_2)/T_1 T_2 = 4.58 [\log \{\alpha_2^2 / (1 - \alpha_2)\} - \log \{\alpha_1^2 / (1 - \alpha_1)\}]$, which is found

to be approximately true with magnesium sulphate and with sulphuric acid.

In solutions of magnesium sulphate or zinc sulphate, the undissociated molecules give rise to complex molecules.

T. H. P.

Conductivity and Ionisation of Electrolytes in Aqueous Solutions as Conditioned by Temperature, Dilution, and Hydrolysis. HARRY C. JONES and C. A. JACOBSON (*Amer. Chem. J.*, 1908, 40, 355—410. Compare Abstr., 1905, ii, 794).—So many conflicting results have been published on the question of the influence of temperature on dissociation that the authors were induced to re-investigate the subject. The method employed was that previously described by Jones and West (Abstr., 1905, ii, 794), the temperature at which observations were made also being the same. Twenty-eight inorganic salts and six organic acids have been investigated; the molecular conductivity and percentage of dissociation at 0°, 10°, 25°, and 35° at eight dilutions are tabulated, also the temperature-coefficients in each case. The results are in agreement with the well established facts that (1) the molecular conductivity of electrolytes increases with rise of temperature; (2) the conductivity increases with increase in dilution up to a certain maximum value; (3) dissociation increases with increase in dilution up to the point of complete dissociation. At the somewhat low temperatures of these observations, no maximum in the conductivity curve, as described by Sack, Kohlrausch, and Noyes, was observed. Further, it was found that the conductivity of water increases as a linear function of the temperature, but the molecular conductivity of electrolytes in aqueous solution increases as a parabolic function of the temperature from 0° to 35°. The increase in conductivity of electrolytes causing the departure from a straight line is largely due to their being more or less hydrated; the rise in temperature diminishes the extent of this hydration, allowing the ions to move with less friction, and thus show an increase of conductivity. In support of this view, those salts which are strongly hydrated in solution are found to exhibit a greater increase in conductivity with rise of temperature than the salts that are slightly hydrated. The conclusion is also drawn from the results given that nearly all, if not all, electrolytes are hydrolysed in dilute solutions, and this greatly influences the true dissociation value. When the temperature-coefficients expressed as conductivity units are examined, they are all found to increase as the dilution increases, and for every salt they increase with rise of temperature; but the organic acids, on the other hand, have decreasing temperature-coefficients with increase of temperature. J. V. E.

Basicity of Acids as Determined by their Conductivities. M. R. SCHMIDT (*Amer. Chem. J.*, 1908, 40, 305—313).—After considering the work of Miolati and Mascetti (Abstr., 1901, ii, 381) on the effect of alkalis on the conductivity of solutions of various acids, and the anomalous behaviour of hydrogen fluoride solutions in this connexion (Pellini and Pegoraro, Abstr., 1907, ii, 860), the author gives his results of a study of the conductivity change when potassium

hydroxide is added to moderately strong solutions of phosphoric acid. Working with 0.2*N*, 0.1*N*, 0.04*N*, and 0.02*N* solutions of phosphoric acid, it was found that in the case of 0.2*N* solutions, the minimum occurs when only about 40% of the amount of potassium hydroxide required for one-third neutralisation had been added. In the more dilute solutions, the minimum shifts continually towards the point corresponding with the salt KH_2PO_4 , reaching it with 0.02*N* solutions. As a possible explanation of this, it is suggested that, as more and more potassium hydroxide is added, the H^+ ions of the phosphoric acid are replaced by K^+ ions, which move more slowly, and, as a result, the conductivity of the mixture decreases. But phosphoric acid being far from completely dissociated in strong solutions, when a small quantity of base is added, practically all the hydrogen ions present are neutralised. Immediately, however, more dissociate, and in sufficient quantity to overbalance the decrease in conductivity caused by the substitution of K^+ ions for the H^+ ions, thus causing the conductivity to rise again.

A minimum thus appears before enough alkali has been added to form the primary salt. Furthermore, as the dilution increases, the phosphoric acid becomes more and more completely dissociated according to the formulation $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + (\text{H}_2\text{PO}_4)^-$, thus lessening the overbalancing effect of secondary dissociation previously mentioned.

J. V. E.

Comparative Investigations on the Formation of Salts and the Basicity of Acids. GIUSEPPE BRUNI (*Zeitsch. Elektrochem*, 1908, 14, 729—734).—The molecular conductivity of an acid of which a fraction x is neutralised is $\Lambda = x(l_M + l_A) + (1 - x)\alpha(l_H + l_A)$, where l_M , l_A , and l_H , are the mobilities of the metallic ion, the anion, and the hydrogen ion respectively, and α is the fraction of the acid which is dissociated. The salt is supposed to be completely dissociated. Assuming that the acid follows Ostwald's dilution law, α can be expressed in terms of known quantities. This gives an expression for the conductivity which reproduces all the peculiarities of the curves obtained by the author (this vol., ii, 935).

T. E.

Certain Phenomena in Gases Subjected to the Action of Spark Discharge or Arc Light. HEINRICH RAUSCH VON TRAUBENBERG (*Physikal. Zeitsch.*, 1908, 9, 713—726).—Measurements have been made of the electrical conductivity of certain gases during, and after, the passage of electricity through them in the form of a spark discharge and of direct and alternating current arcs. The gases examined were hydrogen, oxygen, acetylene, carbon dioxide, air, coal gas, and carburetted hydrogen. The high conductivity, which is observed during the period of the spark or arc discharge in all cases, persists for several hours after the discharge is stopped in the case of acetylene and coal gas. The phenomenon was investigated more closely in the case of coal gas, and found to depend on the material of the electrodes, and on the nature of the discharge. In

some cases the conductivity, which is unipolar in nature, was found to decrease slowly, whilst in others it increased. No evidence of a saturation current could be obtained. The last part of the paper is devoted to a theoretical discussion of the possible modes of electrical transport through the conducting gases.

H. M. D.

Hysteresis of Certain Iron Compounds. G. BERNDT (*Physikal. Zeitsch.*, 1908, 9, 750—752; *Ber. deut. physikal. Ges.*, 1908, 6, 662—666*).—The magnetic properties of ferric oxide, ferric hydroxide (impure), ferric chloride, and ferrous and ferric sulphates have been examined. The oxide and hydroxide exhibit well-developed hysteresis; in the case of the salts, no such effect could be detected. As the strength of the field increases, the magnetic susceptibility of the oxide diminishes considerably, and that of the hydroxide slightly.

H. M. D.

Magnetic Properties of the Oxygenated Metallic Radicles. P. PASCAL (*Compt. rend.*, 1908, 147, 742—744. Compare this vol., ii, 756, 927).—By measuring the magnetic susceptibilities of their solutions, the author has obtained the following values for the molecular magnetic susceptibilities at 23°: of manganese sulphate, $+1500 \times 10^{-5}$; potassium permanganate, $+25.5 \times 10^{-5}$; chrome alum, $+2 \times 629 \times 10^{-5}$; chromic acid, -0.5×10^{-5} ; vanadium chloride, $+139 \times 10^{-5}$; sodium metavanadate, -30.2×10^{-5} . Comparison of each pair of salts shows that oxidation of the metal results in a diminution in the magnetic susceptibility; the molybdates and ferrates also, unlike the salts of molybdenum and iron, are diamagnetic.

The values for vanadium compounds: VCl_2 , $+139 \times 10^{-5}$; $(\text{V}_2\text{O}_5)_2\text{SO}_4$, $2 \times 115 \times 10^{-5}$; vanadium tetrachloride (hydrolysed) ($=\text{V}_2\text{O}_4$), $+66.2 \times 10^{-5}$, and NaVO_3 , -30.2×10^{-5} , indicate that the magnetic properties of the vanadium ion diminish in proportion to the increase in the degree of oxidation; similarly, $\text{U}(\text{SO}_4)_2$ has $+320 \times 10^{-5}$, and $\text{UO}_2(\text{SO}_4)$, -5.57×10^{-5} .

These examples indicate the increasing generality of the law previously enunciated, that when the chemical properties of a metal become masked by its entry into a complex ion or colloid, the magnetic properties are similarly affected and to the same degree. An interesting example of this is afforded by vanadic anhydride, which dissolves in concentrated sulphuric acid to a red solution. The latter on dilution becomes first yellow and then colourless. The anhydride in the red solution has the molecular magnetic susceptibility $-2 \times 85.7 \times 10^{-5}$; in the yellow solution, $-2 \times 31.5 \times 10^{-5}$, and in the colourless solution, $-2 \times 30.2 \times 10^{-5}$. From these values, it is permissible to conclude that the strongly acid solutions contain red sulphovanadic compounds which dissociate on dilution. These complexes doubtless include Berzelius' vanadyl sulphate, $\text{VO}_2(\text{SO}_4)_3$, Ditte's compound, $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{SO}_4$, and Gerland's salt, $4\text{SO}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{O}$.

E. H.

Measurements with Gas Thermometer. ARTHUR L. DAY and J. K. CLEMENT (*Amer. J. Sci.*, 1908, 26, 405—463).—The

* and *Ann. Physik*, 1908, [iv], 27, 712—734.

authors have endeavoured to improve the accuracy of the nitrogen in platinum standard gas thermometer between 0° and 1200° .

Particular attention was paid to uniformly heating the bulb by a series of independently regulated platinum coils whilst the unheated space between bulb and manometer was reduced to a minimum.

The whole furnace being contained in a bomb in which nitrogen was maintained at the same pressure as the thermometer, diffusion and strain on the bulb were obviated, so that much higher gas pressures could be employed than hitherto. The coefficient of expansion of the metal of the bulb was determined with great care.

The melting points of the purest commercially obtainable metals are given as follows: zinc, $418.5^{\circ} \pm 0.1$; silver, $958.3^{\circ} \pm 0.5$; gold, $1059.3^{\circ} \pm 1.0$; copper, $1081.0^{\circ} \pm 0.5$. Exact analyses of the metals are given, but different samples of ostensibly the same metal sometimes differed by 1° in melting point. It is claimed that the determinations of temperature are accurate to within half a degree. R. J. C.

Heat of Fusion, Specific Cohesion, and Molecular Weight at the Melting Point. PAUL WALDEN (*Zeitsch. Elektrochem.*, 1908, 14, 713—724).—For non-associated substances, the ratio L/a^2 is roughly a constant and equal to 3.6 (L =heat of fusion, and a^2 the height to which the liquid rises in a capillary of 1 mm. radius at the melting temperature). The expressions ML/T' and Ma^2/T' (M =molecular weight, and T' absolute melting point) are also roughly constant for non-associated substances. The value of the former is 13.5, and that of the latter, 3.65. For associated substances, the degree of association may be obtained by dividing the value of the expression for any substance into the above constants. The results are in harmony with values obtained by other methods. By combining these results with Trouton's rule and van't Hoff's equations for the depression of freezing point and elevation of boiling point of solutions, it is shown that $E_1/E = 0.64T_1/T$ and $L/L_1 = 0.64T/T_1$, where E_1 , T_1 , and L_1 are the molecular elevation of boiling point, the absolute boiling point, and the heat of evaporation of a liquid, E , T , and L being the corresponding quantities at the freezing point. The application of the equations to some metallic and non-metallic elements and fused salts gives values for the degree of association which agree with what is known on other grounds about the size of their molecules. T. E.

Electrical Heating in Ebullioscopic Determinations and in Fractional Distillation. ERNST BECKMANN (*Zeitsch. physikal. Chem.*, 1908, 64, 506—507. Compare this vol., ii, 663; also Richards and Mathews, this vol., ii, 828).—When, in spite of electrical heating, superheating and bumping occur in ebullioscopic determinations, the difficulty can be got over by passing a current of an indifferent gas through the liquid.

An apparatus is sketched in which electrical heating has been successfully employed for the fractional separation of the chlorides of sulphur. In this way the chloride SCl_2 has been distilled off almost pure at -24° under a pressure of 4 mm. J. C. P.

Quartz Protecting Tubes in Thermal Analysis. P. SCHOEN (*Metallurgie*, 1908, 5, 635—637).—Quartz tubes are to be preferred to porcelain for the protection of thermo-couples in the determination of freezing points of alloys, on account of their greater cheapness, and of the less resistance to the passage of heat. They are also less permeable than porcelain to metallic vapours. They are, however, more readily attacked by oxides. They can be used up to nearly 1500°, at which temperature they soften.
C. H. D.

Cryoscopic Investigations on Solutions of Gases in Liquids. PIETRO FALCIOLA (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 324—330).—The author has extended the investigations of Garelli and Falcicola (Abstr., 1904, ii, 312) to the gases, carbon monoxide, nitrogen, hydrogen, oxygen, methane, and nitrous oxide, and to other solvents than those previously employed.

With water or formic acid, carbon monoxide produces a depression of the freezing point, whilst with acetic acid, benzene, and a number of other organic solvents, the freezing point is raised. Similar elevation of the freezing point of certain solvents is also produced by nitrogen, hydrogen, oxygen, and methane, but is not observed with carbon dioxide, hydrogen sulphide, acetylene, or nitrous oxide.

Benzene, the freezing point of which has been raised by means of carbon monoxide, assumes its normal freezing point gradually in the cold, but rapidly on heating. Bromoform, however, through which carbon monoxide or nitrogen has been passed, maintains its elevated freezing point for some days if kept in the dark and out of contact of the air. The phenomenon does not appear to be due to chemical action, but is probably caused by part of the gas adhering to the solvent and separating with the latter in the solid state.

The following table gives the coefficients of absorption of the various gases, calculated from the equation $c = m\Delta/k$.

	H ₂ .	O ₂ .	N ₂ .	CO.	CH ₄ .	N ₂ O.
Water	—	—	—	0·0222	—	—
Formic acid ...	0·0064	0·2057	0·495	0·0600	0·2285	—
Acetic acid.....	0·0041	0·164	0·1153	—	0·0328	0·891
Benzene	—	—	—	—	0·2286	—
Nitrobenzene ...	—	—	—	—	—	0·2926

T. H. P.

An Electrically Heated Oven, with a Liquid Regulator. L. EHREMANN (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 272—274).—The apparatus described was constructed for the purpose of maintaining a moderately low temperature in an oven. An ordinary electric lamp is used as the source of heat, and the temperature is regulated by means of a tall cylindrical vessel containing very dilute sulphuric acid. A glass tube carrying a platinum wire is inserted through a cork in a tubulure at the bottom of the cylinder, and a long glass tube carrying a second platinum wire is passed through a cork at the top of the cylinder. This upper tube is made to move freely through the cork, so that the distance between the upper and lower platinum wires may be adjusted as desired. The cylinder is inserted in the circuit feeding

the lamp, and by altering the distance between the platinum wires the degree of heat obtained from the lamp may be regulated as desired. A second form of regulator is also described. It consists of a glass vessel containing the acidified water, and in the latter are placed two copper plates, one fixed and the other movable, the method of using this regulator being similar to that mentioned above. In both cases, means are provided for changing the direction of the current from time to time in order to prevent polarisation. W. P. S.

Thermodynamics of Salts containing Water of Crystallisation. HERMANN SCHOTTKY (*Zeitsch. physikal. Chem.*, 1908, 64, 415—448).—The author applies Nernst's theory (Abstr., 1907, ii, 153) to the case of formation of a higher hydrate from a lower one and water, and deduces from it the relationship $Q - A = T(C - C')$, where Q and A are referred to the combination of 1 molecule of water, C is the molecular specific heat of ice, and C' is the heat capacity of the combined molecule of water of crystallisation. For the purpose of testing this formula, the values of Q and $C - C'$ are obtained from thermochemical data, and A is calculated from the tension of the vapour over the hydrates.

The four cases selected for examination are: (1) $\text{CuSO}_4 + \text{H}_2\text{O} = \text{CuSO}_4 \cdot \text{H}_2\text{O}$; (2) $\text{K}_4\text{FeCy}_6 + 3\text{H}_2\text{O} = \text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$; (3) $\text{BaCl}_2 + \text{H}_2\text{O} = \text{BaCl}_2 \cdot \text{H}_2\text{O}$, and (4) $\text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} = \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

In order to supplement the few data already available in these cases, the author has determined (1) the specific heats of the hydrates; (2) the heats of hydration; (3) the dissociation pressures. The values obtained differ in some cases from those recorded by earlier investigators, and are employed to show that the formula $Q - A = T(C - C')$ is qualitatively correct in all four cases, and that for (1) and (3) it is capable of quantitative verification within the limits of experimental error. In the other two cases, the quantitative validity of the formula is only approximate.

The difficulty of determining the dissociation pressures of salt hydrates is discussed, and various forms of apparatus suitable for the determination are described. The sluggishness with which the maximum tension is reached is connected with the character of the efflorescing surface.

The theoretical and experimental work of Johnston (this vol., ii, 358) are adversely criticised. J. C. P.

Thermochemical Equivalence, and the Thermochemistry of Nitrogen. JOHN C. THOMLINSON (*Chem. News*, 1908, 98, 226. Compare Abstr., 1907, ii, 153).—In the belief that the numbers given previously may actually represent the thermal changes taking place, the author calculates from the structural formula he gives for nitrogen pentoxide and nitric acid an approximate heat of formation of 12,504 cal. and 45,447 cal. respectively. The experimental values are 13,000 cal. and 41,600 cal. J. V. E.

Apparent Deviations from Mariotte's Law and their Influence on the Measurement of Small Pressures. KARL SCHEEL and WILHELM HEUSE (*Physikal. Zeitsch.*, 1908, 9, 784—789; *Ber. deut. physikal. Ges.*, 1908, 6, 785—793).—The discrepancies

between the results of previous measurements of the compressibility of gases at low pressures have led the authors to examine the influence of a variation in the ratio of the exposed surface to the volume of the containing vessel in the case of air. In order to obtain a very large surface, one of the containing vessels was filled with about 20 grams of glass wool. For a variation in pressure from 0.07 to 0.7 mm. of mercury, pv remained constant in the absence of the glass wool, but when this was present, pv was found to diminish as the pressure was increased. After drying the glass wool by exhausting the apparatus, and leaving in contact for some time with phosphoric oxide, the variation in pv could no longer be observed.

The authors conclude that the deviations from Boyle's law which Baly and Ramsay found when air was compressed at low pressures in capillary tubes are due to the presence of a film of condensed water on the surface of the glass containing vessels; when this is removed, the apparent deviations disappear, and the same results are obtained whether the gas is compressed in vessels with a small or with a large amount of exposed surface.

It is pointed out that when the McLeod gauge is used for the measurement of small pressures, all traces of water vapour must be removed from the gas and from the walls of the glass vessel.

H. M. D.

Viscosity and Fluidity. EUGENE C. BINGHAM (*Amer. Chem. J.*, 1908, 40, 277—280. Compare *Abstr.*, 1906, ii, 218).—It is found with pure liquids that the fluidities of unassociated substances are approximately a linear function of the temperature, the relation being expressed by the formula $t_1 = A\phi + K_1$, where t is the temperature absolute, ϕ the fluidity, and A and K_1 are constants. Associated compounds, however, especially the alcohols, depart widely from the linear type, except at high temperatures, when the fluidity curves approximate to a straight line. To represent the increase in temperature required to give the fluidity ϕ on account of the association of the substance, use is made of the expression $t_2 = K_2 - B/\phi$, where B and K are constants. Added together, these two equations become $t = t_1 + t_2 = A\phi - B/\phi + C$, which, when tested with Thorpe and Rodger's data (*Trans.*, 1897, 71, 374) for substances not highly associated, gives results in closer agreement with observed facts than does Slotte's equation. With associated substances, such as acids, alcohols, and water, fairly close agreement is also observed. An approximate equation containing four constants, $t = A\phi - B/(\phi + D) + C$, is also used; it gives with associated substances results in as close agreement with observed values as does the above simpler equation with unassociated substances. Tables comparing the values for hexane and water, calculated by the various equations, are given.

J. V. E.

Anomalies in the Viscosity of Emulsions and of Anisotropic Liquids. EMIL BOSE (*Physikal. Zeitsch.*, 1908, 9, 707—708).—The changes observed in the viscosity of anisaldazine in the neighbourhood of the clearing point (this vol., ii, 258) cannot be used as a proof against the emulsion theory of anisotropic liquids. On the other

hand, Vorländer's experiments (this vol., i, 641) indicate that this theory is untenable.

H. M. D.

Influence of Electrolytes on the Viscosity of Colloidal Liquids. MANFREDI ALBANESE (*Arch. exp. Path. Pharm., Suppl.*, 1908, 16—28).—The viscosity of an aqueous solution of gum arabic is lowered (up to 30%) by the addition of electrolytes, but not by other substances. Solutions of certain other colloids, such as egg-albumin, are not affected by electrolytes, unless they have been dialysed previously, in which case the viscosity is somewhat diminished by adding salt.

G. B.

Capillary Properties of Aqueous Solutions of Fatty Acids. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1908, 64, 385—414. Compare this vol., ii, 827).—In contrast with the usually accepted view, the author finds that the heights to which water and fatty acid solutions rise in capillary tubes are almost independent of accidental impurities. For the purest water obtainable, for ordinary distilled water, for conductivity water, and for tap-water, the observed capillary rise is the same to within 0.1 mm. It is also found unnecessary to take special precautions in protecting the capillary tubes from dust; washing out with chromic acid mixture is quite adequate preliminary treatment.

The acids specially examined were *n*- and *iso*-butyric acids, *n*- and *iso*-valeric acids, and *n*- and *iso*-hexoic acids, and the experiments show that the higher an acid stands in the homologous series the greater is its effect in lowering the capillarity of water; the effects of the *n*- and *iso*-acids are nearly equal. In the case of *isobutyric* acid, the variation in the capillarity with concentration is satisfactorily reproduced by the empirical formula $y = 1 - b \log(x/a + 1)$, where *a* and *b* are constants, *x* is the concentration, and *y* is the capillary rise referred to that of water as standard. The other acids examined obey this dilution law only approximately.

In most cases there are considerable differences between the author's measurements and those recorded by Drucker (*Abstr.*, 1905, ii, 680); this is probably to be attributed to the different purity of the acids employed.

Some experiments made on the relative influence of *isovaleric* acid and its barium salt, and on the effect produced by mixtures of the two, support the view that the depression of the capillarity of water is to be attributed to the undissociated part of the acid.

Experiments made with mixtures (1) of *isobutyric* and *isovaleric* acids, and (2) of *isobutyric* and *isohexoic* acids, indicate that the depression of the capillarity of water is an additive property for the fatty acids. In the first case, this fact may be made the basis of an analytical determination of the mixed acids.

J. C. P.

Osmotic Pressure. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1908, 64, 629—632).—The formula for the osmotic pressure of a perfect solution proposed by Lewis (this vol., ii, 465) is identical with that obtained by the author (*Abstr.*, 1895, ii, 107; 1906, ii,

526) on thermodynamic grounds. The formula obtained in this way is valid for imperfect, as well as for perfect, solutions, and is in accordance with the experimental results of Morse and Frazer (Abstr., 1905, ii, 475 ; 1906, ii, 600, 601). C. H. D.

The Vapour Pressure and Osmotic Pressure of a Volatile Solute. HUGH L. CALLENDAR (*Proc. Roy. Soc.*, 1908, A, 81, 336).—If an osmotic membrane is impermeable to the solute, the formulæ for the change of vapour pressure with hydrostatic pressure, and for osmotic pressure, are the same for a volatile as for a non-volatile solute. If, on the other hand, the membrane is permeable to the vapour, but not to the liquid phase, the equation depends on the concentration of the constituents in the vapour phase. C. H. D.

Osmotic Pressure of Sucrose Solutions at 15°. HARMON N. MORSE and B. MEARS (*Amer. Chem. J.*, 1908, 40, 194—213. Compare Abstr., this vol., ii, 671).—In order to ascertain the cause of the osmotic pressure of sucrose solutions at 0° not being in agreement with the gas pressure, as at 20°, measurements at intermediate temperatures have been made. The authors now give results of measurements made at 15°, and from a comparison with those obtained at 0°, 5°, and 10°, previously recorded (*loc. cit.*), they are able to state that sucrose solutions exhibit a temperature-coefficient which is practical identical with the temperature-coefficient of gases. J. V. E.

Electric Osmosis. JOSEPH C. W. FRAZER and HARMON N. HOLMES (*Amer. Chem. J.*, 1908, 40, 319—325).—A description is given of the apparatus used, and also the results of a preliminary investigation of the relative osmosis of a few salts of nitric acid at the concentration 0.001*N*. The observations recorded for nine different salts appear to support the statement made previously (Abstr., 1906, ii, 600) that the osmosis of the nitrates of alkalis and alkaline earths varies inversely as the velocity of the cation divided by its valency, but the osmosis does not seem to be proportional to the specific resistance of the solutions.

It is suggested that some connexion may exist between this phenomenon and the results obtained by Kohlrausch (Abstr., 1903, ii, 403) and others working on the hydration of ions. J. V. E.

Improvement in Cells for the Measurement of Osmotic Pressure. HARMON N. MORSE and B. MEARS (*Amer. Chem. J.*, 1908, 40, 266—277).—A detailed account is given of the weak points of the cell previously used and described (Abstr., 1905, ii, 575); the paper deals, however, in general with the form of cells and the method of closing them for the measurement of osmotic pressure. A new form of cell is described, which is entirely free from the objectionable features of the older one. The upper end of it is glazed inside and out, and has an accurately ground conical aperture at the top for the reception of a brass, cone-shaped collar, which is covered with a caoutchouc cap carrying the manometer

tube. The closing of this cell is rapidly effected by screwing a brass nut down on to the collar. For details of construction and manipulation, the original must be consulted. J. V. E.

Improved Manometers for Measurement of Osmotic Pressure. HARMON N. MORSE and B. F. LOVELACE (*Amer. Chem. J.*, 1908, 40, 325—337).—An apparatus is described by means of which manometers may be compared with others, or with the standard, up to pressures of three hundred atmospheres. Corrections for meniscus, and a method of detecting a temporary or a permanent stretch of the manometer, are also given, as well as a detailed description of the method used by the authors for filling and closing their manometers. J. V. E.

The System Water, and Sodium, Barium, and Copper Chlorides. FRANS A. H. SCHREINEMAKERS and W. C. DE BAAT (*Chem. Weekblad*, 1908, 5, 801—806).—The authors represent the quaternary system water, sodium chloride, barium chloride, and copper chloride by means of a regular tetrahedron, the four angles giving the four components. The method is an extension of that employed to represent a ternary system by means of an equilateral triangle. A. J. W.

Velocity of Reactions in Gases Moving through Heated Vessels, and the Effect of Convection and Diffusion. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1908, 30, 1742—1754).—In studying the changes which take place in mixtures of gases while passing through hot tubes, the velocity coefficient of the reaction is usually calculated by means of the formula derived for reactions occurring in stationary gases. Bodenstein and Wolgast (this vol., ii, 162) have pointed out that this method is inaccurate, since allowance is not made for the mixing of the gases in the tube by diffusion or convection, and they have presented a formula which holds when the mixing of the gases can be considered complete.

In the present paper, these two formulæ and the magnitude of the error arising from their application in various cases are considered. New formulæ are developed, from which the velocity coefficient may be calculated in cases in which neither of the formulæ mentioned holds good, but in which, in the mixing of gases, diffusion plays a more important part than convection. E. G.

Relation between the Velocity of Reaction and the Velocity of Stirring in Non-homogeneous Systems. K. JABŁCZYŃSKI (*Bull. Acad. Sci. Cracow*, 1908, 620—631).—The rate of dissolution of a solid in a liquid increases with stirring. The connexion between the velocity constant k and the velocity of the stirrer n is given by the empirical equation $k_1/k_2 = (n_1/n_2)^x$, where x is a constant, the value of which varies with different apparatus, and even with the same apparatus if taken apart and put together again. This probably accounts for the different values of x obtained by different investigators (Bruner and Tolloczko, *Abstr.*, 1903, ii, 470; Bruner, *Abstr.*, 1904, ii, 315; Sackur,

Abstr., 1906, ii, 261). The evaluation of α is important, since it gives some information as to how far a reaction in a non-homogeneous system is dependent on diffusion (Noyes and Whitney, Abstr., 1897, ii, 479; Nernst, Abstr., 1904, ii, 315). In the same apparatus, so arranged that each experiment can be completed without any disturbance of the parts of the apparatus, the author has examined, at 25°, the solution of a marble plate in hydrochloric acid, the decomposition of hydrogen peroxide by platinised platinum foil, and the solution of a fused zinc plate in hydrochloric acid. The average values of α are 0.93, 0.55, and 0.28 respectively. Hence the author deduces that, for the dissolution of a solid with a perfectly smooth surface, the velocity constant of the reaction is simply proportional to the velocity of stirring (as measured by the revolutions of the stirrer); if the surface of the solid is not smooth, the increase of the velocity constant is slower than the increase of the velocity of stirring, and the more so the rougher the surface. C. S.

Saponification of Glycerides during Ester Exchanges in Homogeneous Systems. ROBERT KREMANN (*J. pr. Chem.*, 1908, [ii], 78, 364—367); MILAN J. STRITAR and RICHARD FANTO (*ibid.*, 408).—Polemical (compare Abstr., 1907, i, 464; this vol., i, 120, 499; ii, 677). G. Y.

Oxidations of Biological Importance. I. HANS EULER and IVAN BOLIN (*Zeitsch. physiol. Chem.*, 1908, 57, 80—98).—Careful experiments have been made on the oxidation of quinol by oxygen in the presence of manganous salts and alkali. It is shown that the velocity of the reaction is almost proportional to the pressure of the oxygen, and that the temperature-coefficient is very small between 0° and 40°. The solutions used were either neutral or slightly acid to phenolphthalein. To obtain such solutions, it is necessary to add dilute alkali, as quinol is decidedly acidic. The effect of the manganese (added as acetate) and of the sodium concentrations has been studied. As the whole reaction cannot be represented by means of the usual unimolecular formula, owing to the fact that part of the quinol is removed in the form of insoluble quinhydrone, the velocity has been determined by measuring the times required in the different experiments for absorbing a given volume (3 or 5 c.c.) of oxygen. The results show that in neutral or slightly acid solutions, manganese salts accelerate the oxidation, and that if the amount of sodium hydroxide added is the same, the rate of oxidation increases less rapidly than the manganese concentration. On the other hand, if the amount of manganese salt is constant, the velocity increases much more rapidly than the amount of alkali added.

The relationship between the effects of the manganese salt and the alkali is compared with that of an enzyme and co-enzyme.

Similar experiments have been made with "laccase" and manganese salts. It is shown that the laccase as prepared by Bertrand's method is slightly acid, and that it has no action on a quinol solution in the absence of manganese salts. It is obvious that the action of the laccase cannot be due to its alkaline nature, as suggested by Dony-

Hénault. Even the addition of 10 c.c. of 0.0001*N* hydrochloric acid to lucerne laccase does not affect the activity of the laccase in the presence of manganous salts.

It is further shown that the active principle of the laccase is not a substance of the enzyme type, as the preparations of laccase can be boiled for three minutes without destroying their activity in the least.

It is shown that salts of hydroxy-acids, for example, rochelle salt, sodium citrate, calcium gluconate, and sodium mucate, accelerate the oxidation of quinol in a marked manner when manganese salts are present, and it is suggested that laccase owes its activity to the presence of such salts. J. J. S.

Some Oxydasic Phenomena Produced by Colloidal Ferrous Ferrocyanide. JULES WOLFF (*Compt. rend.*, 1908, 147, 745—747. Compare this vol., i, 137, 490 ; ii, 573).—In a feebly alkaline solution, colloidal ferrous ferrocyanide acts as an oxydase towards quinol. When a saturated solution of quinol is treated with ammonia to the extent of 1 part in 25,000, and colloidal ferrocyanide to the extent of 1 part of iron in 100,000, abundant crystals of quinihydrone are formed after twelve to fifteen minutes, oxidation being accelerated by shaking. The reaction is still observed with one-twenty-fifth as much iron if the quantity of alkali is increased to 1 part in 2000. Solutions of quinol treated with alkali alone become brown, but rarely deposit crystals, the colloidal iron alone has no action. If too much alkali (1%) is added, the solution is rapidly oxidised by the air, and no crystals are formed. These phenomena can be explained by the alkali facilitating the oxidation of the phenol, and consequently the action of the ferrocyanide, which thus acts as an oxydase. This view is supported by the facts that if the alkali is added some time before the colloidal iron, quinihydrone is no longer obtained, and that, other things being equal, the intensity of the reaction is proportional to the amount of alkali present (within the limits described above). From the latter observation, it would be expected that the alkali-earth oxides and hydrogen carbonates, and feebly alkaline salts, such as disodium hydrogen phosphate, would exercise a much less energetic action. This is actually found to be the case. The important part played by the alkali suggests that the oxidising action on quinol of certain manganese salts with weak acids discovered by Bertrand (*Abstr.*, 1897, ii, 493) is due partly to their alkalinity, all of them being alkaline to methyl-orange. The author finds that the addition to these solutions of a quantity of iron in the form of colloidal ferrocyanide, one-hundredth as great as that of manganese present, suffices to double the rate of oxidation of quinol, and that neutral aqueous manganese sulphate solutions, which are ordinarily almost inactive, increase their activity considerably when treated with traces of pyridine (which does not precipitate manganese). E. H.

Catalysis. IX. Catalytic Reactions induced by Enzymes. SALOMON F. ACREE (*J. Amer. Chem. Soc.*, 1908, 30, 1755—1760).—Attention is drawn to the work of Hudson (this vol., i, 605, 856)

on the inversion of sucrose by invertase, and it is shown that it harmonises completely with the view already advanced by others, that the addition of an enzyme to a reacting system brings about a catalytic reaction, owing to the union of the enzyme with some constituent or "substratum" of the reacting system to form a new product which gives the same end-products as the substratum itself. It is pointed out that this theory of catalysis through the formation of reactive intermediate compounds renders the assumption of a vital energy for such reactions unnecessary.

E. G.

Molecular State of Molten Salts. RICHARD LORENZ and FELIX KAUFLEDER [in part, A. LIEBMANN] (*Ber.*, 1908, 41, 3727—3738).—The molecular weights of lead chloride, potassium nitrate, sodium nitrate, and silver chloride in the fused state at various temperatures between 300° and 600° have been determined by measuring the surface tension of the molten salt. The mean values of K obtained for potassium nitrate and sodium nitrate, namely, 0.7 and 0.25 respectively, are in fair agreement with those recorded by Bottomley (*Trans.*, 1903, 83, 1421). The constants found for silver chloride and lead chloride were respectively 0.8 and 0.9. Since these values are all less than 2.12, the constant for liquids having a normal mol.-wt., the conclusion is drawn that the salts investigated exist in the fused state in a highly associated condition and that the ions are of a complex nature.

W. H. G.

Liquid Crystals. OTTO LEHMANN (*Ber.*, 1908, 41, 3774—3783).—Mainly a historical review of the author's investigations on the subject of liquid crystals.

The view recently put forward by Vorländer (this vol., i, 641), that pseudo-isotropic, crystalline liquids are to be regarded as uniaxial crystals, is combated. It is possible for a biaxial mass to become pseudo-isotropic, that is, apparently uniaxial.

W. H. G.

The Liquid-crystalline State as a General Property of Matter. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 166—168*).—Having shown in previous papers (this vol., ii, 90, 263) that the colloidal-amorphous state of matter is a modification of the crystalline, the author has now studied certain liquid crystals, such as *p*-azoxyphenetole, both microscopically and ultramicroscopically, and states his views of the nature of these crystals as follows. A liquid crystal is a system of chemically or physically associated, solid, crystalline particles, between which vectorial forces of small tension act. The small magnitude of the tension in the case of chemical association is conditioned by the considerable energy expended in building up the complicated molecule in the case of physical association by the expenditure of energy requisite for the association of a number of elementary crystalline particles to one particle.

G. S.

Theory of Colloids. EDUARD JORDIS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 153—166).—A summary of the author's views on the nature of colloidal solutions (compare *Abstr.*, 1907, ii, 344; this vol., ii, 675).

* and *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1323—1327.

The theory developed is in many respects identical with that of Duclaux (summarised in *J. Chim. Phys.*, 1907, 5, 29), and many of Duclaux's results are discussed in detail. Pure hydrosols are not stable; the stability is determined by small amounts of other substances, usually electrolytes, which act as "sol-formers." These substances are in chemical combination with the dissolved colloids, and when they are completely removed, the hydrosol coagulates.

G. S.

Electrical Nature of Colloidal Solutions. NICOLA PAPPADÀ (*Gazzetta*, 1908, 38, ii, 474—480. Compare Abstr., 1907, ii, 754).—The author criticises Duclaux's hypothesis concerning the electrical nature of colloids (compare Abstr., 1904, ii, 162, 243, 325; 1905, ii, 432, 511; 1906, ii, 660, 677; this vol., ii, 760).

T. H. P.

Influence of Colloids on the Absorption of Gases, especially of Carbon Dioxide in Water. ALEXANDER FINDLAY [with W. H. HARBY] (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 169—170).—The absorption of carbon dioxide by blood is not well understood, and it is suggested, in agreement with Wolfgang Ostwald (this vol., ii, 509), that, besides ordinary chemical combination, adsorption on the surface of the colloidal particles may be of importance in this connexion. As the first step in an investigation of the effect of colloids on the solubility of gases, the solubility of carbon dioxide in colloidal solutions of ferric hydroxide, gelatin, arsenic sulphide, silicic acid, albumin, dextrin, soluble starch, and glycogen has been measured at 25°. The first two colloids increase the solubility, the three last mentioned diminish it somewhat, and the other three are without effect.

G. S.

Colloidal Silver (Silver-gel) in Photographic Layers. LÜPP-
CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 170—174).—For the direct production of positives as employed in ferrotype photography, it is necessary that the silver in the parts which are most strongly lighted should be obtained in a more or less white form. This can now be effected with dry collodion plates covered with colloidal substances, such as tannin or gum.

In order to study the deposition of silver in different forms, silver bromide plates have been exposed in a Chapman Jones "plate tester," which allows of graduated illumination. When a plate thus exposed is developed with ferrous oxalate, the silver varies in appearance from greyish-white, on the most highly exposed parts, to greyish-black, on the parts almost in shade, and the difference persists after fixing. The white silver has a much smaller adsorptive power than the black form, and this difference in properties is employed to account for certain phenomena occurring in photographic processes.

G. S.

Freezing of Hydrosols. O. BOBERTAG, KARL FEIST, and H. W. FISCHER (*Ber.*, 1908, 41, 3675—3679).—The paper gives a review of the behaviour of colloidal solutions at temperatures below the freezing point of the solvent. By rapid cooling to -70° , the metal is separated

from Bredig's colloidal suspension of platinum. By freezing a colloidal solution of arsenic trisulphide, Winter (Abstr., 1905, ii, 245) obtained the solid red modification, the authors cool a very dilute solution to -70° , and, after thawing, recover the yellow colloidal solution, which, however, has become very turbid. Colloidal ferric hydroxide, cooled to -70° and thawed, remains clear, but shows a distinct augmentation of the Tyndall phenomenon. Aluminium acetate behaves somewhat similarly. The colloidal silver preparations, protargol, collargol, and lysargin, in the presence of albumin are dark coloured, very turbid, and optically non-homogeneous; by freezing, the silver collects into small lumps, which are distributed irregularly through the clear ice; on thawing, the solution is recovered apparently unchanged.

In connexion with organic colloids, certain dyes and substances of animal and vegetable origin have been examined. Rhodamine, chrysoidine, eosin, and safranin form true solutions; Nile-blue, acid-violet, methyl-violet, and magenta behave as semi-colloids, and night-blue, alkali-blue, Congo-red, and benzopurpurin as pronounced colloids (compare Freundlich and Neumann, this vol., ii, 820; Höber and Chassin, *ibid.*, ii, 875).

On cooling a 10% solution of tannin, a considerable deposition is observed just above the freezing point; on thawing the frozen mass, the tannin partly dissolves, the remainder going into solution by slight warming. Hæmoglobin (Merck), after being cooled to -10° , -70° , and -180° , shows no apparent change. Solutions of gum or starch, cooled to the same temperatures and thawed, are quite turbid, but clarify by keeping. Dried albumin in solution, cooled to -70° to -180° and thawed, gives a turbid solution, which does not again clarify entirely. Solutions of gelatin, caragheen moss, agar-agar, and soap behave in a similar manner on freezing. The water is mostly frozen out from the jelly, so that the first portion of the liquid obtained by thawing is practically free from dissolved substances. After complete thawing, the product is decidedly non-homogeneous, consisting of a mobile liquid and a clotted jelly.

Attempting to explain the varying behaviour of the preceding colloidal solutions on freezing, the authors suggest that the freezing causes the colloidal particles to become aggregated, and that these aggregations may be partly or entirely destroyed by thawing, with the result that a precipitation or a solution is obtained. C. S.

Study of Colouring Matters in Solution. LOUIS PELET-JOLIVET and A. WILD (*Compt. rend.*, 1908, 147, 683—685; *Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 174—177; *Bull. Soc. chim.*, 1908, [iv], 3, 1087—1094).—From a study of the electrical conductivity and the ultramicroscopic state of solutions of various dyes (magenta, methylene-blue, crystal-violet, safranin, crystal-ponceau, naphthol-yellow S, Congo-red, etc.), the conclusion is drawn that dyes are dissociated in aqueous solution into two ions, and that some of them assume the colloidal condition. Addition of electrolytes favours the passage into the colloidal state. The authors' results do not entirely agree with those of Teague and Buxton (Abstr., 1907, ii, 933) and of Freundlich and Neumann (this vol., ii, 820). J. C. C.

Fixation of Different Derivatives of the Same Colouring Matter and Explanation of Dyeing. LOUIS PELET-JOLIVET and N. ANDERSEN (*Compt. rend.*, 1908, 147, 808—810.* Compare preceding abstract).—Wool was placed in solutions containing equivalent quantities of derivatives of certain basic and acidic colouring matters. Other conditions being the same, the hydrochloride of safranine gave a paler tint than the sulphate, and the phosphate a darker tint. The hydroxide gave a tint intermediate between the sulphate and phosphate. The sodium salt of crystal-ponceau produced lighter tints than the magnesium salt; the aluminium salt gave darker tints, whilst the free acid was intermediate between the two latter salts in colouring power.

These experiments confirm the theory of Freundlich and Loser (Abstr., 1907, ii, 155, 534) of the fixation of basic and acidic dyes. The wool is supposed to become negatively charged when placed in water; when treated with a solution of the salt of a basic dye, adsorption of the positively charged organic ion occurs, whilst in the case of the salt of an acidic dye, the positive inorganic ion is adsorbed, causing the fabric to assume a positive charge, which, being smaller than the negative charge produced by an equivalent quantity of a negative dye, accounts for the well-known fact that wool and charcoal fix basic dyes more readily than acidic ones. This accords, moreover, with the effects produced by adding electrolytes to the bath, since positive multivalent ions or hydrogen ions should favour the fixation of the acidic dyes, whilst negative ions should hinder the process. A rational explanation is thus afforded of the action of mordants and of the tanning process.

W. O. W.

Passive State of Metals. Review of the Literature and Theories and Some Experiments on Cobalt, Iron, and Nickel. HORACE G. BYERS (*J. Amer. Chem. Soc.*, 1908, 30, 1718—1742).—A historical and theoretical discussion is given of the work done hitherto on the passivity of metals. Experiments are described which have been carried out with cobalt, iron, and nickel. A plate of the metal connected with a copper conducting wire was suspended as anode in a porous cup, which was placed in a porcelain beaker. Both beaker and cup were nearly filled with solutions of the various electrolytes. The cathodes, two platinum plates of the same size as the anode, were suspended in the beaker parallel to, and at equal distances from, the anode. The amount of the anode dissolved during the passage of the current was measured by its loss of weight.

The results obtained were so varied and conflicting as to render a brief summary impossible. Iron, nickel, and cobalt cannot be rendered passive by the hydrogen acids or their salts. Passivity may take place in electrolytes containing oxygen, and depends on the current density, the temperature, the electrolyte, and the treatment of the metal. The metals may be either passive or active under exactly the same current conditions so long as the current density is below a critical value.

The phenomena of passivity have not yet received any satisfactory explanation. Faraday's view, connecting passivity with the formation of a coating of oxide on the metal, is untenable. The hypotheses of

* and *Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 206—210.

Finkelstein and Müller, according to which the passive state is occasioned by changes in the valency of the metal, are unsatisfactory. Many of the results now obtained cannot be reconciled with Fredenhagen's explanation, which attributes passivity to anodic oxygen or an oxygen alloy. E. G.

Determination of the Atomic Weight of the Simple Ponderable Substance, Pantogen. GUSTAVE D. HINRICHS (*Compt. rend.*, 1908, 147, 797—800. Compare this vol., ii, 573, 574).—The author assumes the existence of a simple fundamental material of atomic weight $1/128$, and thence proceeds to theoretical deductions as to the weight and geometrical forms of the atoms of hydrogen, helium, nitrogen, oxygen, and fluorine. The paper includes a diagrammatic representation of the atoms of these elements, and of their physical properties in the neighbourhood of the absolute zero.

H. O. W.

Atomic Weight of Radium and Other Elementary Substances. HENRY WILDE (*Phil Mag.*, 1908, [vi], 16, 824—830. Compare Abstr., 1907, ii, 149; this vol., ii, 141).—The author still maintains that the true atomic weight of radium is 184. A periodic table is given, based on the numerical relationships previously described.

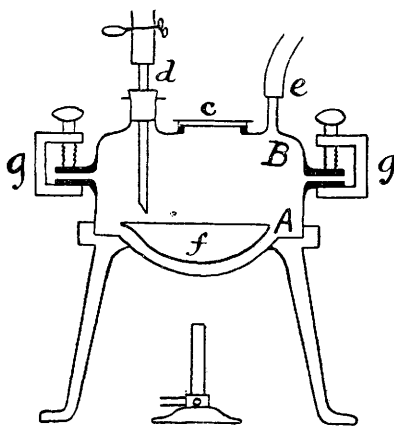
H. M. D.

New Form of Test-tube Holder. H. STOLTZENBERG (*Zeitsch. angew. Chem.*, 1908, 21, 2272).—The advantage of the new form of wire holder described lies in the fact that, not only may the tube or other object held be readily released, but the force by which it is held may be increased by the power of the hand. It thus becomes possible to lift fairly heavy vessels and to shake them without fear of their falling. J. V. E.

Apparatus for Evaporating in a Dish under Reduced Pressure. EDUARD DONATH (*Chem. Zeit.*, 1908, 32, 1107).—The accompanying figure depicts the apparatus described by the author. It consists of two parts, A and B, both being made of stout copper having thick, broad flanges so as to form an air-tight chamber when they are screwed down on to an asbestos washer by screws, g. Into the lower part, A, the evaporating basin, f, is placed upon asbestos fibre.

The upper part, B, is perforated in three places, c, d, and e; c is covered by a thick plate of transparent mica, the liquid to be evaporated is introduced through d, and e is connected to an exhaust pump.

J. V. E



Circulating Pump. H. STOLTZENBERG (*Zeitsch. angew. Chem.*, 1908, 21, 2271—2272).—A new form of small centrifugal pump is described as being an efficient circulator of liquid from a thermostat through condensers, jacketed polarimeter tubes, etc. The power required to drive the pump is very small, and when rotating at 1200 revolutions per min. it is able to lift water to a height of ten metres.

J. V. E.

Inorganic Chemistry.

[Production of Hydrogen Peroxide from Persulphuric Acid.] CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 199958).—When carefully-purified solutions of persulphuric acid are treated with sulphuric acid (D 1.4) at 50—80°, the former rapidly yields hydrogen peroxide with a loss of only 3 or 5% of oxygen. This result is, however, only obtained in the absence of all impurities likely to decompose hydrogen peroxide catalytically (compare *Trans.*, 1904, 85, 1526—1533).
G. T. M.

Generation of Oxygen in a Kipp's Apparatus. LUDWIG WOLTER (*Chem. Zeit.*, 1908, 32, 1066).—The extremely vigorous evolution of oxygen from alkali peroxides when treated with water or dilute acids has been sufficiently modified by admixture with indifferent substances to allow of the generation of the gas in a Kipp's or other gas generation apparatus by this method.

The best results have been obtained with a substance prepared by adding a mixture of 100 parts of sodium peroxide and 25 parts of magnesium oxide to 100 parts of molten potassium nitrate. This, when solidified and broken into pieces of a suitable size, is placed in a Kipp's apparatus and treated with dilute hydrogen chloride. The substance may be kept for some time ready for use by dipping the lumps into molten paraffin wax so as to protect them from the atmosphere.

J. V. E.

Dynamic Allotropy of Sulphur. I. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1908, 64, 513—561).—The investigations of Smith and his collaborators (*Abstr.*, 1903, ii, 139, 284; 1905, ii, 382, 580; 1906, ii, 157; 1907, ii, 20; this vol., ii, 32) have led to results which accord best with the theory that S_A and S_μ are partly miscible in the liquid state, but that the equilibrium curve lies entirely outside the heterogeneous region. Smith's conclusion, that the equilibrium curve cuts the curve of miscibility, is untenable. A bibliography and review of previous literature on the subject are given.

The melting point of rhombic sulphur was determined by immersing capillary tubes containing the powdered sulphur in boiling calcium chloride baths at different temperatures, and was finally fixed at

112.4°. Similar sulphur, heated for an hour at 90° in ammonia to produce equilibrium, melted at 110.9°. The unstable "natural melting point" of rhombic sulphur was then found graphically to be 110.5°, and the melting point of pure rhombic sulphur 112.8°. From 111° onwards, the melting-point curve must be parallel to the concentration axis.

The composition of the vapour in contact with liquid sulphur at different temperatures was measured by blowing a current of air through the molten sulphur at constant temperature, and condensing the current of vapour on the surface of water at 0°. Ammonia gas was introduced as a catalyst, this being subsequently removed by the current of air, the sulphur dioxide formed by partial oxidation then serving to preserve the composition of the vapour unchanged during cooling. The condensed sulphur was analysed by extraction with carbon disulphide. The vapour and liquid curves intersect at 324° and 24.7% S_{μ} .

The vapour-pressure curve of the system S_{λ} — S_{μ} presents either a maximum or a minimum, but it is not yet possible to determine which. This point is to be further investigated. This curve must cut the curve of equilibrium.

C. H. D.

The Boiling Point of Sulphur on the Constant Pressure Air Thermometer. NICHOLAS EUMORFOPOULOS (*Proc. Roy. Soc.*, 1908, *A*, **81**, 339—362).—A detailed account of measurements with a Callendar air thermometer of Jena glass. The various sources of experimental error were very fully investigated, the most important being the changes of volume of the glass bulbs. The mean value of the boiling point of sulphur obtained is 443.58°.

C. H. D.

The Boiling Point of Sulphur. HUGH L. CALLENDAR (*Proc. Roy. Soc.*, 1908, *A*, **81**, 363—366. Compare preceding abstract).—The changes of volume in glass render it an unsuitable material for accurate thermometry. The value for the boiling point of sulphur obtained by Eumorfopoulos is in close agreement with those obtained by other methods, the chief source of error being now the uncertainty as to the true coefficient of expansion of mercury.

C. H. D.

Preparation of Hydrazine. FRITZ RASCHIG (D.R.-P. 198307).—When excess of strong aqueous ammonia reacts with a solution of sodium hypochlorite in the presence of an organic substance to increase the viscosity of the solution, a good yield of hydrazine is obtained. One litre of sodium hypochlorite and 12 c.c. of a solution containing 5% of joiners' glue are added to 3 litres of concentrated aqueous ammonia, the solution heated to drive off ammonia, and concentrated to the crystallising point, when 80—90 grams of hydrazine sulphate are obtained on the addition of sulphuric acid. The product is purified by crystallisation.

G. T. M.

Hydroxylamine. I. ERICH EBELER and E. SCHOTT (*J. pr. Chem.*, 1908, [ii], **78**, 289—342).—The authors review the various formulæ

which have been proposed for hydroxylamine, and assemble the evidence in favour of the view that it is a tautomeric substance, having in alkaline solution the constitution $\text{NH}_2\cdot\text{OH}$, and acting as an acid, but in acid solution behaving as an oxonium base, $\text{NH}_3\cdot\text{O}$, forming salts of the type $\text{NH}_3\cdot\text{O} < \begin{smallmatrix} \text{H} \\ \text{X} \end{smallmatrix}$. This view of the nature of hydroxylamine is applied to the explanation of its properties and of the reactions which it undergoes.

Anhydrous hydroxylamine is readily prepared by dissolving 4—5 grams of the 75% distillate obtained by Uhlenhuth's method (Abstr., 1900, ii, 475) in 100—400 c.c. of absolute alcohol, and cooling the solution to about -18° . Hydroxylamine is deposited from the stronger solutions in white leaflets, and from the more dilute solutions slowly in needles.

Lobry de Bruyn found (Abstr., 1892, 1391) that hydroxylamine reacts with zinc, forming zinc oxide and ammonia. It is now shown that the intermediate product of this reaction is a zinc salt, $\text{Zn}(\text{O}\cdot\text{NH}_2)_2$, and not an additive compound, $\text{Zn}\cdot\text{O}\cdot\text{NH}_3$. A similar calcium salt has been prepared, and indications obtained of the existence of an extremely unstable ferric salt. It is proposed to apply the term hydroxylamites to the salts $\text{NH}_2\cdot\text{OM}'$, $(\text{NH}_2\cdot\text{O})_2\text{M}''$, etc.

Calcium hydroxylamite, $\text{Ca}(\text{O}\cdot\text{NH}_2)_2$, is formed with evolution of gas when calcium filings are treated with anhydrous hydroxylamine at 50° . Ammonia is evolved only if heat is developed, which takes place if water is present. The white salt, which separates towards the end of the reaction, is extremely explosive, being much more dangerous than anhydrous hydroxylamine; when washed with absolute alcohol and dried in a vacuum over sulphuric acid, it is obtained as a white, amorphous powder, which detonates at 180° , and is hydrolysed by water, slowly by moist air, forming calcium hydroxide and hydroxylamine. It is considered that Hofmann and Kohlschütter's calcium salt of hydroxylamine (Abstr., 1898, ii, 380) is a mixture of calcium hydroxylamite and calcium hydroxide.

Zinc hydroxylamite, $\text{Zn}(\text{O}\cdot\text{NH}_2)_2\cdot 3\text{NH}_3\cdot\text{O}$, prepared by the action of anhydrous hydroxylamine on finely-divided pure zinc and treatment of the product with absolute alcohol, is obtained in glistening crystals, loses hydroxylamine, and leaves a residue of zinc oxide when gradually heated, detonates, evolving ammonia, when quickly heated, and is readily hydrolysed by moisture, forming zinc hydroxide.

Haber observed (Abstr., 1898, ii, 23) that hydroxylamine oxidises ferrous salts in ammoniacal or sodium carbonate solution, and stated that the hydroxylamine is itself converted into ammonia. It is now found that under these conditions nitrogen and nitrous oxide are first evolved, ammonia appearing only towards the end of the reaction. The study of the reaction is complicated by the fact that hydroxylamine is decomposed catalytically by ferric hydroxide in neutral or alkaline solution, yielding the same three products. The ferric hydroxide residue is scarlet, becomes brownish-red when heated, does not decolorise permanganate or evolve chlorine from hydrochloric acid, and thus resembles the ferric hydroxide residue obtained from the catalytic

decomposition of hydrogen peroxide. If hydroxylamine is treated with ferric hydroxide in absolute alcoholic solution at about -18° , a brown precipitate is formed, which, after being washed with absolute alcohol, decomposes on treatment with water, forming nitrogen, nitrous oxide, and ammonia, and must therefore contain *ferric hydroxylamite*.

Hydroxylamine silicofluoride, $(\text{NH}_3\text{O})_2\cdot\text{H}_2\text{SiF}_6\cdot 2\text{H}_2\text{O}$, prepared by adding 16% aqueous hydrofluosilicic acid to a 25% aqueous solution of hydroxylamine and allowing the mixture to evaporate, crystallises from boiling methyl alcohol in scales, and is almost insoluble in alcohol, but readily dissolves in water.

Hydroxylamine titanofluoride, $(\text{NH}_3\text{O})_2\cdot\text{H}_2\text{TiF}_6$, prepared by adding 20% hydroxylamine to a cooled solution of hydrofluotitanic acid and evaporating the solution in a vacuum, separates from methyl alcohol in white crystals. With quadrivalent titanium, hydroxylamine gives the same yellow coloration, caused by the formation of a higher oxide of titanium, as is produced by hydrogen peroxide. G. Y.

The Interaction of Nitrous Gases and Oxygen with Water. FRITZ FOERSTER and M. KOCH (*Zeitsch. angew. Chem.*, 1908, 21, 2209—2219. Compare this vol., ii, 941).—In continuation of this investigation (*loc. cit.*), the authors have studied the behaviour towards water of nitric peroxide when greatly diluted with air. The results, which are tabulated, show the proportion of nitric peroxide converted into nitric acid to be greater when the concentration of this gas in the gaseous mixture is greater; it is, however, not directly proportional, being considerably less than would be expected. This may be explained by the fact that with large excess of air the nitrous acid represented in the equation $\text{H}_2\text{O} + 2\text{NO}_2 \rightleftharpoons \text{HNO}_3 + \text{HNO}_2$, being less stable in solution, allows of a more rapid absorption of fresh nitric peroxide than when the excess of air is less. It is also shown that with diluted nitric oxide the increased concentration of nitric acid is not due simply to absorption of more oxides of nitrogen, but, in part, to the nitric acid formed previously leaving the solution with water as $\text{HNO}_3\cdot\text{H}_2\text{O}$. The limiting concentration at the ordinary temperature at which this takes place is indicated by the following: with 1% NO_2 , about 46% HNO_3 ; with 2% NO_2 , about 51.8% HNO_3 , and with 5% NO_2 , more than 55.6%.

From a study of the influence of a large excess of air on the behaviour of the nitrous acid produced in the primary change, it is shown that it completely decomposes, with time, into nitric acid and nitric oxide. Excess of oxygen, when not at the same time under a smaller partial pressure, rapidly oxidises this nitric oxide to nitric peroxide, but, in the case of a large excess of air, there is insufficient time for the nitric oxide that is carried forward from the water solution to be completely oxidised to the peroxide. The quantity of nitric oxide escaping oxidation was ascertained by substituting for the water, dilute alkali hydroxide solution as absorbent, and the quantity of nitrite produced is shown to be greater when the dilution by air is greater.

Nitric peroxide, even when largely diluted by air, is rapidly

oxidised by ozone to nitrogen pentoxide, and when such a gaseous mixture is passed into water, or aqueous nitric acid, an acid solution containing more than 80% HNO_3 may readily be obtained.
J. V. E.

Formation of Colloidal Phosphorus. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1908, [ii], 78, 367—368).—When exposed to diffused daylight in a closed vessel, a clear, colourless solution of white phosphorus in contact with solid white phosphorus gradually becomes opalescent and orange-yellow by reflected, but clear and yellowish-red by transmitted, light. The hydrosol thus formed is unstable, and, after some time, deposits a scarlet crust of red phosphorus on the glass walls of the vessel. The formation of the hydrosol must result from the conversion, under the influence of the diffused light, of the dissolved white phosphorus into the red modification, which is almost insoluble in ether, and separates, therefore, at first in the colloidal form. The strong yellow colour of the hydrosol supplies further evidence that the light red colour of the red phosphorus depends on the finely-divided state of the latter. So soon as red phosphorus is deposited on the walls of the vessel, the solution is free from the hydrosol, partly because the colloid is completely precipitated and partly because the deposit protects the remaining white phosphorus from the action of light.
G. Y.

Ionisation by Phosphorus and Phosphorescence. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1908, 147, 842—844).—It has been shown previously (Abstr., 1905, ii, 72) that the air which has passed over phosphorus is the seat of a true ionisation, and the ions produced have a small mobility. It is now found that when an air current of greater velocity is employed, the phosphorescence becomes elongated in the direction of the current, and with a further increase in the velocity, definitely separates itself from the phosphorus with the production of a dark space. The phosphorus generally retains a slight phosphorescence, but this disappears finally when the velocity is sufficiently augmented. If the tube is sufficiently long, the phosphorescence which assumes the form of a phosphorescent column can be removed several metres from the phosphorus by regulating the air-current. A condenser placed in or beyond, but not before, the phosphorescence becomes charged, whilst an iodide-starch paper (test for ozone) becomes blue in the positions in which the condenser is charged. It is thus shown that the phosphorescence, ionisation, and ozone are produced in the same region, and therefore that the three phenomena are produced, not by the oxidation of the phosphorus itself, but of some substance emanating from it. This might be either phosphorus vapour or phosphorous oxide. From the results obtained by Jungfleisch (Abstr., 1905, ii, 244) and by Schenk, Mihr, and Banthien (Abstr., 1906, ii, 326), the latter supposition seems the more probable. This view is also supported by the observation of the authors, that if the dark space is cut suddenly, phosphorescent bubbles are formed, which travel slowly in opposite directions, disappearing either on collision or, more rarely, of their own accord.

If the dark space contains phosphorous oxide, which is spontaneously inflammable, this phenomenon is explained, the movement of the luminous bubbles being the propagation of explosive waves.

The transformation of phosphorus into phosphoric oxide is a vivid combustion, and it is therefore to be expected that the ions produced would be of the same nature as in other cases of combustion. The analogy between the large ions of phosphorus and those of the gases of flames has been pointed out by Bloch and by Harms (*Abstr.*, 1904, ii, 331), who finds an increase in the mobilities as the phosphorus is approached. The latter result is confirmed by the authors, who obtain values up to 0.1 mm. close to the phosphorus. The mobilities can, however, be greatly increased (up to 2—3 mm.) by inserting a cotton plug beyond the phosphorus to retain the fumes formed on the latter. It seems, therefore, that the phosphorus ions are produced by the combustion of the phosphorous oxide, and rapidly rendered heavy by the presence of liquid or solid particles. E. H.

Sublimation of Arsenic. W. P. A. JONKER (*Chem. Weekblad*, 1908, 5, 783—785).—The sublimation point of arsenic determined by the aid of a thermopile is $616^{\circ}/760$ mm. A. J. W.

The Luminosity of the Bunsen Flame. BURRITT S. LACY (*Zeitsch. physikal. Chem.*, 1908, 64, 633—640. Compare Haber and Richardt, *Abstr.*, 1904, ii, 166).—In order to study the cause of the luminosity in the inner zone, the author has introduced methane into a separated Bunsen flame, 5 mm. above the summit of the inner cone, without producing any effect on the luminosity. Special experiments were made to eliminate the cooling effect of the current of methane. The results are in accordance with Haber and Richardt's view, that the production of the light is a luminescence phenomenon. The presence of methane in the middle zone of the separated flame was confirmed.

The constant $k = [\text{H}_2\text{O}][\text{CO}]/[\text{CO}_2][\text{H}_2]$ was found to be the same whether the gases were taken from a zone just above the green cone or from a higher zone at a temperature 300° lower, being about 3.7. A catalytic influence of the platinum tube used was, however, observed. C. H. D.

Precipitated Silica. HENRY LE CHATELIER (*Compt. rend.*, 1908, 147, 660—662).—The existence of hydrates of silica is questioned on account of the variable amounts of water revealed by analysis. When gelatinous silica, purified from electrolytes by diffusion, was heated in a sealed tube at 320° for six hours, no change in appearance or consistency could be detected. The author draws the conclusion that silica, like chromium trioxide, does not form hydrates, but on account of its absolute insolubility remains in an extremely fine state of division when precipitated. Freshly-precipitated gelatinous silica in distilled water may be used to polish hard substances, such as bronze. R. J. C.

Products of the Arc and Spark Electric Discharge in Liquid Argon. FRANZ FISCHER and GEORGE ILIOVICI (*Ber.*, 1908, 41, 3802—3810).—If compounds of argon are capable of existence, they are probably endothermic, and might be produced at a high temperature and afterwards be preserved by sudden cooling, as in the formation of ozone in liquid oxygen (compare Abstr., 1907, ii, 163, 340). Cadmium was used for the electrodes, and with the spark discharge, after three hours in liquid argon, 3.3 mg. of an olive-green substance, and with the arc after 140 minutes, 22.7 mg. of a black substance, were obtained. These, on examination, proved to contain cadmium nitride, but mixed with cadmium in the case of the arc product. The spectrum of the gas obtained by heating these substances in a vacuum showed the lines of nitrogen, hydrogen, cadmium, and mercury, with some lines of argon, and the gas obtained by the action of phosphoric acid on the substance gave hydrogen, mercury, and argon lines—nitrogen could not be detected, but the product after the action contained ammonia. The nitrogen must have been derived from small traces of air in the argon used.

The spectroscopic examination was carried out in tubes fitted with aluminium electrodes, previously heated at 150° to expel gases. The tube gradually became "hard," and the nitrogen spectrum disappeared, leaving only the argon and hydrogen lines. This behaviour of the spectrum tube makes the source of the argon uncertain, as it is in very small quantities. The conclusion is drawn provisionally that the argon is absorbed by the nitride. W. R.

Electrolytic Soda Industry. Theory of the Bell-chamber Process. ANDRÉ BROCHET (*Compt. rend.*, 1908, 147, 674—676).—The salt solution undergoing electrolysis flows through the apparatus from cathode to anode. If the velocity of the liquid is equal or superior to that of the OH' ions, the yield should be theoretical. The velocity of the OH' ion varies directly as the ionic mobility and current density, and inversely as the conductivity. When the layer of liquid containing only OH anions remains stationary, the concentration of the caustic alkali leaving the apparatus varies directly as the conductivity and inversely as the ionic mobility, but is independent of current density and the nature of the cation. It follows that solutions of potassium chloride give a stronger alkali than common brine. Temperature has no influence on the strength of alkali obtained, but a high temperature economises current.

R. J. C.

Transparent Silver and other Metallic Films. THOMAS TURNER (*Proc. Roy. Soc.*, 1908, A, 81, 301—310. Compare Beilby, Abstr., 1904, ii, 647).—The investigations of Faraday on the conditions of formation of transparent metallic films have been extended. Gold leaf does not undergo any change at 500°, but rapidly becomes transparent at 550°, microscopic examination showing that the originally translucent film has become aggregated to opaque masses, leaving clear spaces between them. Soft gold, which has not

been mechanically strained, does not show this sudden change of properties.

Silver foil becomes slightly transparent in air at 240° , and more rapidly at higher temperatures. Heating to 500° in hydrogen or in charcoal powder does not produce transparency, whilst the effect on gold is independent of the surrounding gas. The presence of oxygen is necessary for the change in silver, although the quantity of oxygen absorbed is very minute. The particles of aggregated silver are smaller and less opaque than those of gold.

Copper undergoes a similar change, but much transparent oxide is formed. This is the origin of the coloured surface films obtained on oxidising copper. Aluminium and alloys of copper and zinc do not become transparent when heated.

C. H. D.

The True Atomic Weight of Silver according to Stas's Experiments. LOUIS DUBREUIL (*Compt. rend.*, 1908, 147, 856—859).—It has been shown previously (this vol., ii, 936) that it is generally impossible to deduce the true value of an atomic weight from the measurement of a single analytical ratio, and that the method of least squares enables the most probable value for the atomic weights in question to be determined in each experiment. Comparison of the values so obtained for the same element gives the means of determining the true atomic weight, and the result is the more probable the greater the number of methods employed. The author has applied this method of calculation to the values obtained by Stas for the analytical ratios of AgCl, I, AgI, Ag₂S, KCl, NH₄Cl, NaCl, LiCl, KBr, NaBr, NH₄Br, AgNO₃, and Ag₂SO₄ compared with Ag, and for the ratios KCl/AgNO₃, NH₄Cl/AgNO₃, AgCl/AgClO₃, AgBr/AgBrO₃, and AgI/AgIO₃, and, as a general mean of them all, has obtained the value 107.9921 for the atomic weight of silver, the extreme values of the series being 108.0313, obtained from the ratio AgI/Ag, and 107.9449, for the ratio KBr/Ag.

Taking into consideration the fact that all the results employed are taken from the work of one experimenter, the conclusion is drawn that silver has the atomic weight 108.

E. H.

Alloys of Silicon and Silver. G. ARRIVAUT (*Compt. rend.*, 1908, 147, 859—861).—Wöhler (*Ann. Chim. Phys.*, 1858, [iii], 54, 222), Warren (Abstr., 1889, 1125; 1893, ii, 474), and de Chalmot (Abstr., 1896, ii, 362) have obtained substances which they considered to be silver silicides, whereas Percy, Moissan (Abstr., 1896, ii, 173; 1904, ii, 560), and Vigouroux (Abstr., 1907, ii, 543) have repeatedly stated that silver and silicon do not combine. In view of this divergence of opinion, the author has examined mixtures of silver and silicon by Tamman's thermal method. The results are given in a table and in the form of curves.

Examination of the latter shows that the liquidus consists of two branches starting from the melting points of silver (950°) and silicon (1415°) respectively, and intersecting at about 800° in a point corresponding with about 5% of silicon. The solidus consists simply of a horizontal line passing through the eutectic point and extending

from 0% to 90% of silicon; thus silver and silicon do not give any point of combination. Consideration of the periods of eutectic crystallisation suggests the existence of mixed crystals of silicon and silver, but this is not confirmed by analysis. In the fusions containing 40—60% of silicon, a small, white pearl is observed on the bluish-grey button of slightly oxidised silicon. This is formed probably owing to the increase in volume of the silicon on solidification. It contains 4.8% of silicon and 94.85% of silver. E. H.

Silver Sub-halides. A. P. H. TRIVELLI (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 358—372).—A critical comparison of the two chief theories regarding the nature of the silver sub-halides. It is shown that the phenomena, which are usually cited in support of the view that the sub-halide is an adsorption compound of colloidal silver and silver halide, can be explained equally satisfactorily in terms of the theory that the sub-halide is a molecular compound. In certain cases, the molecular theory accounts for the observed facts more satisfactorily than the adsorption theory.

In an appendix, it is pointed out that the reducing action of ammonium persulphate can be explained more simply in terms of the molecular theory than by the adsorption hypothesis. The denser portions of the developed image contain more silver and silver sub-halide and less silver halide than the less dense regions. A sodium thiosulphate solution will, in consequence, be more quickly saturated with silver thiosulphate in the less dense parts of the image. In the denser regions, the greater concentration of unchanged sodium thiosulphate will cause the sub-halide to be decomposed to a greater extent, and the resulting greater concentration of free silver is the cause of the more energetic action of the ammonium persulphate. H. M. D.

Reaction between Silver Sulphide and Silver Sulphate. Production of a Dark-coloured Glass. OTTO SACKUR (*Ber.*, 1908, 41, 3356—3359).—Experiments to determine the dissociation pressure of the system $\text{Ag}_2\text{S} + \text{Ag}_2\text{SO}_4 = 4\text{Ag} + 2\text{SO}_2$ were unsuccessful, as, although a constant pressure was obtainable after heating at a constant temperature (above 300°) for some days, repetition of the experiment gave different values. The pressure at 300° is above 10 atmospheres.

When heated in Thüringian glass, the mixture imparts to the glass surface, below 400° , after some time a reddish-brown colour, which absorbs the actinic rays of the spectrum. Such a glass contains several per cent. of silver. W. R.

Preparation and Composition of the Hydrogen Carbonates of Calcium and Barium. EDWARD H. KEISER and SHERMAN LEAVITT (*J. Amer. Chem. Soc.*, 1908, 30, 1711—1714).—Experiments are described which show that calcium hydrogen carbonate is precipitated when potassium or ammonium hydrogen carbonate is added to a solution of calcium chloride at 0° , and that the salt can be separated and analysed if the temperature is not allowed to rise above 1° or 2° . Even at this temperature, the compound slowly decomposes. The results of analysis point to the formula $\text{CaCO}_3 \cdot 1.75\text{H}_2\text{CO}_3$.

Barium hydrogen carbonate can be obtained similarly by the action of ammonium hydrogen carbonate on barium chloride solution at 0°, but it undergoes gradual decomposition, and is therefore difficult to analyse. E. G.

Composition of the Hydrogen Carbonates of Calcium and Barium. EDWARD H. KEISER and LEROY MCMASTER (*J. Amer. Chem. Soc.*, 1908, 30, 1714—1718).—Calcium and barium hydrogen carbonates were prepared in the manner described by Keiser and Leavitt (preceding abstract), except that precipitation was effected in a solution containing gelatin in order to retard decomposition. Analysis was effected by determining the ratio of carbon dioxide to calcium or barium oxide. The results show that the calcium salt has the composition $\text{CaCO}_3 \cdot 1.8\text{H}_2\text{CO}_3$, and the barium salt the composition $\text{BaCO}_3 \cdot 1.5\text{H}_2\text{CO}_3$. E. G.

Preparation of Calcium, Strontium, and Barium Silicides. TH. GOLDSCHMIDT (D.R.-P. 199193).—Calcium silicide may be produced by heating in an ordinary furnace a mixture of silicon and calcium oxide, the reaction being facilitated by the addition of some calcium fluoride and chloride. The interaction takes place as follows: $5\text{CaO} + 5\text{Si} = 2\text{CaSi}_2 + 3\text{CaO} \cdot \text{SiO}_2$. A similar change occurs with the oxides of the other alkaline earths. G. T. M.

Zinc Phosphides. PIERRE JOLIBOIS (*Compt. rend.*, 1908, 147, 801—803).—Zinc and phosphorus were heated together in a crucible until phosphorus vapour ceased to be evolved. The product was freed from excess of zinc either by ignition in a vacuum at 600° or by treatment with mercury or fuming nitric acid. The residual phosphide, Zn_3P_2 , is identical with that described by Vigier (*Bull. Soc. chim.*, 1861, 3, 5), and forms octahedral crystals, $D^{13} 4.55$, which dissolve readily in hydrochloric acid, giving pure phosphine.

The preparation of the phosphide, ZnP_2 , from its elements is also described. This phosphide is non-crystalline, and has $D^{15} 2.97$; at 400°, it undergoes dissociation into phosphorus and Zn_3P_2 .

W. O. W.

Sulphides of the Rare Earths. I. Cerium Sulphides and their Limits of Existence. WILHELM BILTZ (*Ber.*, 1908, 41, 3341—3350. Compare Sterba, *Abstr.*, 1904, ii, 662).—*Cerium disulphide*, Ce_2S_4 , is prepared by heating cerium sulphide in a current of hydrogen sulphide at 580—600°, the experiment being controlled by weighing from time to time; 2 to 3 grams require twenty hours for complete conversion. It forms a dark yellowish-brown, crystalline powder, moderately stable in air and cold water. An oxygenated product, $\text{Ce}_2\text{S}_{2.5}\text{O}_8$, has also been obtained, and as this is of approximately the same weight as the disulphide, a complete analysis is necessary in characterising the compound. Hydrochloric acid (17.7%) dissolves the disulphide in the cold, an odour of hydrogen persulphide is noticed, and afterwards sulphur is precipitated. This is held to prove that the disulphide is not a true analogue of the dioxide, but a

polysulphide, $\text{Ce}_2\text{S}_3\cdot\text{S}$. The related *lanthanum disulphide*, $\text{La}_2\text{S}_3\cdot\text{S}$, is dark yellow, and also gives hydrogen persulphide under similar conditions.

The red sesquisulphide, Ce_2S_3 (Muthmann and Stützel, Abstr., 1900, ii, 142), is obtained on heating the disulphide or the sulphate in a current of hydrogen sulphide at $750\text{--}800^\circ$.

The conversion of the disulphide into the sesquisulphide has been examined up to 1200° . The temperature of decomposition is about 720° ; the lower sulphide is stable at a red heat, and does not react with hydrogen or nitrogen at that temperature, but between 1400° and 1500° it melts and decomposes. The sesquisulphide prepared at 745° ; when heated in a current of hydrogen sulphide for thirty hours at 615° , did not re-absorb sulphur. This irreversibility is only apparent, as by heating the disulphide in a current of hydrogen at 400° the sesquisulphide was obtained, and this product re-absorbed 4.2% sulphur.

The heat of solution of the disulphide, CeS_2 , in hydrochloric acid is 32,500 cal.; that of $\text{CeS}_{1.5}$, 37,800 cal. (39,500 cal. from product prepared at 400°). From these figures, the equation $4\text{CeS}_2 = 2\text{Ce}_2\text{S}_3 + 2\text{S(amorp.)} - 18,600$ cal. is calculated.

By the use of Nernst's equation for heterogeneous equilibria, the decomposition temperature is calculated to be 793° , whereas that found was roughly 720° .
W. R.

Eutectics. I. The Alloys of Lead and Tin. WALTER ROSENHAIN with P. A. TUCKER (*Phil. Trans.*, 1908, A, 209, 89—122).—Alloys of pure lead and pure tin have been studied by thermal and microscopic methods, the curves of ordinary cooling and of differential cooling being taken. The eutectic point is at 62.93% of tin and 180° . Lead forms solid solutions with from 0 to 16% Sn at 180° . Former observers have found the presence of eutectic in alloys containing much less tin, and this is shown to be due to the slowness with which diffusion takes place in the solid alloys. Heating at 175° for six weeks was found to be necessary to bring about equilibrium. On the other hand, tin does not form solid solutions with small quantities of lead.

Alloys containing from 18 to 63% of tin undergo a change, accompanied by development of heat, on cooling to 149° . In alloys containing from 8 to 18% Sn, the transformation takes place at lower temperatures, the passage of the solid solution from the β - to the α -form involving the rejection of a part of the tin. The alloy with 8% Sn appears to remain in the β -form down to the temperature of liquid air. The lead constituent of the eutectic, however, appears to remain in the metastable β -form. The density of the alloys confirms the view that the lead constituent of the eutectic differs from the stable α -solid solution.

A microscopic study of the eutectic alloy shows that it is composed of grains, within each of which the crystallites have a definite orientation. Each grain is to be regarded as a spherulitic crystal of the β -solution, the tin forming a matrix or filling.

The paper is illustrated with photo-micrographs.

C. H. D.

Electrolytic Corrosion of Brasses in Synthetic Sea-Water. AZARIAH T. LINCOLN and G. C. BARTELLS, jun. (*J. Physical Chem.*, 1908, 12, 550—556. Compare Lincoln, Klein, and Howe, *Abstr.*, 1907, ii, 953).—The corrosion of fully annealed copper-zinc alloys was measured, using an artificial sea-water prepared by dissolving salts. The corrosion curves are similar to those obtained in solutions of sodium chloride. With the appearance of the γ -phase, copper ceases to appear in the corrosion product. C. H. D.

Recalculation of the Vapour Pressure of Mercury. T. H. LABY (*Phil. Mag.*, 1908, [vi], 16, 789—796).—The recorded observations of the vapour pressure of mercury have been compared, and the more concordant values have been combined with the object of obtaining a table of most probable values. Two Kirchhoff formulæ are given which satisfactorily express the recorded observations. The vapour-pressure values (in terms of mm. of mercury at 0°) are recorded for every 5° between 15° and 365°, and also for 370°, 380°, 390°, 400°, and 450°. It is also shown that the experimental data of Cailletet, Colardeau, and Rivière for temperatures up to 700° can be satisfactorily expressed by means of a Kirchhoff formula.

H. M. D.

Constitution of Certain Mercuric Compounds with Complex Cations. II. VINCENZO BORELLI (*Gazzetta*, 1908, 38, ii, 421—474. Compare this vol., i, 515).—According to Abegg and Bodländer's principle of electro-affinity (*Abstr.*, 1899, ii, 542), the tendency of the mercuric halogen salts to form complex cations is weaker the stronger the anion combining with the mercuric ion to form the cation, since increase of the electro-affinity of the halogen radicle should be accompanied by an increase in the tendency of the radicle to dissociate according to the scheme: $\text{HgX}'' \rightarrow \text{Hg}'' + \text{X}'$. This is actually found to be the case, the tendency to form these complex ions being greatest with mercuric iodide and cyanide, less marked with the bromide, and so slight with the chloride that the corresponding double salt cannot be isolated. The author has studied the complex salts formed by mercuric iodide, bromide, chloride, and thiocyanate with mercuric perchlorate, the results obtained being parallel with those observed in the case of the similar complex salts yielded by mercuric cyanide. The behaviour of insoluble mercuric compounds of the type HgX'' toward mercuric salts with strong anions is quite analogous to that of the insoluble salts of the type HgX'_2 .

Iodomercury perchlorate, $\text{HgI} \cdot \text{ClO}_4$, forms bundles or mammillary masses of white, opaque prisms, which deliquesce and turn yellow in the air, and are decomposed by water with liberation of mercuric iodide. Cryoscopic measurements in water give values for the molecular weight lower than that calculated for complete dissociation of the compound into its components and allowing for the partial hydrolysis of the mercuric perchlorate according to the equation: $\text{Hg}(\text{ClO}_4)_2 + \text{H}_2\text{O} = \text{Hg}(\text{OH}) \cdot \text{ClO}_4 + \text{HClO}_4$ (compare Heimbucher, *Diss.*, Würzburg, 1904; *Abstr.*, 1904, ii, 465). The depression of the

freezing point of water by mercuric perchlorate is diminished by mercuric iodide, the diminution increasing with the proportion of iodide present in the solution; the complex molecular concentration hence undergoes a corresponding diminution. Similar behaviour is observed when mercuric cyanide is dissolved in an excess of a concentrated solution of mercuric perchlorate. The conductivity of mercuric perchlorate solution is also diminished by the presence in the solution of mercuric iodide, owing to diminution of the ionic concentration and to the lower mobility of the new ions formed. The addition of mercuric iodide or cyanide produces an increase in the molecular concentration of mercuric perchlorate solution when this is not excessively concentrated, and a diminution when an excess of the perchlorate is present. These results are regarded as due to various reactions between the mercuric iodide and the ions, Hg^{++} and ClO_4' , originally present in the solution. The analogy between these results and those obtained with mercuric cyanide indicates that the mercuric iodide unites with the Hg^{++} ions to give complex cations; this view is supported by transport measurements of solutions of mercuric iodide containing excess of the perchlorate.

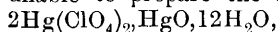
Bromomercury perchlorate, $\text{HgBr}\cdot\text{ClO}_4$, forms bundles or millimetric masses of short, white prisms. When mercuric bromide is dissolved in a solution of mercuric perchlorate, it causes depression of the freezing point and regular elevations of the boiling point, and, consequently, an increase in the concentration. Into these solutions, mercuric bromide enters under the form of the ions HgBr^+ , and also, to a slight extent, of the ions $\text{Hg}_2\text{Br}_2^{++}$. The existence of these complex ions is shown by measurements of the variation of the concentration of mercuric bromide at the electrodes during electrolysis.

Chloromercury perchlorate could not be isolated. The presence of 1 mol. of mercuric chloride per mol. of the perchlorate in solution produces an increase of 0.028% in the original conductivity, but the addition of a further 1.5 mols. of the chloride causes no further increase. The conductivity curve shows that mercuric chloride exhibits a tendency to form the ions HgCl^+ about 500 times less than the tendency of the cyanide to form the ions HgCN^+ .

The author has not succeeded in isolating chloromercury nitrate, $\text{HgCl}\cdot\text{NO}_3$ (compare Morse, Abstr., 1903, ii, 12), but conductivity measurements demonstrate the undoubted presence of the ions HgCl^+ and NO_3^- in solutions containing mercuric chloride and nitrate.

Thiocyanomercury perchlorate, $\text{Hg}(\text{CNS})\cdot\text{ClO}_4$, was obtained as a white, crystalline crust. The addition of mercuric thiocyanate to a solution of mercuric perchlorate produces a diminution in the molecular concentration.

The author has been unable to prepare the compound,



described by Chikashigé (Trans., 1905, 87, 822), the products obtained being basic compounds containing approximately $2\text{Hg}(\text{ClO}_4)_2$ per 3HgO . When mercuric oxide is dissolved in a solution of mercuric perchlorate, it produces diminution of the molecular concentration; the diminution produced increases with the concentration

of the perchlorate solution, as, therefore, does the complexity of the compounds formed.
T. H. P.

Precipitation of Gelatinous Mixtures of Alumina and Silica, and their Relation to Allophane, Halloysite, and Montmorillonite. H. STREMMER (*Centr. Min.*, 1908, 622—632, 661—669).—The gelatinous precipitates obtained from solutions of sodium silicate and aluminium acetate are of very variable composition, depending on the strength of the solutions and on their acidity. In an acid solution there is at first only a turbidity, and the gelatinous precipitate afterwards deposited is richer in silica than that from a neutral solution.

Carbonic acid and acetic acid dissolve the alumina more readily than the silica from the precipitates. The conclusion is drawn that these precipitates do not represent any definite hydrated aluminium silicate, but that they are simply mixtures of gelatinous aluminium hydroxide and hydrated silica. The same relations also exist in the various amorphous minerals of the clay group. The published analyses of these are tabulated, and they show wide variations in composition: for minerals of the allophane group, the ratio $\text{Al}_2\text{O}_3:\text{SiO}_2$ varies from 1:0.31 to 1:1.91; for the halloysite group, 1:1.68 to 1:3.89; and for the montmorillonite group, 1:2.51 to 1:5.32. The conclusion is therefore drawn that these are not definite mineral species, but mixtures in variable proportions of colloidal aluminium hydroxide and hydrated silica.
L. J. S.

Ferromagnetic Nitrogen Compounds of Manganese. EDGAR WEDEKIND and THEO. VEIT (*Ber.*, 1908, 41, 3769—3773. Compare Abstr., 1907, ii, 353; Shukoff, this vol., ii, 484).—With the object of ascertaining whether elements which are gases at the ordinary temperature form ferromagnetic derivatives with manganese, the nitrides of manganese have been investigated. Trimanganese nitride, Mn_3N_2 (compare Prelinger, Abstr., 1894, ii, 16), has only feeble magnetic properties, whilst pentamanganese nitride, Mn_5N_2 , is slightly more magnetic. The nitride, Mn_7N_2 , obtained by the action of ammonia on manganese heated with an oxy-hydrogen blowpipe, has stronger magnetic properties than either of the above nitrides, and is almost as magnetic as manganese boride; it is readily attacked by acids and alkalis.

Chromium nitride, CrN , has only feeble magnetic properties.

W. H. G.

The System Iron-Phosphorus. E. GERCKE (*Metallurgie*, 1908, 5, 604—609).—Alloys rich in phosphorus were prepared by adding red phosphorus to molten iron in a magnesite crucible. The product containing 17.3% P was re-melted with different proportions of iron. The eutectic temperature is 980° ; mixtures low in phosphorus show considerable undercooling. Iron retains up to 1.70% of phosphorus in solid solution, beyond this the eutectic, containing 10.2% P, is present as a constituent. The solid solution undergoes a change of structure, which has not been fully investigated, at 600° .

C. H. D.

The Ternary System Iron-Phosphorus-Carbon. PAUL GOERENS and W. DOBBELSTEIN (*Metallurgie*, 1908, 5, 561—566. Compare Wüst, this vol., ii, 287).—The ternary eutectic point of the system is found to lie at 1.96% C, 6.39% P, and 91.15% Fe, and at 953°. The position of the three binary eutectic curves in the system iron-iron carbide-iron phosphide has also been determined. Both thermal and microscopic methods have been employed.

The microscopic sections are best prepared by etching and heat-tinting, subsequently re-polishing lightly. The oxide film is much more readily removed from cementite than from the phosphide, thus allowing the two to be distinguished.
C. H. D.

The Iron-Carbon Equilibrium. GEORGE B. UPTON (*J. Physical Chem.*, 1908, 12, 507—549).—The results of other observers are examined and recalculated, the silicon and other elements present in the samples examined being calculated as "equivalent carbon." The author concludes that cementite must find a place in the diagram of stable equilibrium, and he assumes the formation of three carbides in all, Fe_6C , Fe_3C , and Fe_2C , of which the first is stable only above 800° and the second above 600°. The brittleness of steel at 500—550° is considered to be due to the change from Fe_3C to Fe_2C . An equilibrium diagram has been constructed on these assumptions.

C. H. D.

Hydrolysis of Ferric Chloride; Influence of Neutral Salts. G. MALFITANO and LEOPOLD MICHEL (*Compt. rend.*, 1908, 147, 803—806. Compare Abstr., 1907, ii, 692; this vol., ii, 111, 288).—The phenomena of the colloidal state are more pronounced and appear more rapidly in solutions of ferric chloride to which potassium chloride has been added than in solutions of ferric chloride alone. The authors have measured the increase in electrical conductivity of solutions of ferric chloride, alone and with varying amounts of potassium chloride, produced by raising the temperature from 18° to 100° for fifteen minutes, and after allowing the solutions to remain for sixteen and twenty-four hours respectively. The results lead to the conclusion that the rate of hydrolysis of the ferric chloride depends on the proportion of potassium chloride present, and that the size of the micro-cells of ferric hydroxide is increased by the addition of this salt. The number of ferric ions being diminished, there are fewer centres of attraction for the ferric hydroxide molecules, and consequently the individual cells are more voluminous.

The chlorides of sodium, ammonium, barium, and magnesium, and also potassium nitrate, behave in a similar manner. Mercuric chloride, on the other hand, being a non-electrolyte, has no appreciable influence on the course of the hydrolysis. Salts containing multivalent negative ions, such as potassium sulphate, behave like the multivalent acids previously studied in hindering hydrolysis.
W. O. W.

Molybdates of Nickel and Cobalt. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1908, [iv], 3, 1012).—The author has been informed by Marckwald that the attribution to the latter by Grossmann and

Schück (this vol., ii, 230) of certain work on nickel and cobalt molybdates is inaccurate. T. A. H.

Antimony Trichloride as Ionising Solvent. Z. KLEMENSIEWICZ (*Bull. Acad. Sci. Cracow*, 1908, 485—494).—The measurements were made by the electrical conductivity method with platinised electrodes in the usual way. The carefully-purified solvent has D^{75} 2.681 and D^{97} 2.647; the smallest conductivity observed amounted to 8.5×10^{-7} reciprocal ohms.

As solutes, the chlorides of potassium, rubidium, ammonium, and thallium were used, and measurements were made up to a dilution of 1024 litres and at different temperatures. The conductivities in dilute solutions are greater, in concentrated solutions (above $N/10$) less, than for the corresponding aqueous solutions. It is probable that the degree of ionisation is less for solutions in antimony chloride than in water, but that the ionic velocity is greater in the former case. The conductivity of the solutions increases regularly with the temperature from 70° to 150 — 200° .

The viscosity of antimony trichloride has been measured from 80° to 200° . The curve obtained by plotting the fluidity (reciprocal of the viscosity) against the temperature appears to show a change of direction at 120° , but a high degree of accuracy is not claimed for the results. G. S.

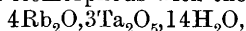
Melting-point Curves for the Systems Bismuth + Chlorine and Bismuth + Bromine. B. G. EGGINK (*Zeitsch. physikal. Chem.*, 1908, 64, 449—505).—After reviewing the various compounds of bismuth with chlorine and bromine which have been described, the author proceeds to a theoretical discussion of the possible liquid-solid equilibria in a system of two components in which two liquid phases may occur. In this discussion, the author uses the graphical method introduced by van Ryn van Alkemade (*Abstr.*, 1893, ii, 363).

The experimental study of the systems bismuth + chlorine and bismuth + bromine has shown that compounds of the formulæ BiCl and BiBr exist, which, on melting at 320° and 287° respectively, both form two liquid phases. Further, an endothermic compound BiCl_4 exists, which is only slightly dissociated in the fused condition. So far as the evidence of the freezing-point curve goes, there are no compounds of the formulæ BiCl_2 , BiBr_2 , and Bi_3Cl_8 ; the author's results are therefore not in harmony with those of Herz and Guthmann (this vol., ii, 199). J. C. P.

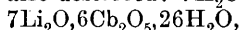
Columbium. CLARENCE W. BALKE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1908, 30, 1637—1668).—A continuation of the investigation of the compounds of columbium and tantalum (*Abstr.*, 1905, ii, 828, 829). The conclusion is confirmed that the coloration produced on the addition of hydrogen peroxide to a solution of columbium in hydrofluoric acid is not due to the presence of titanium, but is probably due to columbium itself. A large quantity of potassium columbium fluoride, K_2CbF_7 , was prepared and carefully purified, and was after-

wards converted into the oxide, which had $D\ 4.8$. This oxide still gave the reaction with hydrogen peroxide, and, in order to study further the question as to whether the reaction might not be due to the presence of some other element, the oxide was converted into the chloride, and the latter fractionally distilled. The whole of the product distilled at about 241° , and no differences could be detected between the fractions obtained. On a spectroscopic examination of the oxide prepared from the chloride, neither tantalum nor titanium lines were observed. Vapour density determinations of the chloride by Dumas' method gave a mean value of 9.45, as compared with the calculated value 9.35 [$Cb = 93.5$]. Specimens of the oxide prepared from the chloride had D varying from 4.48 to 5.02. The chloride had $D\ 2.73-2.77$. A careful determination of the atomic weight of columbium based on the ratio between the chloride and oxide gave as mean of eight determinations the value 93.50 [$O = 16$; $Cl = 34.45$].

A résumé is given of the various columbates described in the literature. Sodium columbate, $Na_2O, Cb_2O_5, 7H_2O$, crystallises in triclinic prisms [$a : b : c = 0.9559 : 1 : 0.8394$; $\alpha = 71^\circ 20'$; $\beta = 105^\circ 30'$; $\gamma = 54^\circ 7'$]. Magnesium columbate, $MgO, Cb_2O_5, 7H_2O$, the silver salt, $Ag_2O, Cb_2O_5, 2H_2O$, the copper salt, $CuO, Cb_2O_5, 3\frac{1}{2}H_2O$, the aluminium salt, $Al_2O_3, 3Cb_2O_5, 12H_2O$, and the cadmium salt, $CdO, Cb_2O_5, 3\frac{1}{2}H_2O$, are described. The potassium salt, $4K_2O, 3Cb_2O_5, 16H_2O$, forms monoclinic crystals [$a : b : c = 0.7120 : 1 : 0.5547$; $\beta = 84^\circ 19'$]. The rubidium salt, $4Rb_2O, 3Cb_2O_5, 14H_2O$, is isomorphous with the salts



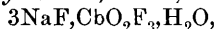
$4Cs_2O, 3Cb_2O_5, 14H_2O$, and $4Cs_2O, 3Ta_2O_5, 14H_2O$, and crystallises in monoclinic prisms [$a : b : c = 0.8815 : 1 : 1.4091$; $\beta = 84^\circ 7'$]. The following columbates are also described: $7K_2O, 6Cb_2O_5, 27H_2O$,



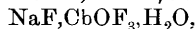
$7Cs_2O, 6Cb_2O_5, 30H_2O$, and $3Rb_2O, 4Cb_2O_5, 9\frac{1}{2}H_2O$.

The following per columbates have been obtained: Na_3CbO_8 , K_3CbO_8 , Rb_3CbO_8 , Cs_3CbO_8 , $MgNaCbO_8, 8H_2O$, $MgKCbO_8, 7H_2O$, $MgRbCbO_8, 7\frac{1}{2}H_2O$, $MgCsCbO_8, 8H_2O$, $CaNaCbO_8, 4H_2O$, and $CaKCbO_8, 4H_2O$.

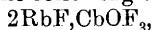
The sodium columbium fluorides, $3NaF, CbOF_3$ and



have been prepared, but the salts, $2NaF, CbOF_3, 2H_2O$ and



described by Marignac could not be obtained. The existence of the potassium salts, $2KF, CbOF_3, H_2O$, $3KF, CbOF_3$, $3KF, HF, CbOF_3$, $5KF, 3CbOF_3, H_2O$, $4KF, 3CbOF_3, 2H_2O$, and $2KF, CbF_5$, described by Marignac, was confirmed. The salt $3KF, HF, CbOF_3$ forms monoclinic needles [$a : b : c = 0.6304 : 1 : 0.4888$; $\beta = 86^\circ 41'$]. The double fluoride, $2RbF, CbF_3$, described by Pennington (Abstr., 1896, ii, 305) could not be obtained, but the following salts were prepared:

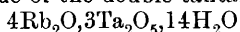


RbF, CbF_5 , and $2RbF, CbO_2F_3, H_2O$. The rubidium tantalum salt, $2RbF, TaO_2F_3, H_2O$, forms thin, white leaflets. The caesium salts, $2CsF, CbOF_3$ and CsF, CbF_5 , are described. The thallium salt,



forms orthorhombic crystals [$a : b : c = 0.4261 : 1 : 1.0129$].

A study has been made of the double tantalates. The salt



forms monoclinic crystals [$a:b:c = 0.8822:1:1.0510$; $\beta = 84^\circ 2'$]. The salts $4\text{Cs}_2\text{O}, 3\text{Ta}_2\text{O}_5, 14\text{H}_2\text{O}$ and $7\text{Cs}_2\text{O}, 6\text{Ta}_2\text{O}_5, 38\text{H}_2\text{O}$ are also described.

The following *pertantalates* have been prepared: Rb_3TaO_8 , Cs_3TaO_8 , $\text{MgNaTaO}_8, 8\text{H}_2\text{O}$, $\text{MgKTaO}_8, 7\text{H}_2\text{O}$, $\text{MgRbTaO}_8, 9\text{H}_2\text{O}$, and $\text{CsNaTaO}_8, 4\frac{1}{2}\text{H}_2\text{O}$.

E. G.

Spectrum and the Bromides of Columbium. WILLIAM M. BARR (*J. Amer. Chem. Soc.*, 1908, 30, 1668—1672).—It has been shown by Hall and Smith (Abstr., 1905, ii, 829) that the hydrogen peroxide test for titanium in a solution of columbium in hydrofluoric acid is not trustworthy. For this reason, spectroscopic examination has been resorted to. Hildebrand (following abstract) has submitted carefully-purified columbium oxide prepared by Balke and Smith (preceding abstract) to a spectroscopic examination, and has found that, whilst nearly all the titanium lines were absent from the spectrum, certain lines were present which are common to both metals. A study has therefore been made of the spectra of specimens of columbium oxide prepared from minerals of different character and from different localities, and purified by Balke and Smith's methods. The results indicate that these methods of purification are efficient, that the spectra of columbium from all sources are identical, and that the lines common to both the columbium and titanium spectra are not due to the presence of titanium in the columbium, and probably not to any other element, but are merely coincident lines.

The "Niobunterbromid" described by Rose (*Ann. Phys. Chem.*, 1858, 104, 441) has been studied, and found to be columbium oxybromide, CbOBr_3 . The dark red compound formed simultaneously is the pentabromide, CbBr_5 , as stated by Rose. Both these salts are described.

A columbium iodide has been prepared from the bromide, and is being investigated.

E. G.

Arc Spectrum of Columbium. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1908, 30, 1672—1684. Compare Balke and Smith, and Barr, preceding abstracts).—The arc spectrum of columbium has been measured between $\lambda 2600$ and $\lambda 6000$, using specimens of the oxide obtained from euxenite, tantalite, columbite, and aeschynite. The results are tabulated.

It has been found that Balke and Smith's method for preparing columbium oxide, free from titanium, is satisfactory, and that the existence of any element common to columbium and titanium is very improbable. The identity of the spectra of columbium from different sources affords strong evidence of its elementary character.

E. G.

Metallographic and Metallurgical Notes. [Thermal Diagrams. Microscopy of Alloys.] K. FRIEDRICH (*Metallurgie*, 1908, 5, 593—604).—I. It was found impossible to obtain thermal

diagrams of the systems platinum-sulphur, gold-selenium, gold-sulphur, gold-arsenic, or zinc-sulphur on account of the volatility of one component. The existence of the sulphide, Zn_2S , is improbable.

II. The use of ultra-violet light in the microscopic study of alloys is not found to have any advantages. C. H. D.

Atomic Weight of Palladium. GEORGE I. KEMMERER (*J. Amer. Chem. Soc.*, 1908, 30, 1701—1705).—The results of previous work on the atomic weight of palladium show considerable variation, and, for this reason, the present investigation was undertaken. The experiments were carried out with (*A*) palladiodiammonium chloride purified by Keller and Smith's method (*Abstr.*, 1893, ii, 73); (*B*) the same salt purified by means of ammonium cyanide instead of the mercuric cyanide used by Keller and Smith, and ammonium salts instead of sodium or potassium salts, and (*C*) palladiodiammonium cyanide, $\text{Pd}(\text{NH}_3\text{CN})_2$. In each case a porcelain boat containing the salt was enclosed in a tube heated by an electric heater, and was reduced to the metal by means of carefully-purified electrolytic hydrogen. The following results were obtained: salt *A*, mean of five experiments, 106.399; salt *B*, mean of four experiments, 106.442; salt *C*, mean of six experiments, 106.458. The mean value of all the determinations gave an atomic weight, 106.434 [$\text{Cl} = 35.473$; $\text{H} = 1.008$; $\text{N} = 14.01$].

E. G.

Mineralogical Chemistry.

Natural Zirconium Oxide Free from Iron. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1908, **21**, 2270—2271).—Of the three forms in which Brazilian zirconium ore occurs, that containing the greatest amount of zirconium is the black, glassy, lump variety ; analysis gave :

ZrO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	SiO ₂ .	ZrSiO ₄ .	Total.
94.12	0.98	3.22	0.43	1.98	100.73

When examined under the microscope, this mineral was found to be composed of black particles embedded in a brownish-yellow, powdery substance. When separated mechanically, the black portion was found to be quite free from iron ; analysis gave :

ZrO ₂ .	SiO ₂ .	TiO ₂ .	Insol.	Total.
97.97	1.72	1.20	0.10	100.99

From this it is evident that the colour previously ascribed to the presence of iron must be caused by the titanium, as, indeed, must be the colour of many other stones and minerals. Crystalline, natural zirconium oxide is feebly radioactive ; it has D 5.41, a value somewhat higher than that, D 5.1, of the artificial, crystalline substance.

J. V. E.

Kröhnkite. Natrochalcite (a New Mineral), and Other Sulphates from Chile. CHARLES PALACHE and CHARLES H. WARREN (*Amer. J. Sci.*, 1908, [iv], 26, 342—348 *).—The specimens described are from copper veins in the mining district of Chuquicamata, in the province of Antofagasta, and include kröhnkite, natrochalcite, blödite, brochantite, atacamite, chalcathite, copiapite, botryogen, sideronatrite, halite, and gypsum.

Kröhnkite.—The large, well-developed crystals are monoclinic, with $a : b : c = 0.5229 : 1 : 0.4357$; $\beta = 56^\circ 17\frac{1}{2}'$; they are twinned on (001), and have a perfect cleavage parallel to (010); hardness $2\frac{1}{2}$. Three types of specimens are distinguished: (i) clusters of octahedroid crystals of a dull greenish-blue colour; (ii) single prismatic crystals and fibrous or acicular aggregates of a pale blue colour; (iii) solid crusts of large, prismatic crystals of a deep vitriol-blue colour. Analysis I gives the usual formula: $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. The water is mainly given off below 150° , but small amounts continue to come off up to 350° . The mineral is fusible without decomposition to a bright green enamel.

Natrochalcite.—This new species occurs as bright emerald-green, monoclinic crystals with an acute pyramidal habit [$a : b : c = 1.423 : 1 : 1.214$; $\beta = 61^\circ 17\frac{1}{2}'$]. Cleavage (001) perfect; hardness $4\frac{1}{2}$. Complete optical determinations are given for this, as also for kröhnkite. Analysis II agrees with $\text{Na}_2\text{SO}_4 \cdot \text{Cu}_4(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. The water is given off gradually above 150° , and between 350° and a low red-heat, sulphuric anhydride is expelled. The mineral readily fuses to a black bead.

Blödite.—Analysis III, of massive, granular material, agrees with the usual formula: $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

	CuO.	MgO.	Na ₂ O.	SO ₃ .	H ₂ O.	Insol.	Cl.*	Total.	Sp. gr.
I.	23.25	—	18.89	47.60	10.72	—	trace	100.46	2.061
II.	41.95	—	8.44	42.10	7.70	0.70	0.05	100.94	2.33
III.	—	12.00	18.20	47.49	21.60	0.50	—	99.70	—

* Cl from atacamite.

L. J. S.

Analyses of Gabbroitic Rocks from Neurode, Silesia. FELIX TANNHÄUSER (*Sitzungsber. k. Akad. Wiss. Berlin*, 1908, 1069—1075).—Nine analyses are given of gabbro, anorthosite, pyroxenite, olivine-gabbro, troctolite, serpentine, diabase, gabbro-aplite, and spessartite.

L. J. S.

Physiological Chemistry.

Heats of Solution of Gases in Blood. MARIO CAMIS (*Mem. Real. Accad. Sci. Torino*, 1908, [ii], 58, 141—169).—The author has measured calorimetrically the heat changes occurring when oxygen and carbon dioxide pass into, or out of, solution in blood. The absorption of 1 gram-mol. of carbon dioxide by the blood is accompanied by the evolution of 5.40 Cal., the corresponding value for oxygen being

* and *Zeitsch. Kryst. Min.*, 1908, 45, 529—538.

10·22 Cal. Taking mean numbers for the daily respiratory exchange, it is calculated that, for a man weighing 70 kilos., this exchange leads to the production of about 127 Cal. per day. The blood pigment and the oxygen absorbed probably react endothermically. The paper concludes with a bibliography. T. H. P.

Estimation of the Respiratory Capacity of Small Quantities of Blood. HEINRICH DRESER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 138—149).—Certain modifications of Haldane's carbon monoxide method, and of Barcroft's gas analysis methods, are proposed. In investigating the effect of certain antipyretics on the respiratory capacity, it was found that many of these produce methæmoglobin formation, and the oxygen so combined is not displaced by carbon monoxide. A comparison of *m*-tolylhydrazine, β -acetylphenylhydrazine (pyrodine), and the semicarbazide of *m*-tolylhydrazine shows that the semicarbazide substitution is much less harmful than the acetyl substitution, as in acetanilide and phenacetin. W. D. H.

Glycine in Normal Blood. ADOLF BINGEL (*Zeitsch. physiol. Chem.*, 1908, 57, 382—388).—By the use of the Fischer-Bergell naphthalenesulphonyl chloride method, it is possible to demonstrate the existence of glycine in normal ox-blood. From 10 litres, 0·2 gram of the glycine compound was obtained. A higher amino-acid, or a peptide-like substance, is also present. W. D. H.

Reaction of the Blood after Intravenous Injection of Acid and Alkali. N. VAN WESTENRYK (*Arch. exp. Path. Pharm., Suppl.*, 1908, 517—527).—That the titration method shows the blood to be alkaline is due to the fact that the acid used may displace a weaker acid in neutral salts. Many indicators are not indifferent chemical substances, but may be themselves acid or basic. By the use of neutral-red and other indicators, the reaction of the blood is shown to be neutral, and remains neutral under various pathological conditions. It alters in experimental acid or alkali poisoning. Alkali poisoning produces stimulation, increasing the action of the heart and kidneys; acid produces the opposite effects. In acid poisoning, the organism remains neutral, as the acid is fixed and neutralised in the muscular tissues. Previous observations that the alkalinity of the blood decreases on destruction of the red corpuscles, are confirmed by the new methods. W. D. H.

Spectrophotographic Investigations on the Action of Hydrocyanic Acid on Blood. LOUIS LEWIN (*Arch. exp. Path. Pharm., Suppl.*, 1908, 337—348).—Details are given of the spectroscopic appearances of blood and hæmoglobin treated with hydrocyanic acid. Cyanomethæmoglobin and cyanohæmatin do not appear to exist; the spectroscopic appearances of their so-called compounds are identical with those of cyanohæmoglobin. Blood so treated catalyses hydrogen peroxide quite typically. The cause of the toxic action of hydrocyanic acid is discussed, and the conclusion is drawn that it is not a blood poison in the biological sense. W. D. H.

Action of Oxidising Salts. ARTHUR R. CUSHNY (*Arch. exp. Path. Pharm., Suppl.*, 1908, 126—137).—The relative activity of oxidising salts on the blood and tissues runs fairly parallel to their oxidising power on simpler chemical compounds. But in many cases other factors step in. The blood corpuscles and pigment react more readily to weak oxidising agents than do muscle or epithelium. In certain cases, also, substances which oxidise blood corpuscles and pigment readily are feeble oxidising agents for simpler chemical substances; the reverse is also seen.

W. D. H.

Hæmolytic Action of Mercury Salts. J. DUNIN-BORKOWSKI (*Bull. Acad. Sci. Cracow*, 1908, 494—505).—The hæmolytic action of mercury salts on the serum-free blood corpuscles (erythrocytes) of different animals has been investigated. With mercuric chloride, the resistance to hæmolysis increases in the order: guinea-pig, sheep, cow, pig, calf, dog. A higher concentration of mercuric chloride than that required to produce complete hæmolysis, agglutinates the erythrocytes.

Mercuric iodide has considerable hæmolytic activity, and mercuric cyanide, although not ionised, is almost as active as the chloride. Potassium cyanide is less active than mercuric cyanide. It follows that hæmolysis does not depend on the concentration of Hg^{++} ions alone, although the ionic concentration probably has some effect, as sodium chloride lessens the activity of mercuric chloride.

The rate of hæmolysis with different concentrations of mercuric chloride has also been measured. With small concentrations, the constants calculated for a unimolecular reaction diminish, and with fairly high concentrations they increase considerably during the reaction, being approximately constant for intermediate concentrations.

The temperature-coefficient for 10° between 18° and 25° is 4.37 for erythrocytes from the guinea-pig, and 2.6 between 18° and 32° for those from the dog. The coefficient is much greater at higher temperatures, owing to the fact that hæmolysis is produced to some extent by heat alone, and, further, the erythrocytes which have been heated alone for some time are much more readily acted on by mercuric chloride than those which have not been heated.

G. S.

Peptolytic Ferments in the Stomach Contents. EMIL ABDERHALDEN and FLORENTIN MEDIGRECEANU (*Zeitsch. physiol. Chem.*, 1908, 57, 317—324).—The observations were made on a dog with a gastric fistula, and confirm those made by Boldyreff, that, after a meal rich in fat, the contents of the duodenum regurgitate into the stomach. Under these conditions, the stomach contents contain a peptolytic ferment, and when neutralised, resolve glycyl-*L*-tyrosine into its constituent amino-acids. Under ordinary conditions, however, the ferment is rendered rapidly inactive by the acid of the gastric juice.

W. D. H.

Influence of the Products of Reaction on the Hydrolysis of Fats by Pancreatic Juice. MILLE. L. KALABOUKOFF and ÉMILE TERROINE (*Compt. rend.*, 1908, 147, 712—715).—Both fatty acids and their sodium salts diminish the rate of hydrolysis; glycerol, on the other hand, has a considerable accelerating action. This acceleration does not take place when a soluble ester, such as monobutyryl, or natural emulsions, such as egg-yolk or cream, or solid fats, such as lard, are submitted to the action of the juice. The action of the glycerol is to be ascribed to the fact that a better distribution of the lipase between the aqueous and oily phases takes place in its presence; other syrupy substances can produce a similar acceleration.

S. B. S.

Digestion in Animals. XXVII. Relationship of Concentration to Absorption in the Intestine. E. S. LONDON and W. W. POLOWZOWA (*Zeitsch. physiol. Chem.*, 1908, 57, 529—546. Compare this vol., ii, 960).—Details are given of the relative amount of absorption in the intestine of the water and sugar contained in solutions of dextrose of different concentrations.

W. D. H.

Absorption of Fat from Intestinal Loops in Dogs. O. H. PLANT (*Amer. J. Physiol.*, 1908, 23, 65—80).—Bile salts increase the absorption of fats from a mixture which contains free fatty acid or soap; they only slightly increase the absorption of neutral oil. Solutions of soap, or biliary solutions of fatty acids, are absorbed more rapidly than emulsified fats. If both bile and pancreatic juice are excluded from the intestinal loop, neutral oil is nevertheless absorbed, and it becomes markedly acid in reaction. Taken as a whole, the experiments favour the view that fats are absorbed in solution rather than as an emulsion.

W. D. H.

Absorption of Iodised Proteins. OTTO VON FÜRTH and M. FRIEDMANN (*Arch. exp. Path. Pharm., Suppl.*, 1908, 214—223).—An iodised protein (iodalbacid) is before absorption in the cat's intestine broken down in large measure so completely that the iodine in the intestinal wall and blood is not in combination as proteose or peptone, but only as alkali iodides.

W. D. H.

Action of Intestinal Astringents on Metabolism. KARL SPIRO (*Arch. exp. Path. Pharm., Suppl.*, 1908, 504—512).—Opium, bismuth subnitrate, and tannigen produce but little change in nitrogenous metabolism in dogs. With opium the C:N ratio in the urine goes up, this is due to a fall in the nitrogen; the nitrogen in the faeces is but little altered. Tannigen, on the other hand, causes a loss of urinary, and an increase of faecal nitrogen, the total excretion of nitrogen being about the normal; a sinking of the C:N ratio in the urine is mainly due to a relative decrease in the excretion of carbon.

W. D. H.

Creatinine Metabolism. G. LEFMANN (*Zeitsch. physiol. Chem.*, 1908, 57, 476—514).—The excretion of creatinine and creatine is

pretty constant in well nourished animals. If either substance is added to the food, it is excreted unchanged. If creatine is given by the mouth or parenterally, it is never changed into creatinine; in inanition it is almost completely excreted as such. Disease of the liver or increased protein catabolism produce first an increase, then a decrease, in creatinine excretion, and when it is lessened, the amount of creatine excreted increases. The liver is the probable seat of creatinine formation. If nephritis is induced by chromates, nearly all the creatinine is changed into creatine, probably by the alteration in the reaction of the urine.

W. D. H.

The Changes in Gaseous Metabolism after Exclusion of the Hepatic Circulation. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1908, 14, 156—179).—Experiments were carried out on ducks, the liver circulation being excluded by ligaturing the portal vein. As birds were employed for the experiments, it was not necessary to make an Eck fistula. The absorption of oxygen and excretion of carbon dioxide were determined both before and after the operation. It was found that the operation caused an increase in the oxygen absorption and in the carbon dioxide excretion, and also an increased respiratory quotient. These results are probably due to the inhibition of glycogen storage, owing to the liver being thrown out of circulation. There is consequently an increased destruction of the carbohydrates, which are thrown into the circulation. The increased respiratory quotient, which is particularly noticeable at some interval after the operation, is probably due to the conversion of the carbohydrate into fat.

S. B. S.

Starvation Metabolism. MIECZYSLAW HALPERN (*Biochem. Zeitsch.*, 1908, 14, 134—142).—The urine of a patient unable to ingest either food or water, owing to cancer in the œsophagus, was analysed. The total daily excretion of nitrogen was 2.058 grams, or, excluding the protein nitrogen excreted, 2.0097 grams. This is less than that found in most other starvation cases, owing probably to the fact that the organism had gradually accommodated itself to a low diet. Other anomalies were also observed, for the ammonia nitrogen was only 3.47% of the total. The excretion of the acetone substances was also small. The purine substances were also small in amount, the daily excretion of purine nitrogen being only 0.05897 gram. The sodium chloride excretion was 0.05265 gram daily, whilst the ratio $N:P_2O_5$ was 6.3 : 1, which is normal and higher than in other starvation cases. The author discusses the possible reasons for the anomalies.

S. B. S.

The Nutritive Value of Protein Cleavage Products. VIII. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1908, 57, 348—362. Compare this vol., ii, 961).—Dogs react differently by feeding on protein cleavage products, some being attacked with vomiting. But in those which do not react in this way, equilibrium and health are well maintained. Complete details of the experiments are tabulated. The same result was obtained also with the products of acid hydrolysis

of flesh and casein. If, however, the greatest part of the tryptophan and tyrosine was removed from the mixture beforehand, the results were not so good.

W. D. H.

Phosphorus in Certain Foods WOLFGANG HEUBNER and M. REEB (*Arch. exp. Path. Pharm., Suppl.*, 1908, 265—272).—The phosphorus-containing substances in foods fall into five groups, namely, inorganic phosphates, phosphatides, nuclein, phosphoproteins, and esters of phosphoric acid. The position of inosic acid and phosphoramidic acid in this classification is uncertain. A method is described for estimating these various compounds, and the results of the examination of various foods, meat, milk, bread, and other vegetable foods, are given in a table.

W. D. H.

Absorption and Assimilation of Organic Compounds of Phosphorus. PIO MARFORI (*Arch. exp. Path. Pharm., Suppl.*, 1908, 378—388).—Natural glycerophosphoric acid differs from the synthetic substance in that its salts, when injected subcutaneously, yield, at least in part, assimilable phosphorus. The phosphorus of lecithin, and, to some extent, that of nucleo-proteins, is also assimilated under these conditions. Nuclein and nucleic acid from yeast, when given by the mouth, did not increase phosphorus assimilation.

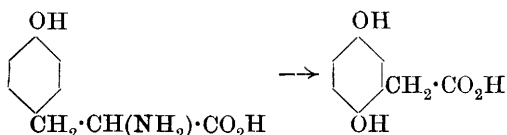
G. B.

The Cleavage of 2:5-Diketopiperazines in the Organism of the Rabbit. II. EMIL ABDERHALDEN and LEONHARD WACKER (*Zeitsch. physiol. Chem.*, 1908, 57, 325—328. Compare this vol., ii, 521).—In the further investigation of this question, it appeared desirable to employ an anhydride which is decomposed by alkali with difficulty. The one selected was *dl*-leucylglycine anhydride, and the experiments confirm those previously reported; this substance is in small measure resolved into its components by the organism of the rabbit.

W. D. H.

The Degradation of Aromatic Substances in the Human Organism. LEON BLUM (*Arch. exp. Path. Pharm.*, 1908, 59, 273—298).—When administered to normal individuals, neither phenylalanine nor tyrosine, normal hydrolysis products of proteins, increase appreciably the aromatic contents of the urine. On the other hand, when given to alcaptonurics, they increase the homogentisic acid excretion in the urine. It has been assumed, therefore, that homogentisic acid is a normal intermediate product of metabolism of aromatic hydrolysis products of proteins, and that alcaptonuric individuals do not possess the power of completely utilising these

products, and that tyrosine in the normal individual is first converted into homogentisic acid. This change can take place in the



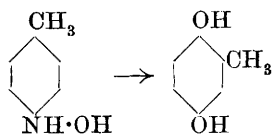
following ways: (a) the degradation may commence in the side-chain,

in which case *p*-hydroxyphenylacetic acid, or hydro-*p*-coumaric acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is first formed, and subsequently converted into homogentisic acid. It was found by Baumann and Schotten that hydro-*p*-coumaric acid, when administered to normal individuals, gave rise to *p*-hydroxybenzoic acid to the extent of 13%, whereas *p*-hydroxyphenylacetic acid was recovered to the extent of 78.6% in the urine. The author found that neither of these acids, on administration to alcaptonurics, caused an increase in the homogentisic acid output.

(b) A change in the relative positions of the hydroxyl group and the side-chain may take place with the formation of *m*- or *o*-tyrosine, which, on secondary oxidation in the para-position and a degradation of the side-chain, could give rise to homogentisic acid. It was found that neither of these tyrosines, when administered to alcaptonurics, increased the homogentisic acid output, and when given to normal individuals they were excreted in the form of the corresponding hydroxyphenylacetic acids to the extent of about 30%.

(c) The side-chain may be degraded to acetic acid, with a concurrent change in the relative position to the hydroxyl group, forming *m*- or *o*-hydroxyphenylacetic acid. Homogentisic acid would be formed from such products by subsequent oxidation in the para-position. This possibility was unlikely, as neither *o*- nor *m*-tyrosine gave rise to homogentisic acid, and it was also found that *m*-hydroxyphenylacetic acid, when administered to normal individuals, was found unchanged in the urine to the extent of 80%. Neither *o*- nor *m*-acid gave rise to increased homogentisic output in alcaptonurics.

(d) The processes of degradation, change of relative positions of the hydroxyl group to the side-chain containing the acid group, and of secondary oxidation, can take place concurrently. A similar change has been observed by Bamberger, who showed that tolylhydroxyl-



amine is converted by hot dilute sulphuric acid into toluquinol. Other examples of similar action are also known, and quoted by the author. A change of this description must take place when tyrosine is converted into homogentisic acid. The results also

indicate that homogentisic acid is a normal intermediate product of metabolism, as none of the products which were not fully destroyed in the normal individual gave rise to increased homogentisic output in alcaptonurics.

m-Tyrosine was prepared by the condensation of *m*-hydroxybenzaldehyde with hippuric acid. The lactimide of *m*-hydroxybenzoylaminocinnamic acid in the form of its acetyl derivative, $\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}$, m. p. 149°, was obtained. On hydrolysis with 10% sodium hydroxide solution, *m*-hydroxybenzoylaminocinnamic acid, $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}$, m. p. 205—206°, was formed, which, on reduction with sodium amalgam, yielded *m*-benzoyltyrosine, $\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}$, m. p. 180°. From this, *m*-tyrosine, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, m. p. 280—281°, was obtained by hydrolysis with 20% hydrochloric acid.

o-Tyrosine was obtained by a similar synthetic method, although all the intermediate products were not obtained pure. *o*-Benzoyltyrosine melts at 176°, and *o*-tyrosine at 249—250°. S. B. S.

Are there Reducing Ferments in the Animal Body? ARTHUR HEFFTER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 253—260).—The reduction processes which occur in animal organs or their extracts, or in vegetable tissues, have been attributed to enzyme action. Boiling does not abolish the action; this and other considerations lead the author to the conclusion that “reductases” do not exist.

W. D. H.

Spectroscopic Properties of Yolk of Egg. LOUIS LEWIN, A. MIETHE, and E. STENGER (*Pflüger's Archiv*, 1908, 124, 585—590).—Attempts are being made to establish relationships between the colouring matters of egg-yolk and blood on account of the close morphological relationship between the blood and yolk. The first step in this direction has been the careful spectroscopic examination of the colouring matter of the yolk. The plates used for photographing the spectra were dyed with isocol. Solutions in water, acetone, alcohol, ether, chloroform, and benzene were examined. The solutions were found to follow Kundt's rule, for example, the absorption bands of the chloroform and benzene solutions were 5—10 μ nearer the red end of the spectrum than the corresponding bands of the other solutions.

There are three characteristic bands at 480, 453, and 427, and feebler bands at 400 and 378. No other yellow colouring matter gives the same absorption bands, and it is thus possible to detect adulterants of yellow of egg by spectroscopic measurements.

J. J. S.

Chemico-physical Investigations on the Crystalline Lens. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 305—316. Compare this vol., ii, 966).—The crystalline lens contains an electro-negative protein, *facoprotein*, which is only soluble in water in the form of acid protein in absence of alkali, or of alkali protein, which is soluble also in absence of salts. The essential material of the lenticular fibre is, in normal conditions, a hydrogel of liquid or gummy consistency. The results are mainly of physiological interest.

T. H. P.

Higher Fatty Acids in the Liver after Removal. JOHN B. LEATHES (*Arch. exp. Path. Pharm., Suppl.*, 1908, 327—336. Compare Abstr., 1904, ii, 355).—A full account of a research previously published, with a description of further experiments on the same lines. The increase of fatty acids previously noted does not invariably occur, but no light can be at present thrown on the nature of the processes involved.

W. D. H.

The Formation of Uric Acid in the Liver of Birds. ERNST FRIEDMANN and H. MANDEL (*Arch. exp. Path. Pharm., Suppl.*, 1908, 199—207).—The experiments recorded were made by perfusing the surviving liver of the goose with various mixtures. If uric acid is added to the perfusion fluid, none is retained or destroyed by the liver. If urea and sodium lactate or malonate are added, there is no increase in uric acid formation. Uric acid formation in the bird's liver is therefore not the simple synthesis it has been considered to be.

W. D. H.

Action of Certain Gases on Autolysis. LUIGI BELLAZZI (*Zeitsch. physiol. Chem.*, 1908, 57, 389—394).—Carbon dioxide favours, and oxygen is indifferent, or feebly inhibitory, towards, autolysis of the liver. W. D. H.

Decomposition of Caffeine by Extract of Ox-Liver. Y. KOTAKE (*Zeitsch. physiol. Chem.*, 1908, 57, 378—381).—Extract of ox-liver decomposes caffeine into xanthine, hypoxanthine, *l*-methyl-xanthine, and paraxanthine. The removal of the methyl groups is prevented by boiling the extract, or by the use of such protoplasmic poisons as toluene or chloroform. The action is therefore attributed to a ferment. W. D. H.

Action of Drugs on the Mammalian Uterus. HAROLD J. FARDON (*Bio-Chem. J.*, 1908, 3, 405—411).—The investigation of a number of drugs shows that the reaction of the uterus is that of a plain muscular organ supplied by sympathetic nerves, of both inhibitory and augmentative nature. Pregnancy and nicotine alter the relative influence of the two sets of fibres. W. D. H.

Inosite [in Flesh]. FRANZ ROSENBERGER (*Zeitsch. physiol. Chem.*, 1908, 57, 464—467. Compare Abstr., 1908, ii, 873).—One factor in the presence or not of inosite, or of its precursor, inositol, in flesh appears to be the time of year, which, as is well known, also affects the quantity of glycogen. W. D. H.

Hydrolysis of Fish Muscle. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 23, 81—89).—The results are compared with those previously published in relation to chicken muscle in the following table, where the figures show percentages of cleavage products :

	Halibut muscle.	Chicken muscle.
Glycine	0·0	0·68
Alanine	?	2·28
Valine	0·79	?
Leucine	10·33	11·19
Proline	3·17	4·74
Phenylalanine	3·04	3·53
Aspartic acid.....	2·73	3·21
Glutamic acid	10·13	16·48
Serine	?	?
Tyrosine	2·39	2·16
Arginine	6·34	6·50
Histidine	0·55	0·47
Lysine	7·45	7·24
Ammonia	1·33	1·67
Tryptophan	present	present
Total	50·25	62·15

The most marked difference is seen to be in the percentage yield of glutamic acid. W. D. H.

Cholesterol in Ox-Bile. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, 521—523).—Cholesterol can be easily prepared from the dried

bile of commerce. Previous saponification is unnecessary. The view is held that cholesterol occurs as such in bile, not as an ester.

W. D. H.

Quantitative Researches on the Exhalation of Alcohols. JULIUS POHL (*Arch. exp. Path. Pharm., Suppl.*, 1908, 427—434).—The result of the experiments recorded is that alcohols of higher boiling points (*tert.*-amyl alcohol; isopropyl alcohol) are exhaled with the breath to a greater degree than those of lower boiling point (ethyl alcohol; methyl alcohol). This unexpected result cannot yet be explained.

W. D. H.

The Distribution of Nitrogen amongst the Various Products in Human Urine. LOUIS C. MAILLARD (*Compt. rend.*, 1908, 147, 710—712).—The mixed urine from ten men of from 22—25 years of age was examined on six consecutive days. Of the total nitrogen excreted, 5.73% was in the form of ammonia, 81.29% in that of urea, 1.65% in that of purine compounds, 1.43% in that of uric acid, 0.22% in that of purine bases, and 11.15% in other forms of combination (creatinine, oxyproteic acids, urochrome, hippuric acid, amino-acids, etc.). The proportion of nitrogen to phosphorus was as 9 : 1.37. Muscular work was without appreciable influence on the total nitrogen excretion, although there was a slight diminution of urea, an undoubted increase in phosphates, and a slight increase in the nitrogen in the undetermined forms.

S. B. S.

Detection of Organic Bases in Urine. R. ENGELAND (*Zeitsch. physiol. Chem.*, 1908, 57, 49—64).—Urine has been treated by the three following methods: 1. Precipitation of the urine with a cold saturated solution of mercuric chloride and sodium acetate (compare Johnson, *Abstr.*, 1888, 506; 1889, 165). 2. Concentration of the urine and precipitation with tannin. 3. Precipitation of urine with a hot saturated solution of mercuric chloride and sodium acetate.

The bases isolated from the precipitate in the first method were creatinine and *as*-dimethylguanidine, the latter of which was obtained as the crystalline *aurichloride*, m. p. 144°.

The precipitate obtained according to the second method contained creatinine and methylguanidine, the latter of which was isolated as its *aurichloride*, m. p. 198°. It has been shown that the methyl- and dimethyl-guanidines are not produced by the action of hydrochloric acid on creatinine.

When the third method of precipitation was used, all the creatinine is removed, as the filtrate no longer gave Weyl's reaction. The bases isolated from the precipitate were creatinine, methylguanidine, vitiatine, histidine, a *base*, $C_{15}H_{36}O_{13}N_8$, similar to some of the protamines, and a *base*, $C_5H_7O_2N_3$, similar to histidine. The last base was isolated as its *picrolonate*, $C_5H_7O_2N_3 \cdot C_{10}H_8O_5N_4$, which crystallises in short needles, decomposing at 244°. The base gives a red coloration with alkali and copper sulphate, and also a dark red colour with an alkaline solution of diazobenzenesulphonic acid.

Iminazole derivatives are found in the urine of most animals, but

herbivorous animals produce larger quantities of these compounds than do the carnivora. J. J. S.

The Regular Occurrence of Indole in the Distillate of Normal Urine. MAX JAFFE (*Arch. exp. Path. Pharm., Suppl.*, 1908, 299—308).—Indole is constantly found in the urine of man and other animals examined. The methods of obtaining and identifying it are given in full, the differences in quantity in various animals noted, and the conditions in which indole derivatives occur discussed.

W. D. H

Urinary Pigments derived from Indole. ALBERICO BENE-DICENTI (*Arch. exp. Path. Pharm., Suppl.*, 1908, 64—74. Compare Abstr., 1907, ii, 980).—After subcutaneous administration, 5-methyl-indole appears in the urine as dimethylindigotin; 2:5-dimethylindole forms a red colouring matter, and α -naphthindole yields a reddish-brown coloration, changing later to bluish-green. G. B.

Excretion of Urobilin in Disease. N. F. SURVEYOR (*Bio-Chem. J.*, 1908, 3, 439—448).—From an examination of 500 specimens of urine in health and disease, the conclusion is drawn that there is no correspondence between the amount of urobilin excreted and the amount of ethereal sulphates in the urine. Urobilin formation is therefore not the result of intestinal putrefaction. Disease of the liver also does not seem to be responsible for its appearance. The method adopted for the estimation of urobilin is the depth of the absorption band in an amyl-alcoholic extract of the urine, and so far as any conclusion can be drawn from the inconstant results found in most diseases, it appears that conditions that lead to hæmoglobin destruction are those most likely to produce increase of the urinary urobilin.

W. D. H.

Microchemical Changes occurring in Appendicitis. OWEN T. WILLIAMS (*Bio-Chem. J.*, 1908, 3, 391—401).—The author considers that intestinal sand (Abstr., 1907, ii, 906) consists largely of calcium salts (soaps) of saturated fatty acids. These soaps are not so easily absorbed as those derived from unsaturated fatty acids.

Action of Radium Emanations [in Diabetes]. E. POULSSON (*Arch. exp. Path. Pharm., Suppl.*, 1908, 443—448).—It is well known that many mineral waters contain radium. Cases of diabetes were treated with radioactive water. In two severe cases, no good was done; in a third case, where the disease was not so malignant, the excretion of sugar was lessened, although whether this was due to the water is uncertain.

W. D. H.

The Degradation of Fatty Acids in Diabetes Mellitus. JULIUS BAER and LEON BLUM (*Arch. exp. Path. Pharm.*, 1908, 59, 321—330).—It has been shown previously (compare Abstr., 1907, ii, 285) that isovaleric acid gives rise to β -hydroxybutyric acid in severe cases of diabetes mellitus, and leucine acts in a similar way; no

great difference could be detected in the relative amounts excreted. Experiments were made in mild cases of the disease, and it was found that *isovaleric* acid exerted but little influence on the excretion of the *hydroxybutyric* acid; *n*-butyric and hexoic acids caused, however, an increased output. Similar results were not obtained in all the cases investigated.

S. B. S.

The Influence of Muscular Work on the Excretion of Sugar in Pancreas Diabetes. Y. SEO (*Arch. exp. Path. Pharm.*, 1908, 59, 341—363).—Experiments were carried out on dogs which had been either wholly or partly deprived of the pancreas. The excretions of nitrogen and sugar were determined during periods of rest and periods of work, when the animals turned a treadmill. In animals in which the pancreas had only been partly removed, it was found that muscular work diminished the excretion of sugar. This was not the case, however, in animals on which total extirpation of the pancreas had been performed. In these cases, the ratio dextrose: nitrogen increased during the periods of work. The conclusion is drawn that increased utilisation of sugar by muscular work can only take place when some functioning pancreas tissue remains in the organism.

S. B. S.

Acidosis in Pancreas Diabetes. EDUARD ALLARD (*Arch. exp. Path. Pharm.*, 1908, 59, 388—396).—Brugsch and others have maintained that acidosis is not found in cases of severe pancreas diabetes. The author cites, however, several experiments made with dogs deprived of the pancreas, in which a comparatively large output of β -hydroxybutyric acid was observed. The phenomenon of acidosis in these cases is, however, a very inconstant one, and it is suggested that it is due to secondary causes. The liver, or other parenchymatous tissue, in the advanced stages of the disease may have lost the power of degrading acetoacetic acid or acetone to simpler substances.

S. B. S.

Radioactivity of Goitrogenic Springs. RÉPIN (*Compt. rend.*, 1908, 147, 703—705. Compare this vol., ii, 796).—The author has measured the radioactivity of the water of fourteen springs, a well, and several torrents situated in districts where goitre is endemic. The springs issuing from faults at the base of high mountains were all found to be radioactive, whilst surface water and torrents fed by glaciers or snow were inactive. Torrent waters when without turbidity are preferred, and the people who use them are free from goitre. A goitrous family living in a non-goitrous district was employing a radioactive well water. The prevalence of goitre in mountainous districts, and the success of distilled water in treating it, also suggests a connexion between radioactive water and the disease. The radioactivity has the character of radiothorium.

R. J. C.

The Pathogenesis of Ochronosis. OSCAR GROSS and EDUARD ALLARET (*Arch. exp. Path. Pharm.*, 1908, 59, 384—387).—The colouring of cartilage in the pathological condition known as ochronosis

is due to the same anomaly in metabolism that produces alcaptonuria, namely, the production of homogentisic acid, which is not destroyed in the organism. The cartilage appears to have the property of attracting this acid and converting it into a dark pigment, producing in this way a form of arthritis, designated by the authors *arthritis alcaptonurica*. Almagia has shown that in cartilage soaked in solutions of sodium urate, concretions are formed similar to those found in cases of gout, and the authors show that cartilage in nearly neutral homogentisic acid solutions acquires a dark colour similar to that observed in cases of ochronosis. Other tissue does not act in this way. S. B. S.

A Case of Chronic Pentosuria. RICCARDO LUZZATTO (*Arch. exp. Path. Pharm., Suppl.*, 1908, 366—377).—The urine of the patient (who has remained in good health for many years) contains generally 0.1% of *l*-arabinose. The amount is not affected by ingestion of large quantities of dextrose, sucrose, or starch, but is increased by galactose, by alkalis, and by intellectual work, and diminished by the ingestion of hydrochloric acid, and apparently also by excessive muscular labour. Pentosuria is therefore quite distinct from diabetes. In order to determine the reducing power of the urine, lead acetate is added, and, after filtration, ammonia; the basic lead precipitate formed carries down all the pentose, and is then redissolved in acid. G. B.

Contents of a Cystic Tumour of the Breast. EMIL ZDAREK (*Zeitsch. physiol. Chem.*, 1908, 57, 461—463).—A complete analysis of the contents of a so-called butter-cyst of the mammary gland is given. It occurred in a woman, forty years of age, and had lasted twelve years before it was removed. It was about the size of an apple. It contained 48% of water, 38.6% of fat, 7.5% of fatty acids, 3% of coagulable protein, 1% of caseinogen, and 1.6% of ash. W. D. H.

Action of Barium Chloride, Adrenaline, and Peptone on the Vaso-motor Apparatus. L. POPIELSKI (*Arch. exp. Path. Pharm., Suppl.*, 1908, 435—442).—The three substances named all act on the peripheral vaso-motor mechanism. Barium chloride and adrenaline cause a rise of pressure by acting on the musculature; Witte's peptone causes a fall by acting on the nerve-endings in the vessels. The substance responsible for the activity of Witte's peptone is named *vaso-dilatin*, it is not a protein, nor is it choline, which when pure produces the opposite effect. Vaso-dilatin is also the substance which renders the blood incoagulable. W. D. H.

Action of Certain Narcotics on Nerve. ALBRECHT BETHE (*Arch. exp. Path. Pharm., Suppl.*, 1908, 75—82).—The excitability of nerve and its reaction to the constant current (polarisation picture) go hand in hand. Solutions of chloral hydrate, ethylurethane, and phenylurethane, which abolish the excitability, also abolish the normal polarisation changes. If the dose of the narcotic is insufficient to completely abolish excitability, the polarisation changes are altered in like measure. When these changes are produced, immersion in

Locke's solution causes the nerve to recover. This reversibility is least easy to obtain after chloral hydrate. W. D. H.

Pharmacological Action of Certain Lactones and the Corresponding Hydroxy-acids. CHARLES R. MARSHALL (*Arch. exp. Path. Pharm., Suppl.*, 1908, 389—394. Compare Abstr., 1906, ii, 788).—Certain tropeines containing a lactone group (Jowett and Hann, *Trans.*, 1906, 89, 357; Jowett and Pyman, *Trans.*, 1907, 91, 92), and possessing an atropine-like action, lose this action when they are converted into salts of the corresponding hydroxy-acids. After the addition of a molecular quantity of alkali hydroxide, this conversion occurs relatively slowly towards the end of the reaction, and the gradual change can be demonstrated pharmacologically. G. B.

Behaviour of Sodium Salicylate in the Organism. ALESSANDRO BALDONI (*Arch. exp. Path. Pharm., Suppl.*, 1908, 54—63).—Sodium salicylate, when administered to dogs, is mostly excreted unchanged in the urine, but a small portion is converted into two crystalline derivatives with acid properties, both yielding a blue coloration with ferric chloride and having a strong reducing action. Of these, one, m. p. 169—170°, has the composition $C_{16}H_{16}O_8N$; the other, m. p. 187—188°, has the composition $C_{15}H_{14}O_8$. Salicyluric acid, which is found in human urine after ingestion of sodium salicylate, cannot be detected in dogs' urine. G. B.

Pharmacological Significance of Twin Ethyl Groups. SIGMUND FRÄNKEL (*Arch. exp. Path. Pharm., Suppl.*, 1908, 181—187).—In order to test the hypothesis, that the hypnotic action of such drugs as veronal (diethylbarbituric acid, $CO<\begin{smallmatrix} NH\cdot CO \\ NH\cdot CO \end{smallmatrix}>CEt_2$) is due to two ethyl groups attached to the same carbon atom of the ring, the author has examined tetra-, penta-, and hexa-ethylphloroglucinol, and also the hexamethyl derivative. None of these substances has a hypnotic action, but they produce strychnine-like convulsions. G. B.

Pharmaco-dynamic Characters of Coumarin. ALEXANDER ELLINGER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 150—163).—The toxic action of cantharidin on the kidneys suggested the examination of other substances with a lactone structure, and coumarin was selected. In rabbits, albuminuria may occur, but only to any extent when the urine is acid. The injury to the kidneys, even in large doses, is never serious. Coumarin, however, in frogs causes deep narcosis, owing to its action on brain and cord; the centres affected include those governing cardiac inhibition and respiration, but the vaso-motor centre is not affected. In rabbits it is, in suitable doses, a harmless narcotic, and has no effect on the heart; large doses injected intravenously paralyse the respiration and produce death. In dogs, also, it is a narcotic, and usually produces vomiting. In large doses it kills them, but without the characteristic symptoms noticed in rabbits. This difference in action is probably related to a difference in

excretion in the two animals, but this part of the work is still in progress.
W. D. H.

Behaviour of Atropine in Various Animals. MAX CLOETTA (*Arch. exp. Path. Pharm., Suppl.*, 1908, 119—125).—Atropine appears to be destroyed in the brain and liver; this is most marked in the rabbit's brain, and least in the cat. This appears to be related to what is termed the "vital reaction difference" of the nervous tissues of various animals, and is not yet explicable on a chemical or physical basis.
W. D. H.

Action of Caffeine on Frogs. CARL JACOB and GOLOWINSKI (*Arch. exp. Path. Pharm., Suppl.*, 1908, 286—298).—The relative difference in the action of caffeine on the two species of frog (*Rana esculenta* and *R. temporaria*) has been attributed to differences in the excitability of the spinal cord. The present research deals mainly with the difference between the muscles of the two species. The difference is mainly one of elasticity and extensibility, and this, as well as the different behaviour of caffeine towards them appears to depend on the sarcolemma of the muscular fibres, and the amount or character of its lipoids.
W. D. H.

The Fate of Synthetic Muscarine in the Animal Body. HERMANN FÜHNER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 208—213).—If muscarine is given subcutaneously to tortoises, it is again obtainable in the urine during the next few days in active form, and but little, if at all, altered in amount. The same is true for curarine.
W. D. H.

Poisons of Amanita Phalloides. JOHN J. ABEL and WILLIAM W. FORD (*Arch. exp. Path. Pharm., Suppl.*, 1908, 8—15. Compare Abstr., 1907, ii, 192).—Further details are given of the properties and actions of the two poisons contained in this fungus, namely, the hæmolysin, which is a glucoside containing pentose, and the toxin. The hæmolysin is easily destroyed by the gastric juice, so that, if taken by the stomach, it does not manifest its hæmolytic properties.
W. D. H.

Action of Atoxyl on the Animal Body. J. IGRSHEIMER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 282—285).—Although sodium *p*-aminophenylarsinic acid may have its proper sphere of action in dealing with diseases due to protozoa (trypanosomiasis, syphilis, etc.), it should be recognised that its other name, *atoxyl*, is an illusory one, and in man it produces effects on the nervous, excretory, and alimentary system. Details are given of its toxic action on a number of dogs and cats.
W. D. H.

Action of Poisons on Enzymatic Processes. KARL G. SANTESSON (*Arch. exp. Path. Pharm., Suppl.*, 1908, 469—481).—It is suggested that the harmful influence of such poisons as hydrocyanic acid on the heart and on plant life is due to interference with intra-

cellular enzymes, the action of which forms the basis of the activity of living cells. In support of this view, experiments are recorded with muscle extract, and the action of the catalase in it was measured by the evolution of gas which occurs when mixed with hydrogen peroxide. This action is favoured by dilute alkali, hindered by dilute acid, by hydrocyanic acid, and also by manganese sulphate in decinormal solution; but in concentration $N/1000$ the development of gas is slightly increased; the favouring action of dilute solutions of manganese salts on other enzymatic processes is well known.

W. D. H.

Poisoning with Potassium Chlorate. L. RIESS (*Arch. exp. Path. Pharm., Suppl.*, 1908, 460—468).—The hæmolysis which follows poisoning with potassium chlorate is of a specially pernicious character, and differs from other cases of hæmolysis in that the corpuscles are broken up, so that irregular clumps of hæmoglobin are formed. The urinary tubules become filled with similar particles, although how they pass the renal epithelium is a difficulty; these tubules, especially in chronic cases, get filled with these particles, which blend so as to form casts of the tubules.

W. D. H.

Post-mortem Action of Corrosive Poisons in the Stomach. ERICH HARNACK and HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm., Suppl.*, 1908, 246—252).—In forensic medicine, the degree of action of a caustic poison after death is sometimes raised. It is shown by experiments on cats that their destructive action on the gastric mucous membrane is more marked after death than during life. The action of potassium cyanide on the blood pigment also occurs post-mortem, but absorption of ammonia from the stomach only takes place during life.

W. D. H.

Chronic Oleic Acid Poisoning. EDWIN S. FAUST (*Arch. exp. Path. Pharm., Suppl.*, 1908, 171—175).—The idea that the anæmia in those afflicted with the tape-worm, *Bothriocephalus*, is due to oleic acid contained as a cholesterol ester in the worm acting as a hæmolytic poison, led to the present research, in which it is shown by experiments on rabbits and dogs that oleic acid administered by the mouth or subcutaneously over long periods of time does act as a hæmolytic agent in the same way as it does *in vitro*; the red corpuscles are diminished in number, and the hæmoglobin is lessened in amount.

W. D. H.

So-called Antitoxic Power of Animal Tissues towards Strychnine. PAUL PELLACANI and FOLLI (*Arch. exp. Path. Pharm., Suppl.*, 1908, 419—426).—Proofs are adduced that the tissues do not possess the power of destroying strychnine; practically the whole of it (98%) can be recovered from the tissues many hours after its introduction.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Estimation of the Reducing Power of Bacteria and Animal Organs. HEINRICH WICHERN (*Zeitsch. physiol. Chem.*, 1908, 57, 365—377).—An important distinction between different micro-organisms is their relative reducing powers, and most methods hitherto employed are defective from the quantitative aspect. It is, however, possible to obtain good results with certain coloured substances, the colour of which disappears on reduction; of these, methylene-blue appears to be the best. Still better results are obtained with ferric chloride and titration with titanium trichloride. This is illustrated by the experiments recorded with various bacteria. The method as applied to pieces of organs is not so useful, although fairly concordant results are obtained with extracts of organs. It is suggested that the same method might be employed for the estimation of the activity of oxydases. W. D. H.

Bacterial Formation of Sulphates in Sewage Purification. CH. ROUCHY (*J. Pharm. Chim.*, 1908, [vi], 28, 439—444).—The opalescence or milkiness of effluents from inefficient bacterial sewage beds is due to the presence of finely-divided sulphur. In the limpid effluents from beds which are working properly, the sulphur has been entirely converted into sulphuric acid, which, reacting on the carbonates in the sewage, is converted into sulphates. This formation of sulphuric acid is, the author thinks, due to the oxidising action of special bacteria, analogous to the nitrifying organisms. T. A. H.

Oxidation by means of Moulds. REGINALD O. HERZOG and A. MEIER (*Zeitsch. physiol. Chem.*, 1908, 57, 35—42. Compare Harden, *Trans.*, 1903, 83, 424).—Cultures of *Penicillium glaucum* were grown in dilute beer wort, and when the evolution of carbon dioxide had reached a constant value, a solution of the ammonium salt of a hydroxy-acid was added. The evolution of carbon dioxide was increased considerably, and each experiment was continued until the evolution had fallen again to the normal value for the medium. In this way, the carbon dioxide due to the decomposition of the hydroxy-acid could be calculated. The following acids were readily attacked: lactic, tartaric, malic, mandelic, β -hydroxybutyric, and in every case the amount of carbon dioxide evolved was considerably in excess of that calculated for the amount of acid destroyed.

Glycollic, citric, pyruvic, and hydroxyisobutyric acids were not affected.

The conclusion is drawn that the process is one of oxidation, but is accompanied by another unknown reaction, which also gives rise to carbon dioxide.

It has been shown that, when the organism has been destroyed by acetone or methyl alcohol, it can still decompose the hydroxy-acids, thus indicating that the reaction is due to an oxidising enzyme. The

activity of the dead cells is not so marked as that of the living, and ceases after some thirty-six hours. J. J. S.

Conversion of Cinnamic Acid into Styrene by means of Moulds. REGINALD O. HERZOG and O. RIPKE (*Zeitsch. physiol. Chem.*, 1908, 57, 43—45. Compare Oliviero, Abstr., 1906, ii, 623).—Styrene is formed when *Aspergillus niger* is grown in dilute beer wort containing ammonium cinnamate (0.25% solution). The amount of hydrocarbon formed can be determined by aspirating sterilised air through the liquid, and then passing it through ten bulbs containing carbon disulphide. The styrene is weighed as its dibromide.

Attention is drawn to the importance of this type of reaction for the explanation of the formation of mineral oil deposits. J. J. S.

Transformations of the Chromogenic Matter of Grapes during Maturation. J. LABORDE (*Compt. rend.*, 1908, 147, 753—755).—It has been shown previously (this vol., ii, 774) that the colouring matter of red grapes can be artificially produced from the œnotannin of the unripe grapes. The object of the present work is to discover how the transformation is effected naturally. The tannins exist in the green pellicles in two forms: (1) soluble in strong alcohol, (2) insoluble in this solvent, the latter being the greater in amount. By determination of the amounts of these tannins in various species of red and white grapes, in varying states of maturity, by means of a colorimetric method described, it is shown that the total quantity of tannin matter diminishes, the proportion of the soluble tannin increases, and that of the insoluble tannin diminishes, during ripening. It is during this change of the insoluble into soluble tannin that the colouring matter of the red grapes appears. Colorimetric examination of the hydrochloric acid solution from the pellicles of grapes just commencing to ripen, before and after heating in an autoclave, shows that they contain untransformed œnotannin; with the ripe grapes this is not observed. The œnotannin in the wine must therefore proceed from other solid parts. The soluble tannin obtained from the pellicles of ripe white grapes gives only an insoluble, brown colouring matter when heated with 2% hydrochloric acid in an autoclave. The change in solubility of the tannin is probably due to diastatic action, and this raises the question whether it is an enzyme which transforms the œnotannin into the colouring matter of red grapes; if so, this enzyme must be absent from the white grapes. All attempts to find such an enzyme have, however, proved unsuccessful. E. H.

Carbohydrates of Coelococcus and Phytelephas. SERGIUS IVANOFF (*J. Landw.*, 1908, 56, 217—228).—Ground *Coelococcus* shavings, when hydrolysed with 6% sulphuric acid, yielded 20% of mannose; *Phytelephas macrocarpa* gave 37%. No other hexose was produced in appreciable quantity. Both substances yielded arabinose when boiled with 2—3% sulphuric acid; xylose could not be detected. Mannose was found to be present in two modifications, as hemicellulose and as mannocellulose. N. H. J. M.

Indole in Flowers. F. WEEHUIZEN (*Pharm. Weekblad*, 1908, 45, 1325—1329).—Indole can be detected in the white flowers of *Murraya exotica* by the action of vanillin or *p*-dimethylaminobenzaldehyde on the alcoholic extract in presence of concentrated hydrochloric acid. Each reagent produces a red coloration, that with *p*-dimethylaminobenzaldehyde being more intense in presence of sodium nitrite. Since phloroglucinol answers to the same test when it is present, the vapour exhaled from the flowers should be allowed to come into contact with the reagents.

A. J. W.

Abnormal Biochemical Products of the Rue Anemone. FREDERICK S. BEATTIE (*Amer. Chem. J.*, 1908, 40, 415—428).—Fasciated specimens of rue anemone (*Syndesmon thalictroides*) contain about 20% of methyl and ethyl isocarboxystyryl-3-carboxylates and 3-methylquinoline-4-carboxylic acid. These substances are not found in the normal plant.

J. C. C.

Preparation of Pure Chitin from Boletus edulis. EMIL SCHOLL (*Monatsh.*, 1908, 29, 1023—1036).—The membranes of *Boletus edulis* consist chiefly of chitin in loose combination with carbohydrates. It has been found possible to prepare pure chitin from this fungus to the extent of 5 to 6% of the dried plant by alternate treatment with boiling water and boiling 10% aqueous potassium hydroxide. The chitin so obtained is chemically identical with animal chitin, and is, unlike Winterstein's fungus-cellulose (*Abstr.*, 1896, ii, 210), completely insoluble in concentrated alkalis. It yields about 78% of crystalline glucosamine hydrochloride when hydrolysed with hydrochloric acid.

W. H. G.

Peptolytic Ferments in Germinating and Ungerminated Seeds of Various Plants. EMIL ABDERHALDEN and DAMMHAHN (*Zeitsch. physiol. Chem.*, 1908, 57, 332—338).—The existence of proteolytic enzymes in plants has been established by the work of Schulze and Winterstein. Schittenhehm found also peptolytic ferments in seeds, and this observation is confirmed; extracts of the seeds of wheat, maize, barley, and lupins produce splitting of glycyl-*l*-tyrosine if the seeds have germinated. In the resting stage, peptolytic ferments are absent.

W. D. H.

Assimilation and Elimination of Nutrients by Oats at Different Periods of Vegetation. L. SEIDLER and ALBERT STUTZER (*J. Landw.*, 1908, 56, 273—278).—Pot experiments with oats in two different soils (a heavy loam mixed with gravel and a chalky gravel mixed with peat), manured with superphosphate and sodium nitrate and with varying amounts of potassium chloride. The plants were analysed (1) four weeks after sowing the seed, (2) when the ears began to form, (3) at the period of full flower, and (4) when the ripening was complete.

As regards nitrogen, it was found that from 50 to 60% of the total amount assimilated was taken up in the first four weeks, and that the ripe plants contained from 6 to 26% less nitrogen than at the third

period. The highest amounts of potassium were also found in the third period, the losses during ripening increasing, with some exceptions, with the amount of potassium chloride applied.

Sodium, calcium, and phosphoric acid seem to be retained by the plants to the end; slight losses of calcium occasionally took place between the third and fourth periods.

N. H. J. M.

Influence of Different Manurial Conditions on the Assimilation of Nutrients and the Structure of Plants. MAX WAGNER (*Landw. Versuchs-Stat.*, 1908, 69, 161—233).—Two series of pot experiments in which mustard, buckwheat, barley, and oats were grown under different manurial conditions. In the second series, plants were taken up and analysed at four periods of growth (May 9 and 29, June 25 and July 13).

As regards the final amount of growth above ground, both the oats and the barley, which ripened completely, generally showed a loss, especially when insufficiently manured. Deficiency of nutrients, especially nitrogen, resulted in a higher relation of roots to above ground growth.

A deficiency of phosphoric acid in soil otherwise sufficiently manured reduced the yield of barley most, then oats, buckwheat, and mustard. When potassium was deficient, barley again suffered most, then oats and mustard, and lastly buckwheat.

Whilst the buckwheat, which remained green to the fourth period, continued to take up the different nutrients to the end, the oats, barley, and mustard showed losses of nitrogen, potassium, and phosphoric acid at the final period.

The relation of grain to straw was considerably affected by the conditions of manuring. In the case of barley, a low relation of grain was most marked when potassium was deficient, whilst with oats, deficiency of nitrogen caused the greatest reduction.

N. H. J. M.

Amount of Nutrients Utilised by Sugar-Beet in the First Year and its Relation to the Amount of Sugar in the Roots. KARL ANDRLÍK and JOSEF URBAN (*Zeitsch. Zuckerind. Böhm.*, 1908, 33, 83—94. Compare *ibid.*, 1906, 31, 149; 1907, 32, 559).—The amount of phosphoric acid assimilated by sugar-beet depends on the manuring and the amount present in the soil, on the rainfall, and on the seed. With a yield of 400 quintals of roots, the amount of phosphoric acid taken up under normal conditions varied from 51.7 to 87.8 kilos., whilst in a dry season the average amount was 48.6 kilos.

The amount of phosphoric acid required to produce 100 parts of sugar also varies according to manurial and climatic conditions. The results of various experiments made from 1902 to 1905 showed that the average amount is 0.97 part of P_2O_5 , the amount deposited in the roots being 48.4% of the total.

N. H. J. M.

Digestibility of Hay from Water Meadows as Compared with Ordinary Hay. KONRAD FRIEDLÄNDER (*Landw. Versuchs-Stat.*, 1908, 69, 245—258).—The hay from water meadows is characterised

by a high percentage of mineral matters and a very high percentage of crude protein. The results of feeding experiments with sheep showed that the digestibility of the crude protein is distinctly higher, and of the true protein appreciably higher, than in the case of ordinary hay. The latter contains, however, a higher amount of carbohydrates.

N. H. J. M.

Studies on the Soils of the Northern Portion of the Great Plains Region: Nitrogen and Humus. FREDERICK J. ALWAY and ROBERT S. TRUMBULL (*Amer. Chem. J.*, 1908, 40, 147—149. Compare Abstr., 1907, ii, 294).—Determinations of total nitrogen, soluble humus, and the nitrogen in the soluble humus in nineteen comparatively heavy soils and one sandy soil from Saskatchewan and Alberta. The percentages of total nitrogen are fairly high in all the soils except the sand, whilst the humus is rather low, although much higher than in the arid soils of California. The proportion of the total nitrogen present in the form of humus is decidedly low. The percentage of nitrogen in the humus is not markedly different from that of soils from humid regions.

The results seem to indicate that the surface soils of the semi-arid portions of Western Canada have the characteristics of humid regions, whilst the sub-soils show the peculiarities of other arid regions.

N. H. J. M.

Isolation of Dihydroxystearic Acid from Soils. OSWALD SCHREINER and EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1908, 38, 1599—1607. Compare this vol., ii, 889).—Four out of six more or less unfertile soils were found to contain dihydroxystearic acid, identical with the one obtained from elaidic acid (Saytzeff, Abstr., 1886, 140). The soil which yielded most of the substance was a grey silt loam from Tennessee, which had been under cultivation for more than fifteen years chiefly in cotton. The soil contains organic matter 3.26, and nitrogen 0.16%. The amount of fairly pure substance obtained from 1 kilo. of soil was about 0.05 gram; the amount actually present is probably far greater.

As regards the toxicity of dihydroxystearic acid, experiments with wheat seedlings show that as little as 20 parts per million is distinctly injurious; 100 parts per million reduced the weight to 53%, whilst 200 parts per million (approximately a saturated solution) had about the same effect. Practically the same results were obtained with dihydroxystearic acid, prepared from elaidic acid, and with the isomeric acid from oleic acid, the weight being reduced to about half of that in the control experiment, and the plants being killed in twelve to fifteen days.

The Takoma soil previously examined (*loc. cit.*), which also contains dihydroxystearic acid, seems to be a good medium for fungi. Rootlets of oak trees growing in the soil were found to be infested with mould, and when freed from soil yielded small quantities of the acid. The conclusion is drawn that the dihydroxystearic acid is produced by the moulds, perhaps by the decomposition of lecithins

into oleic acid, conversion of oleic acid by nitrous acid into elaidic acid, and oxidation of the latter by enzymes or micro-organisms.

N. H. J. M.

Ammonia Question. PAUL EHRENBURG (*Landw. Versuchs-Stat.*, 1908, 69, 259—294. Compare this vol., ii, 60).—Experiments on the production of basic and acid reactions in peaty soil, by application of nitrogen in the form of potassium or sodium nitrate and ammonium salt respectively, and on the effect of the reactions on different plants. Experiments were also made in which ammonium sulphate was applied both with and without calcium carbonate.

As an example of the effect of the two forms of nitrogen (in absence of calcium carbonate) on the growth of plants in an acid soil, it is shown that maize, sorghum, barley, and white mustard during the first periods of growth cause the acidity of the soil to be neutralised when manured with nitrate, and then produce normal growth. At the same time, the assimilation of potassium and other bases tends to maintain the change of reaction within certain limits. The same plants, manured with ammonium sulphate, were able, with the exception of mustard, to make a start under the conditions of slight soil acidity, but after reaching a certain point fell off, owing to the increased acidity resulting from the sulphuric acid of the ammonium salt. Mustard is the most sensitive to ammonium salts, and maize the least sensitive, owing probably to the greater amount of soil it produces.

N. H. J. M.

Old and New Nitrogenous Fertilisers: Calcium Cyanamide, Calcium Nitrate, Ammonia Sulphate, and Sodium Nitrate. VITTORIO NAZARI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 334—342).—The author has investigated the influence of various factors on the fertilising value of calcium cyanamide, and has carried out experiments on the comparative values of calcium cyanamide, calcium nitrate, ammonium sulphate, and sodium nitrate as fertilisers. The crop used, in all cases, was wheat.

The results show that the value of calcium cyanamide is greatly enhanced by the presence in the soil of organic matter in the form of stable manure. The cyanamide acts most beneficially at about 20 cm. below the surface of the soil, and at a depth of 5 cm. gives much less favourable results than at a depth of 35 cm. The best fertiliser to use in association with calcium cyanamide is bone superphosphate, partly owing to the fact that it contains a certain proportion of readily fermentable matter, which serves to nourish the micro-organisms; also, admixture of the cyanamide with gypsum gives better results than admixture with lime, owing to the action of the calcium sulphate on the soil constituents containing insoluble potassium compounds, and to its stimulating action on many of the lower forms of plant life. On treating the soil with equal amounts of nitrogen in the form of the various fertilisers, the best and approximately identical results were obtained with calcium nitrate, ammonium sulphate, and sodium nitrate, calcium cyanamide yielding a considerably inferior crop.

T. H. P.

Danger of Employing Salts of Arsenic in Agriculture.
W. MESTREZAT (*J. Pharm. Chim.*, 1908, [vi], 28, 393—397).—Wines manufactured from untreated vines are found to contain 0·000005 to 0·000008 gram of arsenic per litre, whilst those from vines which have been cultivated on the same soil and in the same manner as the preceding, except that they have been treated three times with various arsenical preparations (as insecticides), contain 0·000020 to 0·000025 gram of arsenic per litre. The danger from this cause is accordingly negligible. Inappreciable quantities of arsenic are found to be inhaled by workmen who have to prepare the arsenic salts for use, whilst the quantities settling on their hands and faces (0·0007 to 0·0012 gram) are probably innocuous. E. H.

Analytical Chemistry.

New Burette Clamp. GUSTAV MÜLLER (*Zeitsch. angew. Chem.*, 1908, 21, 2318—2319).—To a retort stand with a tripod base are fixed one or more clamps so constructed that they may be moved and turned both horizontally and vertically. Hence it is immaterial whether the stand is perfectly level, for the burettes may be always properly adjusted.

A retort stand with the rod fixed in the centre of the oblong base may also be used; the rod should consist of two parts, which may be unscrewed if desired. The base is provided with a hole, so that it may be attached to the wall; the clamps are then fixed to the protruding rod. From the rod may be suspended a variety of laboratory sundries, such as towels, brushes, etc., so as to economise space.

L. DE K.

Rapid Method of Qualitative Analysis. W. BRANCH POLLARD (*Chem. News*, 1908, 98, 211).—One part of the finely-powdered substance is mixed with 1 part of vaseline and 5 parts of sodium peroxide. The mixture is placed on a thick iron plate, or in the cavity of a scorifying mould, and ignited by means of a match or a Bunsen burner. The fused mass is extracted with water, and both the soluble and insoluble matter tested as usual. The soluble portion contains, in the highest state of oxidation, those elements which form soluble sodium salts; the insoluble portion contains the oxides and carbonates of the other metallic elements.

A special test should be made for mercury and sodium. The method is more particularly suited for examining ores and minerals in the field.

L. DE K.

Detection of Hydrogen Peroxide in Milk. W. PERCY WILKINSON and ERNST R. C. PETERS (*Zeitsch. Nahr. Genussm.*, 1908, 16, 515—517).—The reaction described by Feder (*Abstr.*, 1908, ii, 318) is shown by

the authors' experiments to depend on the actual quantities of hydrogen peroxide and formaldehyde present, and also on the proportion of these two substances to each other. The strongest reaction is obtained when from 0.004 to 0.013% of formaldehyde and about 0.005% of hydrogen peroxide are present in the milk. If the amount of hydrogen peroxide is increased to 0.5%, a coloration is not obtained. Ferric salts, nitrates, etc., also influence the reaction, so that a positive reaction is not a definite proof of the presence of hydrogen peroxide. The test proposed by the authors (Abstr., 1908, ii, 907) for distinguishing between raw and heated milk may be applied conversely to the detection of hydrogen peroxide; it is not affected by the presence of nitrates or ferric salts.

W. P. S.

Pringsheim's Method for Estimating Chlorine, Bromine, and Iodine in Organic Compounds. ERIK J. VIRGIN (*Arkiv Kem. Min. Geol.*, 1908, 3, No. 12, 1—6).—The author has investigated the method proposed by Pringsheim (compare Abstr., 1904, ii, 146, 447; 1905, ii, 609) for estimating halogens in organic compounds by means of sodium peroxide.

With 1:4-dichloronaphthalene tetrachloride, 3:4-dichlorophenol, and *p*-bromoaniline, this method gives low results, whilst with *p*-dibromobenzene and iodoform good results are obtained.

The method is only applicable to substances which burn quietly with the sodium peroxide, and give no smoke or flame outside the crucible. As it is impossible to tell beforehand if this will be the case, and as there is no definite limit between quiet and vigorous combustion, the method is not to be recommended.

T. H. P.

Kjeldahl's Method. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, 57, 523—526).—Some practical details in the employment of this method are given as the result of the author's experience. Among other points, the omission of the addition of mercuric oxide is recommended.

W. D. H.

Micro-chemical Reactions of Arsenic Applicable to Medico-Legal Investigations. GEORGES DENIGÈS (*Compt. rend.*, 1908, 147, 596—597).—A description of the technique is given for identifying arsenic by microscopical methods, the reagents employed being silver nitrate in solutions acidified by acetic acid, and in ammoniacal solutions. The reactions are carried out with a drop of arsenical liquid, which has been evaporated to dryness with certain precautions, on an object glass.

S. B. S.

Mercurous Nitrate as a Microchemical Reagent for Arsenic. GEORGES DENIGÈS (*Compt. rend.*, 1908, 147, 744—745. Compare preceding abstract).—The reagent is prepared by triturating crystallised mercurous nitrate (10 grams) with nitric acid (D 1.39, 10 c.c.) and adding water (100 c.c.). A small drop of the solution (in nitric acid) to be tested is evaporated to dryness on a glass plate by a gentle heat, and the residue treated with a drop of ammonia, which is also evaporated. To the residue, when quite cold, a drop of the mercurous reagent of a volume insufficient to completely cover it is added.

After two minutes, the drop of reagent is spread over the entire residue by means of a very finely-pointed glass rod, care being taken not to scratch the glass and to keep the rod in a continuous circular motion for 20—30 turns. After another two minutes, if arsenic is present, examination under the microscope (magnifying 40—50 or 100 diameters) reveals thick macles and crystallites, often arranged in a double fan-shape and coloured brownish-yellow, and groups of almost colourless tablets with rounded ends. When the residue is very small, only an extremely small drop (not more than 1—2 mm. diameter) must be used. The test can only be effected successfully by exact attention to all the above details. E. H.

Simplified Apparatus for the Estimation of Carbon in Iron. THEO. GRZESCHIK (*Chem. Zeit.*, 1908, 32, 1092).—An improvement of the apparatus generally used. Close to the end of the inner tube of the condensing arrangement is sealed a concave disk, on which is placed the sample, and when the condenser is placed in the flask the disc should dip slightly into the chromic acid mixture. After transmitting a current of purified air and connecting the apparatus with the train of absorbers, heat is applied with a small flame, and, owing to the disc, a more even distribution of heat is effected. Instead of using a breakable glass tube for connecting the condenser with the water supply, an indiarubber tube is substituted. The distance between the condenser and flask is about 2 mm. The acid rises to a considerable height in the tube, but there is no danger of loss.

L. DE K.

A Boat Funnel. H. STOLTZENBERG (*Zeitsch. angew. Chem.*, 1908, 21, 2271).—To facilitate filling the boat used for combustions, the author describes a nickel funnel made the shape and length of the boat and having a narrow slit underneath. This funnel is supported over the boat, which stands on a small nickel tray, and it allows of the substance being evenly distributed along the boat in an expeditious manner; if overfilled, the substance may be collected from the nickel tray. J. V. E.

Apparatus for the Estimation of Carbon Dioxide, etc. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 267—271).—The piece of apparatus described consists of a flat-bottomed flask provided with a hollow glass stopper, through the centre of which is fused the stem of a tapped funnel; the latter serves as a reservoir for the dilute acid, or other reagent, used in the estimation. A narrow glass tube extends from the stopper of the bottle to the top of the funnel, and a second tube leading from the stopper serves as the delivery tube of the apparatus. The top of the funnel is closed by means of a stopper provided with a small hole, which, on turning the stopper, is brought opposite a similar hole in the neck, so that the pressure in the flask may be equalised when necessary. The apparatus may be used for the estimation of carbon dioxide in carbonates, nitrogen in urea and ammonia (by using the sodium hypobromite method), and in the analysis of hydrogen peroxide, persulphates, etc. W. P. S.

Separation of the Alkali Metals in the Electrolytic Way. JACOB S. GOLDBAUM and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1908, **30**, 1705—1711).—In earlier papers (Abstr., 1907, ii, 574, 988), it has been shown that halide salts of various metals, and particularly those of the alkalis and alkaline earths, can be readily analysed electrolytically with the aid of a mercury cathode and a rotating silver anode. Results are now recorded which have been obtained with ammonium chloride, bromide, and thiocyanate, and the chlorides of caesium, rubidium, lithium, and which prove the accuracy of the method.

An account is given of experiments on the separation of the alkali metals. Freudenberg (Abstr., 1893, ii, 506) has shown that trustworthy separations of metals may be obtained by arranging the pressure so that it exceeds the polarisation value of one metal and continues below that of the other. Working on this principle, separations of sodium from potassium, ammonium, caesium, rubidium, and lithium, of potassium from rubidium, caesium, and lithium, of caesium from rubidium, and of lithium from rubidium and caesium, have been successfully effected. The decomposition values of potassium and ammonium salts are so near to one another that these elements could not be separated.

It is suggested that this method of separation may prove useful in the estimation of small quantities of the alkali metals which occur in silicates. E. G.

Volumetric Alkalimetric Method for Determining Alkaline Earths in Manures and Soils. OTTO FOERSTER (*Landw. Versuchs-Stat.*, 1908, **69**, 235—243).—The substance (4—5 grams of quicklime or 8—10 grams of carbonate) is heated with *N*-hydrochloric acid (200—250 c.c.) in a 400 or 500 c.c. measuring flask for half an hour, then filled to the mark, and the whole filtered. A portion of the filtrate (100 c.c.), after adding the indicator, is treated with *N*/2 sodium hydroxide until the colour changes, then with 1—2 c.c. of *N*/2 acid, and boiled for a few minutes. When there is no, or only slight, precipitation of sesquioxides, the solution may be at once titrated back with *N*/2 alkali, and the number of c.c. used added to the number previously obtained. It is, however, usually advisable to dilute the cooled solution to 200 c.c. with water free from carbon dioxide and, after filtering, to titrate 100 c.c.

The approximate neutralisation of the acid solution is very desirable, as in this way most of the sesquioxides are separated. There must, however, always be an excess of acid so as to avoid the precipitation of calcium hydroxide.

It is pointed out that calcium silicates, owing to the readiness with which they are decomposed, are practically basic compounds. Calcium, in the form of hydrated silicate (or even after being ignited for half an hour), can be determined by the above method. N. H. J. M.

Volhard's Copper Titration. OTTO KUHN (*Chem. Zeit.*, 1908, **32**, 1056—1057).—The author agrees with Theodor (this vol., ii, 898) that Volhard's process gives very satisfactory results. He has, however,

introduced a slight modification so as to avoid the harmful influence of free nitric acid, which has a solvent action on the copper thiocyanate precipitate.

The solution of the alloy in nitric acid is mixed with ammonia until a permanent precipitate has formed, which is then redissolved by adding a decided excess of sulphurous acid; the solution is then heated to boiling, and precipitated with ammonium thiocyanate, the excess of which is estimated in the filtrate with silver solution as usual. The nitric acid may, of course, be expelled completely by evaporating with sulphuric acid, but this would render the course somewhat more complicated.

L. DE K.

Volumetric Estimation of Mercury by means of the Thiocyanate, Iodometric, and Acidimetric Processes. ERWIN RUPP (*Chem. Zeit.*, 1908, 32, 1077—1079).—*Thiocyanate Process.*—The solution, which must contain the mercury as mercuric nitrate or sulphate and be absolutely free from mercurous nitrate, also from chlorine and nitrous acid, is titrated with $N/10$ ammonium thiocyanate, using 2 c.c. of 10% iron-alum solution as indicator; 1 c.c. of thiocyanate = 0.01 gram of mercury. When the solution has been prepared by dissolving mercury in nitric acid, the oxidation is conveniently completed with potassium permanganate, the excess of which is then removed with a pinch of ferrous sulphate.

Iodometric Process.—Twenty-five to fifty c.c. of the solution, containing about 0.1—0.25 gram of the salt, are mixed in a stoppered flask with 1—2 grams of potassium iodide, 10—20 c.c. of 10% potassium hydroxide are added, and then 3 c.c. of 40% formaldehyde diluted with 10 c.c. of water. After shaking for two minutes, 10 c.c. of glacial acetic acid are added, and then 25 c.c. of $N/10$ iodine. When all traces of metallic mercury have disappeared, the excess of iodine is titrated with $N/10$ thiosulphate; no indicator is wanted. One c.c. of iodine solution = 0.01 gram of mercury.

Acidimetric Process.—This is based on the strong affinity of mercury for cyanogen. The mercury should be present as chloride, which may be effected, if necessary, by addition of 1 gram of potassium chloride; any free acid is carefully neutralised with potassium hydroxide, using phenolphthalein as indicator, and 20 c.c. of $N/2$ potassium cyanide are added. The excess of cyanide is then titrated with $N/2$ hydrochloric acid, using methyl-orange as indicator; 2 mols of cyanide = 1 at. of mercury. The titration may also be performed by simply adding the cyanide solution until the liquid turns pink.

Notwithstanding the great stability of the cyanide, it is completely decomposed by potassium iodide with formation of potassium cyanide, which may then be titrated with $N/2$ hydrochloric acid. Mercuric oxide may also be titrated with acid in presence of potassium iodide, from which it liberates the hydroxide. Instead of standardising the cyanide with $N/2$ acid, it may be also checked against a solution of mercuric chloride of known strength.

L. DE K.

Volumetric Estimation of Mercuric Oxide. ERWIN RUPP and W. F. SCHIRMER (*Pharm. Zeit.*, 1908, 53, 928).—Mercuric oxide

cannot be estimated by dissolving in hydrochloric acid and titrating the excess of this with alkali; but it may be titrated by dissolving about 0.25 gram in 10—20 c.c. of water containing 2—3 grams of potassium iodide, and titrating with $N/10$ hydrochloric acid, using methyl-orange as indicator. Heating on the water-bath promotes the solution of the oxide.

Another plan is to boil 0.25 gram of the oxide with 50 c.c. of water and 2 grams of mercuric cyanide. When all is dissolved, 1 gram of salt is added, and when cold the solution is titrated with $N/10$ hydrochloric acid, using methyl-orange as indicator.

The process may be employed for the testing of ointments. Two grams of the sample are boiled with 2 grams of mercuric cyanide and 50 c.c. of water until all the oxide has dissolved, 1 gram of salt is added, and the solution titrated with $N/10$ acid. On account of a slight saponification taking place, owing to the liberation of potassium hydroxide, the potassium iodide process is unsuitable for the testing of fatty ointments.

L. DE K.

Estimation of Manganese by means of Potassium Ferri-cyanide. HERMANN BOLLENBACH and E. LUCHMANN (*Chem. Zeit.*, 1908, 32, 1101—1102, 1114—1115).—The solution, which must be free from metals precipitable by hydrogen sulphide, and also from ferrous iron, cobalt, nickel, chromium, and reducing substances, is mixed with an excess of potassium ferricyanide. A decided excess of aqueous sodium hydroxide is added, and the manganese dioxide is collected and washed with hot water. The filtrate is acidified with excess of dilute sulphuric acid, and the potassium ferrocyanide formed in the reaction titrated with permanganate as usual. Two mols. of ferrocyanide = 1 at. of manganese.

In presence of ferrous iron, an aliquot part of the solution should be titrated with permanganate, and an allowance should be made.

L. DE K.

New Method of Attacking Ferro-compounds, particularly Ferro-silicon. PAUL NICOLARDOT (*Compt. rend.*, 1908, 147, 676—678).—In decomposing ferro-silicon by chlorine at a red heat, it is impossible to retain all the silicon chloride. The author finds that ferro-silicon is completely decomposed by heating with commercial sulphur chloride at 70° for three minutes. Ferro-titanium is somewhat less easily decomposed, whilst ferro-chromium requires a temperature above 120°. The process is carried out in a 250 c.c. flask, closed by a small graduated dropping funnel of special shape. The apparatus is evacuated, and exactly 2 c.c. of sulphur chloride cautiously introduced. On completion of the action which is started by heating, a few drops of ammonia solution are introduced, and the flask is filled up with water as it gradually cools. The products are estimated in the usual way.

R. J. C.

Separation of Tungstic Acid from Silica. PAUL NICOLARDOT (*Compt. rend.*, 1908, 147, 795—797).—This separation is most readily effected by heating the mixture at 500° in a current of air charged

with chloroform vapour, which, unlike carbon tetrachloride, does not give a deposit of carbon at this temperature. The tungsten is thus removed as a mixture of oxychlorides. W. O. W.

Reduction of Stannic Oxide. DAVID B. DOTT (*Pharm. J.*, 1908, 81, 585).—When stannic oxide (0.15 gram) is heated with hypophosphorous acid (0.5 gram) over a Bunsen flame during thirty minutes, it is converted into stannous phosphate or pyrophosphate, which is readily soluble in warm hydrochloric acid. Silica remains unaffected by this treatment, and, if present, can be filtered from the hydrochloric acid solution of the tin. T. A. H.

Physico-chemical Analysis of Mineral Water. ERNST HINTZ and LEO GRÜNHUT (*Zeitsch. angew. Chem.*, 1908, 21, 2359—2368. Compare *ibid.*, 1903, 16, 842).—A mathematical paper comprising a reply to Roloff's criticism of the formulæ used by the authors for calculating the middle dissociation value from the specific conductivity. The formulæ used by Roloff are deduced and shown to be only applicable in special cases, and a complete derivation of the authors' formula is given for the first time. Roloff's assumptions respecting the calculation of the freezing point are discussed, and examples given showing an error of +5.8% from the observed values when use is made of his mode of calculation.

J. V. E.

Assay of Turpentine and Estimation of Mineral Oil in Rosin Spirit. R. ADAN (*Bull. Soc. chim. Belg.*, 1908, 22, 389—396).—Herzfeld's sulphuric acid process is quite untrustworthy for the detection of petroleum products in turpentine or rosin spirit, but Burton's nitric acid method gives satisfactory results provided the temperature is lowered to -10° . Some samples, although pure, may still give 1—2% of insoluble oils.

Petroleum in turpentine or rosin spirit may also be detected by collecting the distillate passing over between 120° — 150° . In the absence of petroleum, the fraction is miscible in all proportions with aniline or acetic anhydride.

Pure turpentine should practically distil over at 162° . In the case of rosin spirit, the bulk of the distillate collects between 165° — 175° , and the distillation is not quite finished even at 180° . This fact facilitates its detection in mixtures. It may be also identified by Grimaldi's test with tin and hydrochloric acid, which gives a green coloration, and also by its odour.

L. DE K.

Estimation of Essential Oils in Spices. R. REICH (*Zeitsch. Nahr. Genussm.*, 1908, 16, 497—509).—The method described by Mann (*Abstr.*, 1902, ii, 432) gives trustworthy results if the point at which the solvent has been removed completely can be exactly determined, and for this purpose the author recommends the following modification as giving the best result. The solution of the ethereal oil in ether, or pentane, is placed in the evaporation flask, and the solvent is evaporated almost completely. A few drops of isopropyl

chloride are then added to the flask, and the drying is continued until the current of air and other gases issuing from the platinum jet no longer gives a green flame when allowed to impinge against a heated copper gauze. The method is trustworthy for estimations of essential oils of cinnamon, cassia, cloves, peppermint, aniseed, thyme, ginger, and camphor, but cannot be used in the case of oils of carraway, lemon, eucalyptus, and turpentine, as these contain extremely volatile substances.

W. P. S.

Detection of Small Quantities of Methyl Alcohol in the Presence of Ethyl Alcohol. LEONHARDT E. HINKEL (*Analyst*, 1908, 33, 417—419).—The following method, in which the alcohols are oxidised to their corresponding aldehydes, and the formaldehyde then detected by means of morphine hydrochloride, is stated to be capable of detecting the presence of methyl alcohol in ethyl alcohol when the proportion of the former alcohol is not less than 5%. One c.c. of the mixed alcohols is placed in a small distilling flask, and the oxidising agent is added. If ammonium persulphate is used, 0.8 gram of the salt is added, followed by 3 c.c. of dilute sulphuric acid (1:5); or in the case of potassium dichromate, 1.5 grams of the salt and 1.5 grams of pure sulphuric acid are employed. In both cases, the mixture is diluted with water to 20 c.c. and distilled, the distillate being collected in test-tubes in five separate portions of 2 c.c. each. The first two portions, which will contain all the acetaldehyde, are rejected; to each of the remaining portions are added a few drops of 0.5% morphine hydrochloride solution, and concentrated sulphuric acid is run into each tube so as to form a layer at the bottom. In the presence of formaldehyde (resulting from the oxidation of the methyl alcohol), a violet ring will be formed at the junction of the two liquids. Pure ethyl alcohol always yields a trace of formaldehyde on oxidation, but the reaction obtained when 5% of methyl alcohol is present cannot be confused with the coloration due to the ethyl alcohol.

W. P. S.

Apparatus for Polarising at 87°. ALBERT P. SY (*J. Amer. Chem. Soc.*, 1908, 30, 1790—1791).—Apparatus is described for determining the rotatory power of sugar solutions at 87°. It consists essentially of a jacketed polariscope tube heated by means of a current of water from an instantaneous water heater. For details, the description and diagram in the original must be consulted.

E. G.

Influence of Clarification with Lead Acetate on the Estimation of Invert Sugar. O. SCHREFELD (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 634, 947—956).—It has been shown by Prinsen-Geerligs (this vol., ii, 991) and others that, under certain conditions, lævulose and, in less degree, dextrose are partly precipitated from their aqueous solutions by basic lead acetate. The author has carried out experiments to ascertain whether the use of this reagent for clarifying solutions of commercial sugar products interferes with the estimation of invert sugar by the reduction of Fehling's solution.

The results show that the reducing power of invert sugar may be lowered by basic lead acetate, this being especially the case with low products and with high contents of invert sugar. When neutral lead acetate is employed, there is, however, little danger of low results being obtained.

T. H. P.

Optically Active Non-saccharine Substances in Sugar Beet which are Eliminated by the Action of Lime in the Purification of the Sap, and their Polarimetric Estimation. FRANZ HERLES (*Zeitsch. Zuckerind. Böhm.*, 1908, 33, 94—98).—Polarimetric determinations in beet juice before and after boiling with lime generally resulted in lower figures after treatment with lime. The differences varied between 0.0% and 0.4%. Beet juice therefore contains, as a rule, some optically active non-sugar which is either precipitated or destroyed by the lime employed during the process of purification.

N. H. J. M.

Colour Reactions of the Carbohydrates Based on the Formation of Furfuraldehyde from them. Reactions with Indole and Carbazole. C. FLEIG (*J. Pharm. Chim.*, 1908, [vi], 28, 385—392).—When 0.5 c.c. of a dilute solution of sucrose or other carbohydrate (many proteins also react) is treated with 3—4 c.c. of pure hydrochloric acid, the mixture boiled momentarily (if any coloration is thereby produced the carbohydrate solution should be diluted and less of it used), and 3—4 drops of a 0.1% alcoholic solution of indole added, a yellow-orange or reddish-orange coloration is produced. One to two drops of a 0.01% solution of sucrose diluted to 0.5 c.c. will give this reaction. Most of the sugars, starches, dextrans, glucosides, etc., react, but the polybasic alcohols, sorbitol, dulcitol, etc., are inactive. If sulphuric acid is used in place of hydrochloric acid, a blank experiment containing no carbohydrate must be made for comparison. The reaction with carbazole (which is given by the same substances as give the indole reaction) is obtained by adding 1—2 drops of a saturated alcoholic solution of carbazole and 1 c.c. of pure sulphuric acid to 0.5 c.c. of the carbohydrate solution, when a reddish-violet ring is formed at the junction of the two liquids. A blank experiment is necessary also in this case, since at certain temperatures carbazole and sulphuric acid react, giving red or violet colorations.

E. H.

Polarimetric Estimation of Starch. CARL J. LINTNER (*Zeitsch. Nahr. Genussm.*, 1908, 16, 509—512).—Sulphuric acid may be used in place of hydrochloric acid in the method described previously by the author (*Abstr.*, 1907, ii, 823). 2.5 Grams of the finely-ground flour are mixed in a mortar with 10 c.c. of water and 20 c.c. of sulphuric acid, D 1.7 (77%); at the end of twenty-five minutes the mass is washed into a 100 c.c. flask by the aid of dilute sulphuric acid (1:3), 5 c.c. of 8% phosphotungstic acid solution are added, and the process then continued as described (*loc. cit.*). When sulphuric acid is used, barley starch has $[\alpha]_D^{20}$ 191.7°, and this value differs for each kind of starch. Unless the value be determined for each starch, the hydrochloric acid method is to be preferred, as, in this case, the value is fairly constant.

W. P. S.

Estimation of Tartaric Acid in Wines by Evaporation. W. MESTREZAT (*Ann. Chim. anal.*, 1908, 13, 433—436).—The evaporation method proposed by Pasteur and modified by Reboul is considered to be more trustworthy than the official (French) method for the estimation of tartaric acid in wines. The following way of carrying out the estimation is recommended: 50 c.c. of the wine are evaporated to such an extent that the residue, when cold, is semi-fluid. After the lapse of five days, the crystals of potassium hydrogen tartrate which have formed are washed with 40% alcohol saturated previously with potassium hydrogen tartrate, and are then titrated in the usual manner.

W. P. S.

Estimation of Malic Acid. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 266—267*).—It is pointed out by the author that the untrustworthiness of both the American official method and the process described by Cowles (Abstr., 1908, ii, 904) for the estimation of malic acid is mainly due to the use of precipitants which are insoluble in alcohol, and that, at the same time, calcium malate is appreciably soluble in 85% alcohol. Malic acid is best precipitated by means of a solution of barium bromide in 96% alcohol, the solution being rendered slightly ammoniacal before use, and the precipitation made in the presence of an excess of alcohol.

W. P. S.

Detection of Benzoic Acid in Butter. LUCIEN ROBIN (*Ann. Chim. anal.*, 1908, 13, 431—433).—The author modifies the method described by Halphen (Abstr., 1908, ii, 906) in order to prevent the formation of an emulsion when the butter is extracted. A portion of the butter is melted together with 50 c.c. of water, 15 c.c. of alcohol, and 0.5 gram of sodium hydrogen carbonate; the aqueous portion is then separated, acidified with sulphuric acid, heated, and filtered. The filtrate is shaken with ether, and the ethereal extract, after being washed with a mixture of 20 c.c. of water and 5 c.c. of alcohol, is shaken with 25 c.c. of the same water-alcohol mixture to which has been added 0.3 gram of sodium hydrogen carbonate. The aqueous portion, containing the benzoic acid as its sodium salt, is separated and evaporated to dryness; the residue is heated with 5 c.c. of sulphuric acid and 10 drops of fuming nitric acid until sulphuric acid fumes are given off, and the solution is then poured into 50 c.c. of cold water. After rendering the solution ammoniacal, a few drops of ammonium sulphide are added, when an orange-red coloration develops rapidly if the butter contains benzoic acid.

W. P. S.

Colour Reactions of Aromatic Aldehydes with Phenols and Various Cyclic, Heterocyclic, and Open-chain Compounds. C. FLEIG (*Bull. Soc. chim.*, 1908, [iv], 3, 1038—1045).—When an acid is added to a solution of an aromatic aldehyde in alcohol also containing one of a variety of substances of which the following may be mentioned as types, phenol, gallic acid, camphor, menthol, aniline, pyrrole, indole, mercaptan, and isobutyl alcohol, a coloration, usually yellow, orange, red, or violet, or in some cases a

* and *Bull. Soc. chim. Belg.*, 1908, 22, 413—414.

play of colours, is produced. The acid used may be sulphuric, hydrochloric, lactic, or a mixture of the last two. The colours given by menthol and terpin are similar to those yielded by cholesterol and biliary acids.

The aminophenols yield orange-red colorations, which turn yellow and finally disappear on addition of excess of acid. With alkalis they also change to yellow, but on the further addition of acid in excess become red. These changes are explained by assuming the existence in the solution of a tautomeric substance *d*; this, on addition of sodium hydroxide, forms a product $\text{Na}d$, which is yellow in presence of excess of alkali and red in presence of excess of acid.

These colour reactions can be applied in the detection of free hydrochloric acid in gastric juice, and possibly to the detection of mineral acids in adulterated wines. T. A. H.

Colorimetric Estimation of Benzaldehyde in Almond Extracts. ALPHEUS G. WOODMAN and E. F. LYFORD (*J. Amer. Chem. Soc.*, 1908, 30, 1607—1611).—The reagents required are magenta decolorised by sulphurous acid and alcohol free from aldehyde. The former is prepared by dissolving 0.5 gram of magenta in 100 c.c. of water, and adding a solution containing 20 grams of sulphur dioxide. When decolorised, the solution is diluted to one litre. The alcohol is purified by distilling over silver oxide. To the distillate are added 25 grams of *m*-phenylenediamine hydrochloride per litre, a rapid current of air is drawn through the solution for three hours, and the alcohol is again distilled, the first 100 c.c. being rejected. The method as used with commercial almond extract may be outlined as follows:

Ten grams of the sample are diluted to 50 c.c. with the purified alcohol. Of this, 2 c.c. are placed in a Hehner cylinder and diluted with alcohol to 20 c.c. Three standard solutions are made up by diluting 2, 4, and 6 c.c. of benzaldehyde solution (alcohol containing 1 mg. of benzaldehyde per c.c.) to 20 c.c. and placing them in similar colorimeter tubes. The tubes are then placed for some time in water at 15°, and to the contents of each are added rapidly 20 c.c. of the magenta reagent, also at 15°. After ten minutes, the unknown sample is matched with the nearest standard in the usual manner by withdrawing part of either liquid. The depth of colour is proportional to the amount of benzaldehyde present. L. DE K.

Detection of "Saccharin" (*o*-Benzoic-sulphinide) and other Artificial Sweetening Materials in Beverages and Foods. ALBERTO BIANCHI and ETTORE DI NOLA (*Boll. chim. farm.*, 1908, 47, 599—605. Compare this vol., ii, 440).—The authors give the following modification of the method devised by Villiers and others (compare Abstr., 1904, ii, 599) for the detection of *o*-benzoic-sulphinide in foods. The liquid, or, in the case of a solid, a suitable liquid extract, is freed from alcohol, heated to boiling, and acidified with about 20 drops of acetic acid per 100 c.c. The liquid is shaken, cooled, and mixed with about 10 c.c. of 20% lead acetate solution per 100 c.c. After half an hour, the excess of lead is precipitated by means of a solution containing 10% of sodium sulphate and 10% of

sodium phosphate, double the volume of lead acetate used being always sufficient. The filtered liquid, concentrated to 70–80 c.c. if necessary, is acidified with 6–8 c.c. of dilute sulphuric acid (1:3), and shaken in a separating funnel with its own volume of a mixture of equal parts of ether and benzene. The benzene-ethereal extract is then slowly evaporated in a flat-bottomed glass dish. The residue is tested for (1) *o*-benzoisulphinide by tasting, and by fusion with sodium hydroxide at 270°; (2) salicylic acid by extracting with a small quantity of alcohol, diluting the alcoholic solution, and adding ferric chloride. If salicylic acid is found, it must be destroyed before the residue is tested for *o*-benzoisulphinide (compare Villiers, etc., *Abstr.*, 1904, ii, 599).

The above method also serves for the detection of the ammonium ("sucramine"), sodium ("sucrose"), and magnesium derivatives of *o*-benzoisulphinide, and of the so-called extract of sugar-cane, which is a solution of *o*-benzoisulphinide in glycerol.

"Dulcine" or "sucrol" (*p*-phenetolcarbamide) may be detected by treating a small portion of the residue left by the benzene-ethereal extract (above) with silver nitrate (compare Ruggeri, *Ann. Lab. Centr. Gabelle*, 3, 143).
T. H. P.

Microchemical Studies. A. BOLLAND (*Monatsh.*, 1908, 29, 965–994).—A paper dealing with the microchemical detection of the following substances: methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, amylamine, hexylamine, neurine, ethylenediamine, pentamethylenediamine, choline, betaine, methylguanidine, α -aminovaleric acid, parvoline, pilocarpine, piperine, coniine, conhydrine, ψ -conhydrine, hyoscyne, cornutine, ergotinine, colchicine, emetine, lobelliine, solanine, solanidine, chelidonine, chelerythrine, sanguinarine, strophantin, digitalin, picrotoxin, and santonin. The appearance, crystallographic and optical properties of the precipitates obtained on treating the tartrates of these substances with various reagents are described.

The refractive indices of the following alkaloids, determined by the immersion method, are given: solanine, solanidine, colchicine, conhydrine, ψ -conhydrine, and ergotinine; also of the tartrates of morphine, thebaine, quinine, cinchonidine, coniine, nicotine, hydrastine and cocaine.
W. H. G.

Colour Reactions of Proteins. C. FLEIG (*Ann. Chim. anal.*, 1908, 13, 427–431).—The following colour reactions are given by the proteins which contain a carbohydrate group in their molecule, namely, ovalbumin, ovoglobulin, serum-albumin, and particularly the glucoproteins (mucin). The test is best carried out by mixing a few drops of a 20% solution of the reagent with a dilute solution of the protein and pouring the mixture on to the surface of a little concentrated sulphuric acid contained in a test-tube. Orcinol, catechol, pyrogallol, phenol, menthol, camphor, terpene, carbazole, thiophen, and pyrrole give red colorations; resorcinol and indole blue, and phloroglucinol, reddish-brown.
W. P. S.